



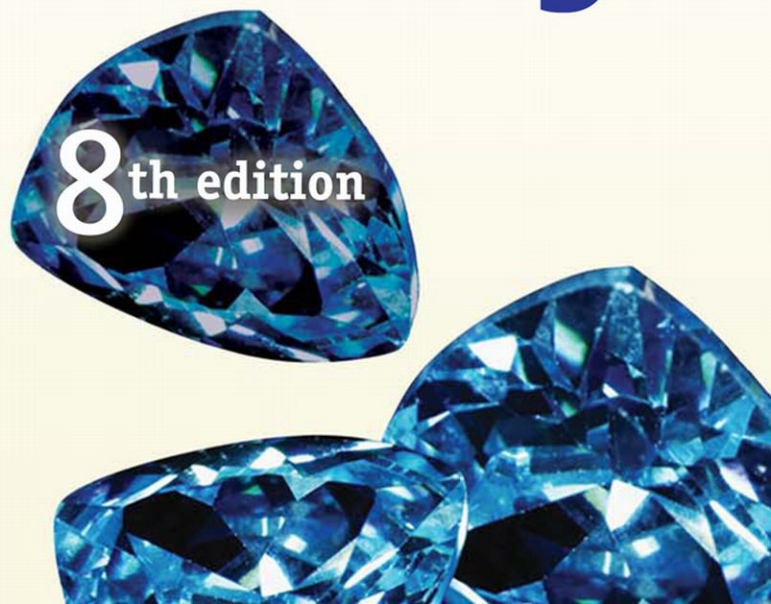
Basic Concepts of

# Chemistry

Leo J. Malone

Theodore Dolter

8<sup>th</sup> edition







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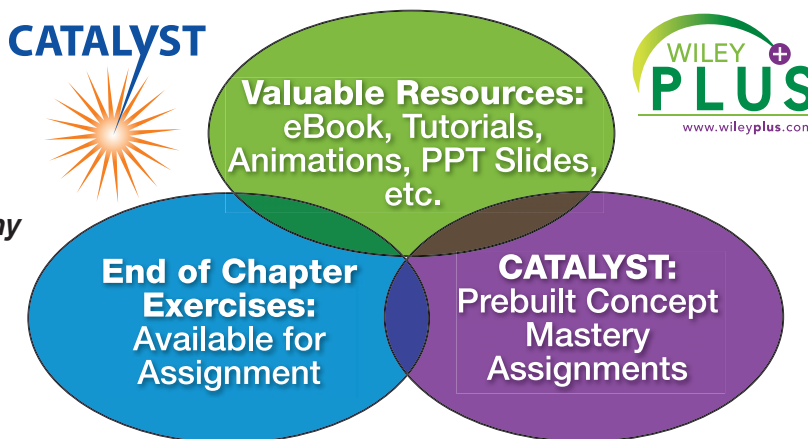
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- + **To succeed in general chemistry, students need to work a diverse range of problems, which facilitate chemical understanding and problem solving.**

**Review Problem 4.53**  
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. Use minimal integer numbers to balance the reaction. Include physical states in your answer, e.g.,  $N_2H_4(aq)$ .

Charge:  $\uparrow$   $\downarrow$   $\rightarrow$   $\leftarrow$   $\rightleftharpoons$   $e^-$   $state$   $NR$

$H_2O^{2+}$

**Show Answer**

**Link to Text** **Office Hours** **Chem FAQ** **Key Tables**

**Question Attempts: 3 of 3 used**

- + **Instructors save time assigning and grading homework and students are provided with the necessary practice that is so important to mastering chemical understanding.**

**Additional Exercise 4.126**  
How many milliliters of 0.10 M HCl must be added to 35.3 mL of 0.40 M HCl to give a final solution that has a molarity of 0.25 M?

Significant digits are disabled.

**Show Hint**

**Link to Text** **Link to Text**

**Hint**  
**Additional Exercise 4.126**  
This problem is a variation of concentration problems. Remember that the concentration is  $Concentration (M) = \text{moles solute}/\text{Volume (L)}$ . Develop an expression for the moles of solute that is present in the original 35.3 mL of 0.40 M HCl as well as for each addition of the 0.10 M HCl. Something like  $\text{total moles HCl} = \text{moles HCl from } 0.40 \text{ M HCl solution} + \text{moles HCl from } 0.10 \text{ M HCl solution}$ . Going back to our definition of concentration, then  $0.25 \text{ M} = (\text{total moles HCl})/(\text{V}_1 + \text{V}_2)$  where  $V_1$  is the initial volume, 35.3 mL converted to liters, and  $V_2$  is the volume, in L, of 0.10 M HCl added to the solution. The next step is solve for  $V_2$ .

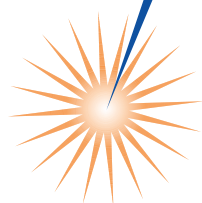
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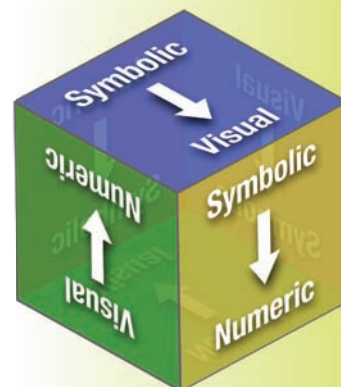
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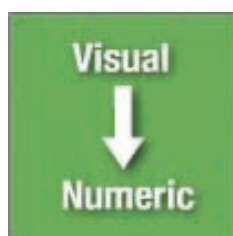
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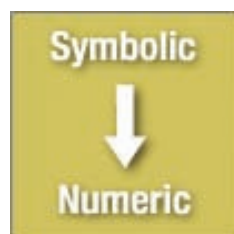
VISUALIZING REACTIONS T02/S01

Enter a balanced chemical equation for the reaction visualized. Do not include states.

Charge:  $\oplus$   $\ominus$   $\rightarrow$   $\rightleftharpoons$   $e^-$  *state* NR

$\text{NH}_4^+ \text{O}_2 \rightarrow$

Question Attempts: 0 of 1 used [Submit Answer](#)



TITRATION T01/S01

A 30 mL sample of an aqueous acetic acid solution was titrated with 24.0 mL of a 0.0940 M aqueous potassium hydroxide solution according to the balanced equation. Calculate the molarity of the acetic acid solution.

$\text{KOH} + \text{HCO}_2\text{CH}_3 \rightarrow \text{KCO}_2\text{CH}_3 + \text{H}_2\text{O}$

Significant digits are disabled; the tolerance is +/-2%

| Molar Mass (g/mol)        |         |
|---------------------------|---------|
| $\text{HCO}_2\text{CH}_3$ | 60.0528 |
| KOH                       | 56.1057 |

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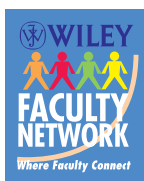
**– Jacob Follman, Student at Penn State University**



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# BASIC CONCEPTS OF CHEMISTRY

8<sup>th</sup>  
EDITION

**LEO J. MALONE** *St. Louis University*

**THEODORE O. DOLTER** *Southwestern Illinois College*



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### **LEO J. MALONE**

Leo Malone is a native of Kansas where he received his B.S. in Chemistry from Wichita State University in 1960 and M.S. in Chemistry in 1962. At WSU he worked under the direction of Dr. Robert Christian. He moved on to the University of Michigan where he received his Ph.D. in 1964 under the direction of Dr. Robert Parry. Dr. Malone began his teaching career at Saint Louis University in 1965 where he remained until his retirement as Professor Emeritus in 2005. Although his early research at SLU involved boron hydride chemistry, he eventually concentrated his efforts on the teaching of basic chemistry and in the field of chemical education.

### **THEODORE (TED) O. DOLTER**

Ted Dolter received his B.S. in Chemistry from St. Louis University in 1987, where he was a student of Dr. Malone's. He went on to the University of Illinois where he received a Masters of Chemical Education in 1990. He concurrently earned a secondary teaching certificate, and it was there that he received most of his training in modern educational theory. After six years of teaching high school chemistry and evening courses at Southwestern Illinois College, he joined the faculty at SWIC full time. In 2004, he was elected to the Department Chair position, where he currently serves and is involved in the department's outcomes assessment initiative.

Professor Dolter's background in educational training and his knowledge of the needs of the growing numbers of community college students compliment Dr. Malone's years of traditional university educational experience. Together, they have produced a text that remains flexible and applicable to the rapidly changing face of today's post-secondary student population.

# BRIEF CONTENTS

|                                   |   |             |
|-----------------------------------|---|-------------|
| <b>PROLOGUE</b>                   | <b>Introduction to the Study of Chemistry</b>           | <b>2</b>    |
| <b>CHAPTER 1</b>                  | <b>Measurements in Chemistry</b>                        | <b>14</b>   |
| <b>CHAPTER 2</b>                  | <b>Elements and Compounds</b>                           | <b>50</b>   |
| <b>CHAPTER 3</b>                  | <b>The Properties of Matter and Energy</b>              | <b>78</b>   |
| <b>CHAPTER 4</b>                  | <b>The Periodic Table and Chemical Nomenclature</b>     | <b>108</b>  |
| <b>CHAPTER 5</b>                  | <b>Chemical Reactions</b>                               | <b>136</b>  |
| <b>CHAPTER 6</b>                  | <b>Quantities in Chemistry</b>                          | <b>168</b>  |
| <b>CHAPTER 7</b>                  | <b>Quantitative Relationships in Chemical Reactions</b> | <b>196</b>  |
| <b>CHAPTER 8</b>                  | <b>Modern Atomic Theory</b>                             | <b>220</b>  |
| <b>CHAPTER 9</b>                  | <b>The Chemical Bond</b>                                | <b>252</b>  |
| <b>CHAPTER 10</b>                 | <b>The Gaseous State</b>                                | <b>292</b>  |
| <b>CHAPTER 11</b>                 | <b>The Solid and Liquid States</b>                      | <b>330</b>  |
| <b>CHAPTER 12</b>                 | <b>Aqueous Solutions</b>                                | <b>362</b>  |
| <b>CHAPTER 13</b>                 | <b>Acids, Bases, and Salts</b>                          | <b>396</b>  |
| <b>CHAPTER 14</b>                 | <b>Oxidation–Reduction Reactions</b>                    | <b>436</b>  |
| <b>CHAPTER 15</b>                 | <b>Reaction Rates and Equilibrium</b>                   | <b>470</b>  |
| <b>CHAPTER 16</b>                 | <b>Nuclear Chemistry</b>                                | <b>510</b>  |
| <b>CHAPTER 17</b>                 | <b>Organic Chemistry (WEB)</b>                          | <b>w-2</b>  |
| <b>CHAPTER 18</b>                 | <b>Biochemistry (WEB)</b>                               | <b>w-42</b> |
| <b>Foreword to the Appendices</b> |   | <b>A-1</b>  |
| <b>APPENDIX A</b>                 | <b>Basic Mathematics</b>                                | <b>A-1</b>  |
| <b>APPENDIX B</b>                 | <b>Basic Algebra</b>                                    | <b>A-10</b> |
| <b>APPENDIX C</b>                 | <b>Scientific Notation</b>                              | <b>A-19</b> |
| <b>APPENDIX D</b>                 | <b>Graphs</b>   | <b>A-27</b> |
| <b>APPENDIX E</b>                 | <b>Calculators</b>                                      | <b>A-31</b> |
| <b>APPENDIX F</b>                 | <b>Glossary</b>   | <b>A-36</b> |
| <b>APPENDIX G</b>                 | <b>Answers to Problems</b>                              | <b>A-45</b> |



# CONTENTS

## PROLOGUE

### Science and the Magnificent Human Mind 2

- A The Origin of Matter 4
- B The Mystery of Fire 9
- C The Scientific Method 10

## CHAPTER 1

### Measurements in Chemistry 14

#### PART A THE NUMBERS USED IN CHEMISTRY 16

- 1-1 The Numerical Value of a Measurement 16
  - 1-2 Significant Figures and Mathematical Operations 19
  - 1-3 Expressing Large and Small Numbers: Scientific Notation 22
- MAKING IT REAL:** Ted Williams and Significant Figures 22

#### PART A SUMMARY 25

#### PART B THE MEASUREMENTS USED IN CHEMISTRY 26

- 1-4 Measurement of Mass, Length, and Volume 26
  - 1-5 Conversion of Units by the Factor-Label Method 30
- MAKING IT REAL:** Worlds from the Small to the Distant—  
Picometers to Terameters 31
- 1-6 Measurement of Temperature 38

#### PART B SUMMARY 41

- Chapter Summary 41
- Chapter Problems 43

## CHAPTER 2

### Elements and Compounds 50

#### PART A THE ELEMENTS AND THEIR COMPOSITION 52

- 2-1 The Elements 52
- MAKING IT REAL:** Iridium, the Missing Dinosaurs, and the Scientific Method 55
- 2-2 The Composition of Elements: Atomic Theory 56
  - 2-3 Composition of the Atom 58
  - 2-4 Atomic Number, Mass Number, and Atomic Mass 60
- MAKING IT REAL:** Isotopes and the History of Earth's Weather 62

#### PART A SUMMARY 64



**PART B COMPOUNDS AND THEIR COMPOSITION 64**

2-5 Molecular Compounds 64

2-6 Ionic Compounds 67

**MAKING IT REAL:** Ionic Compounds and Essential Elements 71**PART B SUMMARY 71**

Chapter Summary 72

Chapter Problems 74

**CHAPTER 3****The Properties of Matter and Energy 78****PART A THE PROPERTIES OF MATTER 80**

3-1 The Physical and Chemical Properties of Matter 80

3-2 Density—A Physical Property 84

**MAKING IT REAL:** Identifying a Glass Shard from a Crime Scene by Density 88

3-3 The Properties of Mixtures 89

**PART A SUMMARY 93****PART B THE PROPERTIES OF ENERGY 94**

3-4 The Forms and Types of Energy 94

3-5 Energy Measurement and Specific Heat 96

**MAKING IT REAL:** Body Solutions—Lose Weight (actually money) While You Sleep 99**MAKING IT REAL:** Dark Matter and Energy 100**PART B SUMMARY 101**

Chapter Summary 102

Chapter Problems 104

**CHAPTER 4****The Periodic Table and Chemical Nomenclature 108****PART A RELATIONSHIPS AMONG THE ELEMENTS AND THE PERIODIC TABLE 110**

4-1 The Origin of the Periodic Table 110

4-2 Using the Periodic Table 112

**MAKING IT REAL:** The Discovery of a Group VIIA Element, Iodine 114**PART A SUMMARY 116****PART B THE FORMULAS AND NAMES OF COMPOUNDS 116**

4-3 Naming and Writing Formulas of Metal-Nonmetal Binary Compounds 117

4-4 Naming and Writing Formulas of Compounds with Polyatomic Ions 121

**MAKING IT REAL:** Ionic Compounds in the Treatment of Disease 124

4-5 Naming Nonmetal-Nonmetal Binary Compounds 125

4-6 Naming Acids 127

**PART B SUMMARY 129**

Chapter Summary 130

Chapter Problems 132



## CHAPTER 5

## Chemical Reactions 136

**PART A THE REPRESENTATION OF CHEMICAL CHANGES AND THREE TYPES OF CHANGES 138**

5-1 Chemical Equations 138

5-2 Combustion, Combination, and Decomposition Reactions 143

**MAKING IT REAL:** Life Where the Sun Doesn't Shine—Chemosynthesis 146**PART A SUMMARY 147****PART B IONS IN WATER AND HOW THEY REACT 147**

5-3 The Formation of Ions in Water 148

5-4 Single-Replacement Reactions 150

5-5 Double-Replacement Reactions—Precipitation 153

**MAKING IT REAL:** Hard Water and Water Treatment 158

5-6 Double-Replacement Reactions—Neutralization 159

**PART B SUMMARY 161**

Chapter Summary 162

Chapter Problems 164

## CHAPTER 6

## Quantities in Chemistry 168

**PART A THE MEASUREMENT OF MASSES OF ELEMENTS AND COMPOUNDS 170**

6-1 Relative Masses of Elements 170

6-2 The Mole and the Molar Mass of Elements 173

6-3 The Molar Mass of Compounds 177

**PART A SUMMARY 181****PART B THE COMPONENT ELEMENTS OF COMPOUNDS 182**

6-4 The Composition of Compounds 182

**MAKING IT REAL:** Calcium in Our Diets—How Much Are You Getting? 186

6-5 Empirical and Molecular Formulas 187

**PART B SUMMARY 190**

Chapter Summary 191

Chapter Problems 192

## CHAPTER 7

## Quantitative Relationships in Chemical Reactions 196

**PART A MASS RELATIONSHIPS IN CHEMICAL REACTIONS 198**

7-1 Stoichiometry 198

7-2 Limiting Reactant 203

**MAKING IT REAL:** Alcohol—The Limiting Reactant in Breathalyzers 207

7-3 Percent Yield 208

**PART A SUMMARY 210**

**PART B ENERGY RELATIONSHIPS IN CHEMICAL REACTIONS 211**

- 7-4 Heat Energy in Chemical Reactions 211  
**MAKING IT REAL:** Hydrogen—The Perfect Fuel 213

**PART B SUMMARY 214**

- Chapter Summary 214  
 Chapter Problems 215

**CHAPTER 8****Modern Atomic Theory 220****PART A THE ENERGY OF THE ELECTRON IN THE ATOM 222**

- 8-1 The Emission Spectra of the Elements and Bohr's Model 222  
**MAKING IT REAL:** Roses Are Red; Violets Are Blue—But Why? 223  
**MAKING IT REAL:** Solving Crimes with Light 227

- 8-2 Modern Atomic Theory: A Closer Look at Energy Levels 227

**PART A SUMMARY 232****PART B THE PERIODIC TABLE AND ELECTRON CONFIGURATION 233**

- 8-3 Electron Configurations of the Elements 233  
 8-4 Orbital Diagrams of the Elements (Optional) 240  
 8-5 Periodic Trends 242

**PART B SUMMARY 245**

- Chapter Summary 246  
 Chapter Problems 248

**CHAPTER 9****The Chemical Bond 252****PART A CHEMICAL BONDS AND THE NATURE OF IONIC COMPOUNDS 254**

- 9-1 Bond Formation and Representative Elements 254  
 9-2 Formation of Ions and Ionic Compounds 255

**PART A SUMMARY 259****PART B CHEMICAL BONDS AND THE NATURE OF MOLECULAR COMPOUNDS 260**

- 9-3 The Covalent Bond 260  
**MAKING IT REAL:** Nitrogen: From the Air to Proteins 263  
 9-4 Writing Lewis Structures 264  
 9-5 Resonance Structures 269

**PART B SUMMARY 271****PART C THE DISTRIBUTION OF CHARGE IN CHEMICAL BONDS 272**



- 9-6 Electronegativity and Polarity of Bonds 272
- 9-7 Geometry of Simple Molecules 275
- 9-8 Polarity of Molecules 278
- 9-9 Formal Charge (Optional) 280
- MAKING IT REAL:** Enzymes—The Keys of Life 281
- PART C SUMMARY** 284
- Chapter Summary 285
- Chapter Problems 287

## CHAPTER 10

### The Gaseous State 292

#### **PART A THE NATURE OF THE GASEOUS STATE AND THE EFFECTS OF CONDITIONS 294**

- 10-1 The Nature of Gases and the Kinetic Molecular Theory 294
- MAKING IT REAL:** Ozone—Friend and Foe 296
- 10-2 The Pressure of a Gas 297
- 10-3 Charles's, Gay-Lussac's, and Avogadro's Laws 301

#### **PART A SUMMARY 309**

#### **PART B RELATIONSHIPS AMONG QUANTITIES OF GASES, CONDITIONS, AND CHEMICAL REACTIONS 309**

- 10-4 The Ideal Gas Law 310
- 10-5 Dalton's Law of Partial Pressures 313
- 10-6 The Molar Volume and Density of a Gas 316
- MAKING IT REAL:** Defying Gravity—Hot-Air Balloons 319
- 10-7 Stoichiometry Involving Gases 319

#### **PART B SUMMARY 321**

- Chapter Summary 322
- Chapter Problems 324

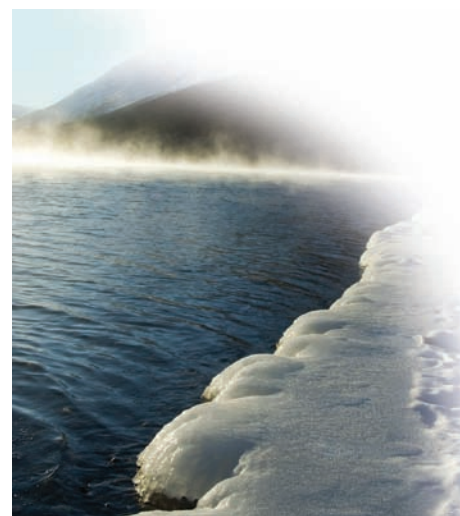
## CHAPTER 11

### The Solid and Liquid States 330

#### **PART A THE PROPERTIES OF CONDENSED STATES AND THE FORCES INVOLVED 332**

- 11-1 Properties of the Solid and Liquid States 332
- 11-2 Intermolecular Forces and Physical State 334
- 11-3 The Solid State: Melting Point 338
- MAKING IT REAL:** The Melting Point of Iron and the World Trade Center 341

#### **PART A SUMMARY 342**



**PART B THE LIQUID STATE AND CHANGES IN STATE 343**

- 11-4 The Liquid State: Surface Tension, Viscosity, and Boiling Point 343  
**MAKING IT REAL:** The Oceans of Mars 348  
 11-5 Energy and Changes in State 349  
 11-6 Heating Curve of Water 352

**PART B SUMMARY 355**

- Chapter Summary 356  
 Chapter Problems 358

**CHAPTER 12****Aqueous Solutions 362****PART A SOLUTIONS AND THE QUANTITIES INVOLVED 364**

- 12-1 The Nature of Aqueous Solutions 364  
 12-2 The Effects of Temperature and Pressure on Solubility 367  
**MAKING IT REAL:** Hyperbaric Therapy 369  
 12-3 Concentration: Percent by Mass 370  
 12-4 Concentration: Molarity 373  
 12-5 Stoichiometry Involving Solutions 377

**PART A SUMMARY 381****PART B THE EFFECTS OF SOLUTES ON THE PROPERTIES OF WATER 382**

- 12-6 Electrical Properties of Solutions 382  
 12-7 Colligative Properties of Solutions 384  
**MAKING IT REAL:** Osmosis in a Diaper 389

**PART B SUMMARY 390**

- Chapter Summary 390  
 Chapter Problems 392

**CHAPTER 13****Acids, Bases, and Salts 396****PART A ACIDS, BASES, AND THE FORMATION OF SALTS 398**

- 13-1 Properties of Acids and Bases 398  
 13-2 Brønsted–Lowry Acids and Bases 400  
 13-3 Strengths of Acids and Bases 404  
 13-4 Neutralization and the Formation of Salts 408  
**MAKING IT REAL:** Salts and Fingerprint Imaging 411

**PART A SUMMARY 412**

**PART B THE MEASUREMENT OF ACID STRENGTH 412**

13-5 Equilibrium of Water 412

13-6 The pH Scale 415

**PART B SUMMARY 419****PART C SALTS AND OXIDES AS ACIDS AND BASES 420**

13-7 The Effect of Salts on pH—Hydrolysis 420

13-8 Control of pH—Buffer Solutions 423

**MAKING IT REAL:** The pH Balance in the Blood 425

13-9 Oxides as Acids and Bases 426

**MAKING IT REAL:** Acid Rain—The Price of Progress? 428**PART C SUMMARY 428**

Chapter Summary 429

Chapter Problems 431

**CHAPTER 14****Oxidation–Reduction Reactions 436****PART A REDOX REACTIONS—THE EXCHANGE OF ELECTRONS 438**

14-1 The Nature of Oxidation and Reduction and Oxidation States 438

**MAKING IT REAL:** Lightning Bugs (Fireflies)—Nature's Little Night-Lights 443

14-2 Balancing Redox Equations: Oxidation State Method 444

14-3 Balancing Redox Equations: Ion-Electron Method 447

**PART A SUMMARY 451****PART B SPONTANEOUS AND NONSPONTANEOUS REDOX REACTIONS 452**

14-4 Predicting Spontaneous Redox Reactions 453

14-5 Voltaic Cells 457

**MAKING IT REAL:** Fuel Cells—The Future Is (Almost) Here 462

14-6 Electrolytic Cells 462

**PART B SUMMARY 464**

Chapter Summary 465

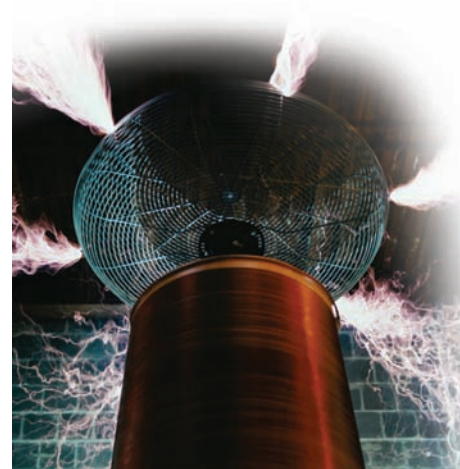
Chapter Problems 466

**CHAPTER 15****Reaction Rates and Equilibrium 470****PART A COLLISIONS OF MOLECULES AND REACTIONS AT EQUILIBRIUM 472**

15-1 How Reactions Take Place 472

15-2 Rates of Chemical Reactions 475

15-3 Equilibrium and Le Châtelier's Principle 479

**MAKING IT REAL:** The Lake That Exploded 483**PART A SUMMARY 484**

**PART B THE QUANTITATIVE ASPECTS OF REACTIONS AT EQUILIBRIUM 485**

- 15-4 The Equilibrium Constant 485
- 15-5 Equilibria of Weak Acids and Weak Bases in Water 489  
**MAKING IT REAL:** Buffers and Swimming Pool Chemistry 496
- 15-6 Solubility Equilibria 497
- PART B SUMMARY 502**
- Chapter Summary 502
- Chapter Problems 505

**CHAPTER 16****Nuclear Chemistry 510****PART A NATURALLY OCCURRING RADIOACTIVITY 512**

- 16-1 Radioactivity 512
- 16-2 Rates of Decay of Radioactive Isotopes 516
- 16-3 The Effects of Radiation 518  
**MAKING IT REAL:** Radioactivity and Smoke Detectors 520
- 16-4 The Detection and Measurement of Radiation 521

**PART A SUMMARY 523****PART B INDUCED NUCLEAR CHANGES AND THEIR USES 524**

- 16-5 Nuclear Reactions 524
- 16-6 Applications of Radioactivity 526
- 16-7 Nuclear Fission and Fusion 529  
**MAKING IT REAL:** Revisiting the Origin of the Elements 534

**PART B SUMMARY 534**

Chapter Summary 535

Chapter Problems 537

**CHAPTER 17 (WEB)****Organic Chemistry w-2****PART A HYDROCARBONS w-4**

- 17-1 Bonding in Organic Compounds w-4
- 17-2 Alkanes w-8
- 17-3 Alkenes and Alkynes w-13  
**MAKING IT REAL:** The Age of Plastics w-16
- 17-4 Aromatic Compounds w-17

**PART A SUMMARY w-19**



**PART B OTHER CLASSES OF ORGANIC COMPOUNDS W-20**

17-5 Alcohols and Ethers w-20

17-6 Aldehydes and Ketones w-22

17-7 Amines w-24

17-8 Carboxylic Acids, Esters, and Amides w-25

**MAKING IT REAL:** Aspirin—An Old Drug with a New Life w-28**PART B SUMMARY w-29**

Chapter Summary w-30

Chapter Problems w-32

**CHAPTER 18 (WEB)****Biochemistry w-42****PART A THREE BASIC TYPES OF BIOCHEMICAL COMPOUNDS w-44**

18-1 Lipids w-44

**MAKING IT REAL:** Soap—Dissolves Away Fat w-48

18-2 Carbohydrates w-49

18-3 Amino Acids and Proteins w-53

**PART A SUMMARY w-57****PART B BIOCHEMICAL COMPOUNDS AND LIFE FUNCTIONS W-58**

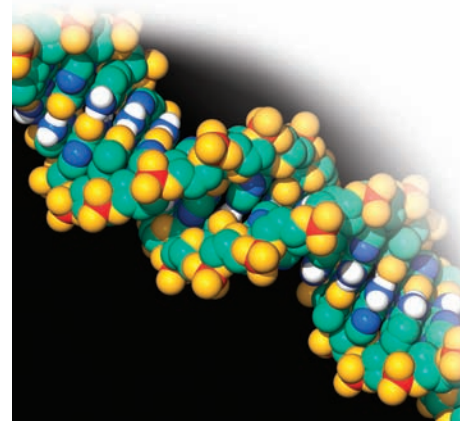
18-4 Enzymes w-58

18-5 Nucleic Acids and Genetics w-60

**MAKING IT REAL:** The Origin of Life w-64**PART B SUMMARY w-65**

Chapter Summary w-66

Chapter Problems w-68

**FOREWORD TO THE APPENDICES A-1****APPENDIX A: BASIC MATHEMATICS A-2****APPENDIX B: BASIC ALGEBRA A-10****APPENDIX C: SCIENTIFIC NOTATION A-19****APPENDIX D: GRAPHS A-27****APPENDIX E: CALCULATORS A-31****APPENDIX F: GLOSSARY A-36****APPENDIX G: ANSWERS TO CHAPTER PROBLEMS A-45****PHOTO CREDITS PC-1****INDEX I-1**





# PREFACE

Leo Malone, sole author of the first seven editions, has joined forces with Ted Dolter to create **Basic Concepts of Chemistry, Eighth Edition**. Professor Dolter's academic background in chemical education and professional duties as chairman of the chemistry program at Southwestern Illinois College uniquely qualifies him to integrate this new dimension of outcomes assessment into Basic Concepts of Chemistry. Although the new edition continues its focus on the preparatory and basic chemistry market, it now includes emphasis on chapter objectives and their assessment.

## Why Did We Write This Book?

---

*Basic Concepts of Chemistry* was originally written in 1981 to address the needs of students planning to take the general chemistry course, but with little or no background in chemistry. Over the next seven editions, its mission has evolved, so that in this new eighth edition we have focused on integrating meaningful assessment and timely feedback into the book as well as the accompanying online course management course (WileyPLUS). This book has been used extensively in one semester, general-purpose courses, where professors find students at a variety of levels. For some of these students a main sequence in chemistry may follow, but for others the course precedes a semester of organic and biochemistry. Still others enroll to satisfy a science requirement or a one semester stand-alone chemistry requirement. The text was written at a level and with the functionality designed to accommodate the needs of each of these groups of students, by structuring itself so that an instructor could emphasize or omit certain clearly delineated sections.

## Basic Concepts of Chemistry Today

---

Today, more and more students are entering post secondary education with a wider variety of learning styles and varied levels of preparedness. Recent data on student populations indicate that many of them are visual and kinesthetic learners and it is vital that textbook authors both recognize and integrate this pedagogy into their books. We have focused hard on accomplishing this goal. Furthermore, the students that take this course have very diverse math backgrounds and we have provided many valuable resources to allow those students with weak math skills to succeed in this course. To accommodate the visual and kinesthetic learner and to support those students with weaker math backgrounds, we have introduced several new features, principle among these is a focus on outcomes assessment.

## The Role of Outcomes Assessment in this Edition

---

Surveys of programs across the country show that chemistry is being taught in numerous ways. From packed lecture halls to intimate classrooms, from Ph.D.s to adjunct instructors to teaching assistants, chemistry education is being delivered in multiple formats, often within the same institution. Outcomes Assessment is an

attempt to insure consistency in evaluating student achievement across these multiple formats. By delineating the expected outcomes or objectives for each chapter, and then devising assessment tools, such as homework and exam questions, lab experiments, group work, and the like, that are designed to target those specific objectives, schools can insure that all students in all sections are being served. By incorporating outcomes assessment into the curriculum, students can receive the same topical instruction and be evaluated against the same standard.

Implementing and justifying an outcomes assessment program can be time consuming. To that end, the authors, having already been through an outcomes assessment program, have designed a text with objectives and assessments already in place, along with the required information needed to show how all of it ties together. Each Part within chapters includes a list of the relevant objectives for that chapter.

### PART A THE PROPERTIES OF MATTER

#### SETTING A GOAL

- You will learn how a sample of matter can be described by its properties and how they can be quantitatively expressed.

#### OBJECTIVES

- 3-1** List and define several properties of matter and distinguish them as physical or chemical.
- 3-2** Perform calculations involving the density of liquids and solids.
- 3-3 (a)** Describe the differences in properties between a pure substance and a mixture. **(b)** Perform calculations involving percent as applied to mixtures.

These are measurable outcomes that the student should master by the completion of that part. Assessments of varying complexity follow each section so that the student, upon completion, can evaluate to what degree the material has been internalized.

#### ASSESSING THE OBJECTIVE FOR SECTION 4-3

**EXERCISE 4-3(a) KNOWLEDGE:** For which of the following metals must a charge be placed in parenthesis when naming one of its compounds? Co, Li, Sn, Al, Ba

**EXERCISE 4-3(b) ANALYSIS:** Name the following compounds.

- (a)  $\text{Li}_2\text{O}$     (b)  $\text{CrI}_3$     (c)  $\text{PbS}$     (d)  $\text{Mg}_3\text{N}_2$     (e)  $\text{Ni}_3\text{P}_2$

**EXERCISE 4-3(c) ANALYSIS:** Provide the formula for the following chemicals.

- (a) aluminum iodide    (c) tin(IV) bromide

- (b) iron(III) oxide    (d) calcium nitride

**EXERCISE 4-3(d) SYNTHESIS:** Using an M to represent the metal and an X to represent the nonmetal, write theoretical formulas for all possible combinations of M and X with charges of +1, +2, +3 and -1, -2, and -3.

*For additional practice, work chapter problems 4-18, 4-20, 4-22, and 4-24.*

At the end of each chapter summary, there is an objectives grid which ties the objectives to examples within the sections, assessment exercises at the end each section, and relevant chapter problems at the end of each chapter. This grid has utility for both the student and instructor so that both can easily locate tools within the text to help address a specific student problem.



| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES      | OBJECTIVES     |                                    |
|---------|---|---------------|----------------|------------------------------------|
|         |   |               | EXERCISES      | CHAPTER PROBLEMS                   |
| 5-1     | Write a chemical equation from a word description of the reaction.  | 5-1           | 1a, 1b, 1e, 2c | 10, 11, 12, 13                     |
|         | Balance a simple chemical equation by inspection.   | 5-1, 5-2, 5-3 | 1c, 1d         | 2, 3, 4, 5                         |
| 5-2     | Classify certain chemical reactions as being combustion, combination, or decomposition reactions.                                     | 5-3           | 2a, 2b, 2c     | 14, 15, 16, 18, 19, 20, 21, 22, 23 |
| 5-3     | Write the ions formed when ionic compounds or acids dissolve in water.  | 5-4           | 3a, 3b, 3c     | 24, 25, 26, 27                     |
| 5-4     | Given the activity series, complete several single-replacement reactions as balanced molecular, total ionic, and net ionic equations. | 5-5           | 4a, 4b, 4c, 4d | 28, 29, 30, 33                     |
| 5-5     | Given a table of solubility rules, determine whether a specific ionic compound is soluble or insoluble in water.                      | 5-6           | 5a, 5b, 5c     | 34, 35, 40, 42                     |
| 5-6     | Write balanced molecular, total ionic, and net ionic equations for precipitation reactions.   | 5-7, 5-8, 5-9 | 5d, 5e         | 44, 45, 46, 47, 48, 49             |
|         | Write balanced molecular, total ionic, and net ionic equations for neutralization reactions.  | 5-10          | 6a, 6b         | 55, 56, 57, 58                     |

#### Other changes to the eighth edition include:

- Emphasizing outcomes assessment, each Chapter Part now begins with **Setting Goals**, which serves to preview the important topics within that Part. **Section Objectives** are presented alongside these Goals so that students can realistically link the text's goals to the objectives required of them.
- **Assessing the Objectives** are a collection of problems that appear at the end of each section, and provide students with the opportunity to assess their understanding of each section's objectives. The representative problems are divided into three cognitive levels: *Knowledge*, *Analysis*, and *Synthesis*. Each level is progressively more sophisticated and prompts the students to gauge their conceptual understanding of the section content.
- Every concept in the text is clearly illustrated with one or more **step by step examples**. Most examples, in addition to a *Procedure* and *Solution* step, are followed by two new steps *Analysis* and *Synthesis*. The *Analysis* step discusses the problem in light of the reasonableness of the answer, or perhaps suggests an alternate way to solve the problem involving different learning modes. The concluding *Synthesis* step gives the student the opportunity to delve deeper, asking the student to extend their knowledge. These added steps promote critical thinking and facilitate deeper conceptual understanding.
- **Making it Real** essays have been updated to present timely and engaging real-world applications, emphasizing to the student the relevance of the material they are learning. For example, in the high-interest field of forensics we describe how glass shards from crime scenes can be identified by their density in Chapter 3, and then in Chapter 8, explore how the refractive index of glass is also used as important evidence in solving crimes. In Chapter 7, we take a look at the chemical reactions involved in the breathalyzer and in Chapter 13, how salts are used to analyze fingerprints.
- New to this edition are end of chapter **Student Workshop** activities. These are intended to cater to the many different student learning styles and to engage them in the practical aspect of the material discussed in the chapter. Each "Student Workshop" includes a statement of purpose and an estimated time for completion.

## Organization

The **Prologue** is a unique feature which introduces the origin of science in general and chemistry in particular. There are no quizzes, exercises, or problems; rather, it is meant to be a relaxing, historical glimpse at the origin of this fascinating subject and how it now affects our lives. Our intent is build interest and engage the student in further study. We recognize the changing needs of students and balance that with the requirements to successfully study chemistry. As such, we continue to provide the necessary support for students continuing on in the study of chemistry. **Chapter 1, Measurements in Chemistry**, provides the necessary math tools in a non-threatening way. In **Chapter 2, Elements and Compounds**, the elements are introduced starting from what we see and sense about us (the macroscopic) to the atoms of which they are composed and finally into the structure within the atom (the microscopic and submicroscopic.) We do the same for compounds in the second part of this chapter. **Chapter 3, The Properties of Energy and Matter** continues the discussion of matter and its properties. Some additional yet relevant math concepts such as density, percent composition, and specific heat are introduced in this chapter as properties of matter. **Chapter 4, The Periodic Table and Chemical Nomenclature**, allows us to draw in one of the primary tools of the chemist, the periodic table. We see its functionality and organization, and begin using it in a thorough discussion of how to name most common chemicals, whose structure was discussed in chapter 2.

In **Chapter 5, Chemical Reactions** we discuss the broad range of chemical interactions that can occur. The quantitative aspects of chemistry are discussed in **Chapter 6, Quantities in Chemistry** and **Chapter 7, Quantitative Relationships in Chemical Reactions**. These chapters were split from a single, larger chapter in the 7th edition, and have been moved forward ahead of **Chapter 8, Modern Atomic Theory** and **Chapter 9, The Chemical Bond**. Still, the two latter chapters can be moved ahead of Chapter 5 without prejudice, depending on the preferences of the instructor, and the ease with which the material can be incorporated into the overall curriculum.

**Chapter 10, The Gaseous State**, begins a three chapter in depth study of the states of matter by examining the unique and predictable behaviors of gases. This is followed by similar discussions of the condensed states of matter in **Chapter 11, The Liquid and Solid States**, which includes a thorough but understandable discussion of intermolecular forces and how those affect the properties of matter. This discussion continues in **Chapter 12, Aqueous Solutions**, where we discuss both the qualitative and quantitative aspects of solute-solvent interactions. This chapter serves as a wrap-up of the quantitative relationships introduced in Chapters 6 and 7.

**Chapter 13, Acids, Bases and Salts**, begins a discussion of specific classes of chemicals, and goes into depth as regards the ways acids and bases can react together and with their environment. A second class of reaction is explored in depth in **Chapter 14, Oxidation-Reduction Reactions**. The relationship of these types of reactions to the creation of batteries and electrical currents is explained.

The remaining chapters offer a survey of topics that are of general chemical interest, and are appropriate for those looking to expose their students to a broad set of topics. **Chapter 15, Reaction Rate and Equilibrium**, introduces the concepts of Kinetics and Equilibrium and gives a taste of the sophisticated mathematical treatment these topics receive. **Chapter 16, Nuclear Chemistry**, explores how radioactivity is a phenomenon associated with certain elements and isotopes. **Chapter 17, Organic Chemistry**, gives the briefest introduction to organic functional groups, structure, and bonding. **Chapter 18, Biochemistry**, gives a similar treatment to common biochemical structures like carbohydrates, proteins, lipids, and nucleic acids.

## Supplements

### WileyPLUS with CATALYST

WileyPLUS is a powerful online tool that provides a completely integrated suite of teaching and learning resources on one easy to use website. WileyPLUS integrates Wiley's world-renowned content with media, including a multimedia version of the text, PowerPoint slides, digital image archive, online assessment, and more.

WileyPLUS with CATALYST partners with the instructor to teach students how to think their way through problems, rather than rely on a list of memorized equations, by placing a strong emphasis on developing problem solving skills and conceptual understanding. WileyPLUS with CATALYST incorporates an online learning system designed to facilitate dynamic learning and retention of learned concepts. CATALYST was developed by Dr. Patrick Wegner (California State University, Fullerton) to promote conceptual understanding and visualization of chemical phenomena in undergraduate chemistry courses.

CATALYST assignments have multiple levels of parameterization and test on key concepts from multiple points of view (visual, symbolic, graphical, quantitative). Hundreds of end-of-chapter problems are available for assignment, and all are available with multiple forms of problemsolving support.

*Study Guide/Solutions Manual by Leo J. Malone* is available to accompany this text. In the Study Guide/Solutions Manual, the same topics in a specific section are also grouped in the same manner for review, discussion, and testing. In this manner, the Study Guide/Solutions Manual can be put to use before the chapter is completed. The Study Guide/Solutions Manual contains answers and worked-out solutions to all problems in green lettering in the text.

*Experiments in Basic Chemistry by Steven Murov and Brian Stedjee*, Modesto Junior College. Taking an exploratory approach to chemistry, this hands-on lab manual for preparatory chemistry encourages critical thinking and allows students to make discoveries as they experiment. The manual contains 26 experiments that parallel text organization and provides learning objectives, discussion sections outlining each experiment, easy-to-follow procedures, post-lab questions, and additional exercises.

*Instructor's Manual and Test Bank* by Leo J. Malone, St Louis University; Ted Dolter and Steve Gentemann, Southwestern Illinois College; and Kyle Beran, University of Texas-Permian Basin. The Instructor's Manual consists of two parts; the first part includes hints and comments for each chapter by Ted Dolter, followed by daily lesson plans by Steve Gentemann. The second part of the manual contains answers and worked-out solutions to all chapter-end problems in the text by Leo Malone. The test bank by Kyle Beran consists of multiple choice, short answer, and fill in the blank questions.

*Instructor's Manual for Experiments in Basic Chemistry*, written by the lab manual authors, contains answers to post-lab questions, lists of chemicals needed, suggestions for other experiments, as well as suggestions for experimental set-ups.

*Power Point Lecture Slides*, created by Wyatt Murphy, of Seton Hall University, these slides contain key topics from each chapter of the text, along with supporting artwork and figures from the text. The slides also contain assessment questions that can be used to facilitate discussions during lecture.

*Digital Image Archive*. The text web site includes downloadable files of text images in JPEG format.

*Computerized Test Bank* The IBM and Macintosh compatible version of the entire Test Bank has full editing features to help the instructor customize tests.

Most of the resources listed above can also be accessed at [www.wiley.com/college/malone](http://www.wiley.com/college/malone).







## ACKNOWLEDGMENTS

A revision of this magnitude involves efforts spanning several years and requiring the input of many people. In particular, Dr. Malone thanks his colleagues at Saint Louis University for their helpful comments in previous editions of this text. He's grateful to his wife Meg, who demonstrated patience and put up with occasional crabbiness during the new text's preparation. Dr. Malone also appreciates the support of his children and their spouses: Lisa and Chris, Mary and Brian, Katie and Rob, and Bill. They and their eleven children were both a source of great inspiration and a large amount of noise.

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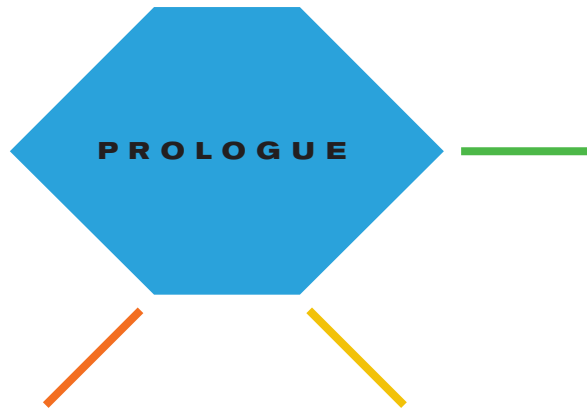
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# **BASIC CONCEPTS OF CHEMISTRY**



# Science and the Magnificent Human Mind

**W**hat could be more peaceful than a campfire silhouetted by the night sky? Actually, the sky and the fire were the source of remarkable achievements of the human race but in different ways. Observations of the sky and the stars provided the keys, in an ongoing process, that are unlocking the secrets of space, time, and the history of the cosmos.

The use of fire, an awesome force of nature, provided the protection and the warmth that allowed the human race to thrive in a hostile world. Eventually, the use of fire would be the instrument of huge advances in civilization. The

Prologue relates how the study of the stars and the use of fire led us to the world of science that serves us so ably today.

- A The Origin of Matter
- B The Mystery of Fire
- C The Scientific Method

**AMONG THE ANIMAL KINGDOM**, only humans have the ability to take their minds beyond simple survival. We also analyze, ponder, and predict the future based on observations. This has led us to a remarkable understanding of all that we see and otherwise sense about us. So this Prologue is dedicated to how the wonderful workings of our minds have allowed us to establish the realm of modern science. In Section A, we examine how the first stirrings of curiosity about the night sky led eventually to the still developing understanding of what has happened since the beginning of time. As presented here, we are preempting the use of some terms and concepts that will be explained more thoroughly in later chapters. The readings in the Prologue are meant to tweak your interest, not necessarily to be learned. In Section B, we see how the taming of fire by our ancient ancestors propelled us into huge scientific discoveries and the basis of chemistry. Finally, in Section C, we take note of how science in general and chemistry in particular have progressed from random discoveries and serendipity to the complex technical world in which we exist today. After proceeding through the Prologue, we will build the topic of chemistry from the most basic substances of the universe to the complex world of chemistry that serves us in so many ways today.



## A THE ORIGIN OF MATTER

Somewhere in ancient time, many thousands of years ago, someone looked up at the night sky and wondered what this display of bright dots meant. It was a great landmark in our existence, as humans became able to expand their minds beyond just the concerns of everyday survival and existence. With the power of abstract reasoning, our earliest ancestors began to observe, consider, and speculate about the world around them. Surely the glittering display of bright stars in the heavens would have attracted the attention of their newly inquisitive minds. One can only imagine what they must have thought they were observing. They probably sensed that something very vast and mysterious was involved, but they would not have known that the secrets of our very existence are indeed “written in the stars.” What cosmologists have garnered from the night sky in just the past few decades has given us a tantalizing yet still incomplete understanding of the beginning, evolution, and ultimate destiny of our entire universe.

From observations of the cosmos, many of the mysteries of the origin of all that we see, from the paper in front of us to the farthest reach of the cosmos in infinite space, have been revealed. On a small piece of dust in the universe, called Earth, we peer out into distant space and back into ancient time. We observe the flickering points of light that we call stars—the visible flashes from distant suns, some like our own. Magnification of the heavens tells us that some of what appear as individual stars to the naked eye are actually groups of stars called *galaxies*, each containing hundreds of billions of individual stars. It was the motions of these galaxies in the heavens that provided modern scientists with the clues about the origin of everything. One observation divulged that groups of galaxies seem to be pushing away from each other, indicating a dynamic, continually expanding universe. A logical conclusion from this is that the galaxies were closer together in the past. In fact, if we go back a little less than 14 billion years, the entire cosmos was coalesced into a single, infinitely dense point known as the *singularity*. The spontaneous expansion of this point (which is referred to as “the big bang”) marked the beginning of time and space. At the very start of time, the two components of the universe—the stars, planets, and other forms of *matter* (which has mass) as well as the heat, light, and other forms of *energy* (which has no mass)—were to evolve from the *singularity*. How the singularity came to be and what was present before time began is unknown to science and may never be known. But, immediately after the big bang, there was only energy and unbelievable heat. It wasn’t for another 10,000 years that our infant universe expanded and cooled enough so that some of the energy of this nascent system evolved into the basic building blocks of nature.

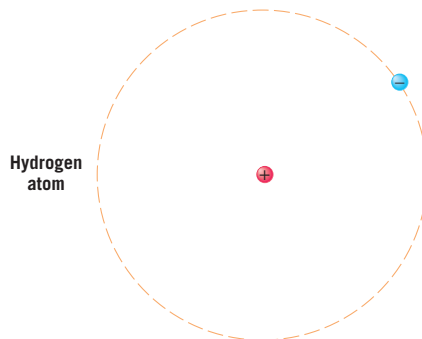
The first matter was composed of three basic particles known as *protons*, *neutrons*, and *electrons*, which evolved from energy and even more fundamental particles. At first they existed independently in the hot, dense universe. These particles exist in the world of the submicroscopic—they are way too small to see with even the most powerful magnification. The proton carries a positive electrical charge; the neutron, about the same mass as a proton, carries no charge. The third particle, the electron, tiny compared to protons and neutrons (about 1/2000 the mass), carries a negative charge equal but opposite to the charge on the proton. From these three particles, the entire stuff of the universe would eventually evolve.

About 400,000 years after the big bang, a hugely significant event occurred. The particles slowed down enough so that the attractive forces between a positively charged proton and a negatively charged electron could hold the two particles

together. Significantly, the electron and proton did not directly attach to each other. Instead, the electron settled into a stable orbit around the central proton. Why this happened is not easily explained but is understood in the realm of *quantum mechanics*. Quantum mechanics is the science that deals with the forces involved in the very small dimensions of these particles. For now we can accept some results of more complex theories without going into detail.

A model of the hydrogen atom, with an electron in a set orbit, was first advanced by Niels Bohr in 1923. It compares the orbiting of the electron around the proton to the motion of the Earth around the sun. In fact, the nature of the electron in the atom is now known to be more complex, but this classical orbiting model serves us well at this point, so we will use it. The proton and the electron together now formed a neutral *atom*. Normal matter is composed of variations of these tiny particles called atoms. The smallness of atoms is a stretch for the human mind to comprehend. In fact, the period at the end of this sentence contains a number of atoms comparable to the number of grains of sand in the Sahara Desert (about  $10^{17}$ , or one hundred million billion atoms).

The proton is the center of this tiny two-particle universe and is known as the *nucleus* of the atom. The vast volume of the atom is empty space in which the electron exists. If the minute size of the atom isn't hard enough to imagine, the dimensions within the atom itself are equally difficult for our modest and limited minds to fathom. Imagine that the nucleus was the size of a basketball. In that case, the electron, which defines the total size of the atom, would exist in a volume with a two-mile radius. This model represents an atom of the element *hydrogen*, which accounted for 90% of the atoms initially formed in the big bang. An *element* is a basic form of matter.

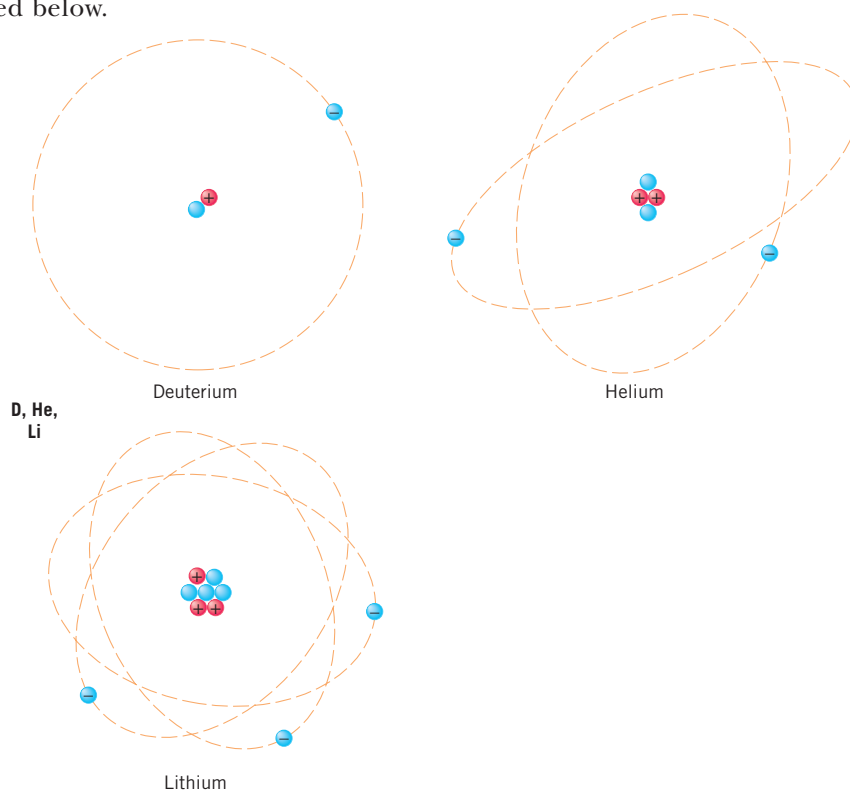


What of the other 10% of the matter that was formed? Some of the nuclei of hydrogen contained one neutron as well as one proton. This form of hydrogen is often referred to as *deuterium* or *heavy hydrogen*, but it is not a unique element. About one out of 30,000 hydrogen atoms are actually deuterium atoms. Atoms of a certain element that have a specific number of neutrons are known as *isotopes*. So, initially, the element hydrogen existed as a mixture of two isotopes, normal hydrogen and a very small amount of deuterium.

The earliest universe contained another type of nucleus that had two protons and two neutrons. When combined with two electrons, these nuclei formed the atoms of a second element known as *helium*. The atoms of a specific element have a definite number of protons in the nucleus, and that is what determines the identity of an element. At this point in time, essentially only two elements, hydrogen and helium, existed in the entire cosmos.

It is believed that there may also have been trace amounts of a third element, known as *lithium*, among the first atoms formed after the big bang. Lithium is identified by the presence of three protons along with four neutrons in the

nuclei of its atoms. The three other atoms in the primeval universe are illustrated below.



Chemistry makes use of a good amount of convenient symbolism. The elements are represented by *symbols* that are usually the first one or two letters of their English, Latin, or, in one case, German, names. Thus H stands for hydrogen, He for helium, and Li for lithium. To represent the information about the content of an isotope's nucleus, we use *isotopic notation*. The number in the upper-left-hand corner is known as the *mass number*, which is the total number of protons and neutrons. The number in the lower-left-hand corner is the *atomic number*, which is the number of protons in that specific element. The atomic number and the element's symbol are redundant because each element has a specific atomic number.

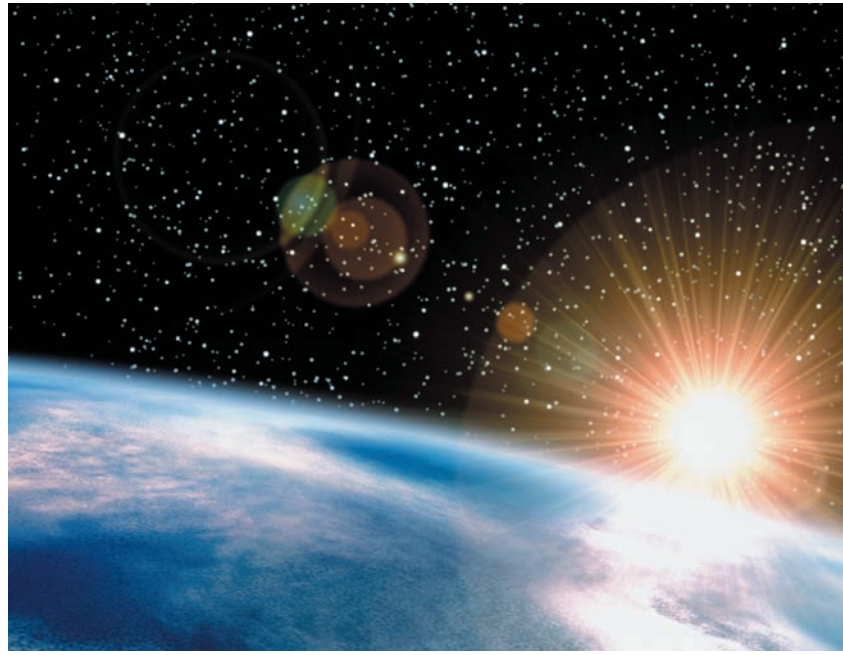


The complete list of elements, along with their symbols, is shown inside the front cover.

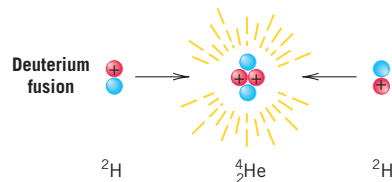
For a time after the formation of the original neutral atoms, the universe turned completely dark. However, about 1 billion years after the big bang, some of the hydrogen and helium began to gather into individual clouds of gas. We are not sure why this happened, but it did. However, this was a significant event because within the regions of gas, an elementary attractive force of nature, *gravity*, began to have its way. Gravity caused some of the individual clouds of gas to contract. Changes began to occur in the clouds as the atoms moved closer together. As the clouds contracted, the temperature within increased dramatically. Heat relates to the velocity of the atoms. Heat causes expansion, which actually counteracts gravity. However, gravity continued to predominate in the huge cloud, so further contraction and heating occurred. Crushing pressures and high temperature began to build in the center of the cloud.

In the dynamic, churning center of the cloud, the extremely hot hydrogen nuclei, now stripped of their orbiting electrons, collided frequently with each other. However, the fact that they had the same electrical charge meant that they actually

did not touch but were repelled from each other (like charges repel; unlike charges attract). At some point, however, a phenomenal event happened in the evolution of our cosmos. Colliding protons had enough velocity and energy to overcome the repulsive forces between the two nuclei, thus merging or fusing together to form a single nucleus. This process is called *nuclear fusion*. Some of the mass of the two fusing nuclei converted back into energy (i.e., Einstein's law,  $E = mc^2$ ). It was like starting a campfire. Once the fire starts, it continues until the wood is consumed. The heat generated from the fusion of the atoms within the cloud was enough to counteract the pull of gravity, thus stabilizing the size of the cloud. The cloud of gas began to glow and, at that time, a star was born. The universe began to light up and appear much like we see it today, except that the stars were much closer together. (See Figure P-1.) Fusion powers all of the stars, including our own sun. (Nuclear fusion has only been understood since the late 1930s.)



**FIGURE P-1 A Typical Star**  
Our sun is a typical star, generating massive amounts of energy from the fusion of hydrogen to form helium.



The fusion of protons to form helium occurs in several steps that are somewhat complex. The fusion of deuterium nuclei to form a helium nucleus, which was mentioned previously, however, occurs in one simple step and is illustrated below.

Many of the earliest stars were massive (many times larger than our own sun) and used up their hydrogen fuel in the core of the star in the course of several million years. Our own sun uses its fuel much more slowly, so even though it is over 4 billion years old, it will go on at this rate for many more billion years. So far, however, in our early universe, the number of elements had not changed—just a minuscule increase in the amount of helium as a result of fusion. It is what happened next in the stars that led to the formation of heavier elements.

As the supply of hydrogen began to diminish in the core of the star, the fusion of protons began to wane and no longer supplied enough energy to keep the size of the star stable. So again gravity predominated and contraction recommenced. With the increasing pressure came increasing temperatures. Eventually the heat was high enough and the nuclei crushed together enough to cause the helium nuclei (with a +2 charge) to fuse to form the first elements heavier than lithium. (Stars in this stage are known as *red giants*.) This process occurs at a higher temperature than the proton fusion because of the higher nuclear charge to be overcome by the colliding nuclei. The fusion of helium in a series of steps eventually led to heavier elements such as carbon (mass number 12) and oxygen (mass number 16).

In time, the helium was exhausted and the contraction-heating process took over once again. Another stage of elemental formation would begin, forming even heavier elements such as aluminum and silicon. Each stage of this cycle was a result of higher temperatures and higher pressures within the star and led to the creation of heavier and heavier elements.



**FIGURE P-2 A Supernova**  
The bright star in the center of the photo is actually an exploding star. Heavy elements are being formed in this explosion.

This process of fusion, contraction, higher temperature, and pressure followed by more fusion only goes so far. The fusing of lighter elements to form elements up to the mass of iron (26 protons and 30 neutrons) releases energy. Formation of any element heavier than that does not release energy, so the fusion process stops abruptly at that point. It is as if iron forms the ashes of the nuclear fire. When a fire is reduced to ashes, the fire goes out. However, in the stepwise evolution of a star, the first 26 or 27 elements were formed. Yet we have many other familiar elements that are much heavier than iron, such as gold and uranium. What is their origin if not from the interior of a star? The spectacular results of what happens when a huge star exhausted the fuel in its now mainly iron core is what produced the heaviest of the elements.

Other messages from space have given us insight into creation of the heavier elements. In 1987, an extremely bright star was found in the heavens from an observatory in Chile. Only an ordinary dim star had been there the night before. The astronomers became immediately aware that they were witnessing the explosion of a star known as a *supernova*. (See Figure P-2.) This phenomenon had been previously known but was now being witnessed. Apparently, the star had suddenly exhausted the supply of fuel for fusion in its core. Without an energy source to counteract gravity, the star again collapsed. This time the collapse did not stop, causing densities, temperatures, and pressures to go to the extreme. But in a matter of seconds, the collapsing star rebounded in a cataclysmic explosion, propelling the outer layers of the star into outer space along with a huge flux of neutrons (formed when electrons are forced into a proton). Elements such as iron dramatically increased their mass by adding neutrons during and after the explosion. The more massive atoms formed at this time eventually underwent nuclear changes that produced elements with higher and higher atomic numbers such as silver, lead, and gold.

To summarize the sequence of events: (1) A star explodes, sending elements formed by fusion in the star rushing into space along with huge numbers of neutrons. (2) The atoms of the original elements absorb neutrons, increasing the atomic mass. (3) The heavier elements undergo nuclear changes, leading to elements with high atomic numbers. (The heaviest naturally occurring element found on Earth is uranium-238.)

For billions of years, giant clouds of hydrogen have formed and contracted into new generations of stars. Each generation had more and more of the heavier elements. (In fact, astronomers have identified stars with few heavy elements, indicating that they date to near the beginning of time.) Blasted by the force of supernovae, this matter drifted through cold, dark space. About 4.6 billion years ago, a cloud of hydrogen containing the dust and debris from previous stars condensed to form our sun, with enough star dust left over to form eight (or more) planets and many other smaller solid bodies trapped in perpetual orbits around this star. On the third planet out from this ordinary star, atoms of some of the lighter elements assembled into living systems. It sounds somewhat melodramatic, but we are indeed children of the stars.

## The Origin of the Chemical Bond

So far, we have encroached into the disciplines of astronomy and physics. Chemistry came into being when atoms began to bond to each other. Let's return to the early universe, about the time clouds of neutral hydrogen atoms (nuclei and orbiting electrons) were beginning to form. At first, the new hydrogen atoms were very hot. When two hydrogen atoms collided, they bounced away from each other like recoiling billiard balls. When they cooled sufficiently, however, another important event occurred. The two neutral atoms stuck together. The electrons of the two atoms acted like glue, holding the two atoms together.

The sharing of electrons between two atoms is known as a *covalent chemical bond* or simply a *chemical bond*. If it weren't for the fact that two atoms are more stable bonded together than existing apart, the universe would still be just a collection of



gaseous atoms—no continents, no oceans, no moons, no us. The two hydrogen atoms joined together to form a molecule. A *molecule* is composed of two or more atoms chemically bonded together. This is illustrated by the formula  $H_2$ , where the subscript 2 indicates the number of hydrogen atoms present in the molecule. The hydrogen molecule is the primeval molecule. It is the way hydrogen exists except at a very high temperature that forces the atoms apart.

As the universe became enriched in other elements, chemical bonds formed between other elements. In the farthest reaches of space, we have detected many other molecules that have formulas such as  $H_2CO$  (formaldehyde whose molecules contain two hydrogens, one carbon, and one oxygen),  $HCN$  (hydrogen cyanide),  $H_2O$  (water),  $NH_3$  (ammonia), and even more complex species. Like the primeval molecule,  $H_2$ , the atoms in these molecules are held together by chemical bonds. (There is another type of bond that held lithium and hydrogen together in the early universe called an ionic bond. It will be described in Chapter 2.) On Earth, we find molecules ranging from the simplest two-atom hydrogen molecule to those of DNA, which contain millions of atoms.

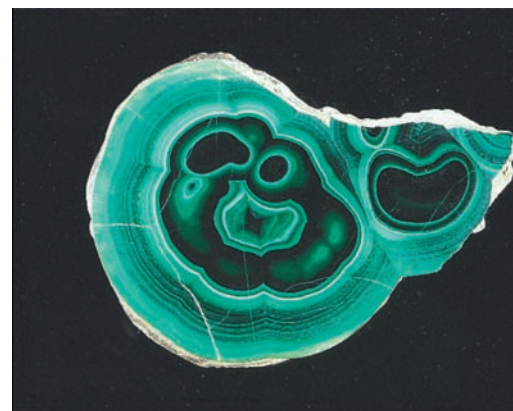
In Chapter 1, we begin our journey into chemistry by emphasizing mathematical skills related to chemistry. In Chapter 2, we then examine the types of matter found in our beautiful planet with its air, oceans, and solid earth. We will then develop and master the topic one step at a time while continuing to emphasize the “big picture.”

## B THE MYSTERY OF FIRE

At about the same time (give or take 100,000 years) that humans may have started to wonder about the meaning of the night sky, they did something more immediately practical with their new ability to reason. It would change their destiny and order in the realm of all other animals. They tamed and put to use one of the most powerful forces in nature: fire.

It is difficult to imagine how our ancient ancestors could have managed without fire. Humans do not have sharp night vision like the raccoon, but fire brought light to the long, dark night. We have no protective fur like the deer, but fire lessened the chill of winter. We do not have sharp teeth or powerful jaws like the lion, but fire rendered meat tender. Humans are not as strong or as powerful as the other large animals, but fire repels even the most ferocious of beasts. It seems reasonable to suggest that the taming of fire was one of the most monumental events in the history of the human race. The use of fire made our species dominant over all others.

Let's fast-forward in time to near the end of the Stone Age, about 10,000 years ago, when fire became the agent that launched us into the world of chemistry. In the Stone Age, weapons and utensils were fashioned from rocks and a few chunks of copper metal (an element) that were found in nature. Copper was superior to stone because pounding could easily shape it into fine points and sharp blades. Unfortunately, native copper was quite rare. But about 7000 years ago this changed. Anthropologists speculate that some resident of ancient Persia found copper metal in the ashes remaining from a hot charcoal fire. The free copper had not been there before, so it must have come from a green stone called malachite (see Figure P-3), which probably lined the fire pit. Imagine the commotion that this discovery must have caused. Hot coals could transform a particular stone into a valuable metal. Fire was the key that launched the human population into the age of metals. The recovery of metals from their ores is now a branch of chemical science called *metallurgy*. The ancient Persians must have considered this discovery a dramatic example of the magic of fire.



**FIGURE P-3 Malachite** Malachite is a copper ore. When heated with charcoal, it forms metallic copper.

Other civilizations used chemistry in various ways. About 3000 B.C., the Egyptians learned how to dye cloth and embalm their dead through the use of certain chemicals found in nature. They were very good at what they did. In fact, we can still determine from ancient mummies the cause of death and even diseases the person may have had. The Egyptians were good chemists, but they had no idea why any of these procedures worked. Every chemical process they used was discovered by accident.

Around 400 B.C., while some Greeks were speculating about their various gods, philosophers were trying to understand and describe nature. These great thinkers argued about why things occurred in the world around them, but they were not inclined (or able) to check out their ideas by experimentation or to put them to practical use. At the time, however, people believed that there were four basic elements of nature—earth, air, water, and fire. Everything else was simply a specific combination of these basic elements. Of the original four elements, fire was obviously the most mysterious. It was the transforming element; that is, it had the capacity to change one substance into another (e.g., certain rocks into metals). We now call such transformations “chemistry.” Fire itself consists of the hot, glowing gases associated with certain chemical changes. If fire is a result of an ongoing chemical transformation, then it is reasonable to suggest that chemistry and many significant advances in the human race are very much related.

The early centuries of the Middle Ages (A.D. 500–1600) in Europe are sometimes referred to as the Dark Ages because of the lack of art and literature and the decline of central governments. The civilizations that Egypt, Greece, and Rome had previously built began to decline. Chemistry, however, began to grow during this period, especially in the area of experimentation. Chemistry was then considered a combination of magic and art rather than a science. Many of those who practiced chemistry in Europe were known as *alchemists*. Some of these alchemists were simply con artists who tried to convince greedy kings that they could transform cheaper metals such as lead and zinc into gold. Gold was thought to be the perfect metal. Such a task was impossible, of course, so many of these alchemists met a drastic fate for their lack of success. However, all was not lost. Many important laboratory procedures such as distillation and crystallization were developed. Alchemists also discovered or prepared many previously unknown chemicals, which we now know as elements and compounds.

Modern chemistry has its foundation in the late 1700s when the use of the analytical balance became widespread. Chemistry then became a quantitative science in which theories had to be correlated with the results of direct laboratory experimentation. From these experiments and observations came the modern atomic theory, first proposed by John Dalton around 1803. This theory, in a slightly modified form, is still the basis of our understanding of nature today. Dalton’s theory gave chemistry the solid base from which it could serve humanity on an impressive scale. Actually, most of our understanding of chemistry has evolved in the past 100 years. In a way, this makes chemistry a very young science. However, if we mark the beginning of chemistry with the use of fire, it is also the oldest science.

From the ancient Persians five millennia ago, to the Egyptians, to the alchemists of the Middle Ages, various cultures have stumbled on assorted chemical procedures. In many cases, these were used to improve the quality of life. With the exception of the Greek philosophers, there was little attention given to why a certain process worked. The “why” is very important. In fact, the tremendous explosion of scientific knowledge and applications in the past 200 years can be attributed to how science is now approached. This is called the scientific method, which we will discuss next.

## C THE SCIENTIFIC METHOD

In ancient times, scientific advances were discovered by accident. This still occurs to some extent, but we have made great strides in how we approach science such that most modern advances occur by design. Consider the case of *tamoxifen*, a chem-

ical that is saving the lives of thousands of women in the United States alone. It is thought to dramatically reduce the chances of recurrence of breast cancer, a frightening disease that now strikes about one in nine American women. In 1998, the Food and Drug Administration (FDA) approved use of the drug to prevent breast cancer in women with a high risk of the disease. But the drug also has undesirable side effects. It may increase the chances of other types of cancer in some women and, in a few cases, causes depression, irritability, and short-term memory loss. However, knowing how tamoxifen works led scientists to produce an improved drug. In December 2004, the drug *anastrozole* was found to be at least as effective as tamoxifen but with fewer side effects. It is now under large-scale testing. How tamoxifen was discovered in the first place and what led to the potentially improved drug are examples of how the *scientific method* improves our lives. But the first step in the scientific method is a long way from producing a useful drug. It simply involves making *observations and gathering data*. As an example, imagine that we are the first to make a simple observation about nature—"the sun rises in the east and sets in the west." This never seems to vary and, as far as we can tell from history, it has always been so. In other words, our scientific observation is strictly *reproducible*. So now we ask "Why?" We are ready for a hypothesis. A **hypothesis** is a *tentative explanation of observations*. The first plausible hypothesis to explain our observations was advanced by Claudius Ptolemy, a Greek philosopher, in A.D. 150. He suggested that the sun, as well as the rest of the universe, revolves around the Earth from east to west. That made sense. It certainly explained the observation. In fact, this concept became an article of religious faith in much of the Western world. However, Ptolemy's hypothesis did not explain other observations known at the time, which included the movement of the planets across the sky and the phases of the moon.

Sometimes new or contradictory evidence means a hypothesis, just like a broken-down old car, must either receive a major overhaul or be discarded entirely. In 1543, a new hypothesis was proposed. Nicolaus Copernicus explained all of the observations about the sun, moon, and planets by suggesting that Earth and the other planets orbit around the sun instead of vice versa. Even though this hypothesis explained the mysteries of the heavenly bodies, it was considered extremely radical and even heretical at the time. (It was believed that God made Earth the center of the universe.) In 1609, a Venetian scientist by the name of Galileo Galilei built a telescope to view ships still far out at sea. When he turned the telescope up to the sky, he eventually produced almost unquestionable proof that Copernicus was correct. Galileo is sometimes credited with the beginning of the modern scientific method because he provided direct experimental data in support of a concept. The hypothesis had withstood the challenge of experiments and thus could be considered a theory. A **theory** is a *well established hypothesis*. A theory should predict the results of future experiments or observations.

The next part of this story comes in 1684, when an English scientist named Sir Isaac Newton stated a law that governs the motion of planets around the sun. A **law** is a *concise scientific statement of fact to which no exceptions are known*. Newton's law of universal gravitation states that planets are held by gravity in stationary orbits around the sun. (See Figure P-4.)



**FIGURE P-4 The Solar System** The Copernican theory became the basis of a natural law of the universe.



In summary, these were the steps that led to a law of nature:

1. Reproducible observations (the sun rises in the east)
2. A hypothesis advanced by Ptolemy and then a better one by Copernicus
3. Experimental data gathered by Galileo in support of the Copernican hypothesis and eventual acceptance of the hypothesis as a theory
4. The statement by Newton of a universal law based on the theory

Variations on the scientific method serve us well today as we pursue an urgent search for cures of diseases. An example follows.

### The Scientific Method in Action



**FIGURE P-5** The Pacific Yew The bark of this tree is a source of an anticancer drug known as Taxol.

The healing power of plants and plant extracts has been known for thousands of years. For example, ancient Sumerians and Egyptians used willow leaves to relieve the pain of arthritis. We now know that extracts of the common willow contain a drug very closely related to aspirin. This is the observation that starts us on our journey to new drugs. An obvious hypothesis comes from this observation, namely, that there are many other useful drugs among the plants and soils of the world. We should be able to find them. There are several recent discoveries that support this hypothesis. For example, the rosy periwinkle is a common tropical plant not too different from thousands of other tropical plants except that this one saves lives. The innocent-looking plant contains a powerful chemical called *vincristine*, which can cure childhood leukemia. Another relatively new drug called Taxol has been extracted from the Pacific yew tree. (See Figure P-5.) Taxol is effective in treating ovarian cancer and possibly breast cancer. Others include cyclosporine, isolated from a fungus in 1957, which made organ transplants possible, and digoxin, isolated from the foxglove plant, used for treatment of heart failure. In fact, many of the best-selling medicines in the United States originated from plants and other natural sources. Besides those mentioned, other drugs treat conditions such as high blood pressure, cancer, glaucoma, and malaria. The search for effective drugs from natural sources and newly synthesized compounds is very active today. These chemicals are screened for potential anticancer, antiarthritic, and anti-AIDS activity. Since the greatest variety of plants, molds, and fungi are found in tropical forests, these species are receiving the most attention. The introduction of a new medicine from a plant involves the following steps.

1. *Collection of materials.* “Chemical prospectors” scour the backwoods of the United States and the tropical forests such as those in Costa Rica, collecting and labeling samples of leaves, barks, and roots. Soil samples containing fungi and molds are also collected and carefully labeled.
2. *Testing of activity.* Scientists at several large chemical and pharmaceutical companies make extracts of the sample in the laboratory. These extracts are run through a series of chemical tests to determine whether there is any antidisease activity among the chemicals in the extract. New methods such as high-throughput-screening (HTS) allow certain chemical companies to screen thousands of chemicals in a single day. If there is antidisease activity, it is considered a “hit” and the extract is taken to the next step.
3. *Isolation and identification of the active ingredient.* The next painstaking task is to separate the one chemical that has the desired activity from among the “soup” of chemicals present. Once that’s done, the particular structure of the active chemical must be determined. A hypothesis is then advanced about what part of the structure is important and how the chemical works. The hypothesis is tested by attempting to make other more effective drugs (or ones with fewer side effects) based on the chemical’s structure. It is then determined whether the chemical or a modified version of it is worth further testing.

4. *Testing on animals.* If the chemical is considered promising, it is now ready to be tested on animals. This is usually done in government and university labs under strictly controlled conditions. Scientists study toxicity, side effects, and the chemical's activity against the particular disease for which it is being tested. If, after careful study, the chemical is considered both effective and safe, it is ready for the next step.
5. *Testing on humans.* The final step is the careful testing on humans in a series of clinical trials carefully monitored by agencies such as the FDA. Effectiveness, dosage, and long-term side effects are carefully recorded and evaluated. All told, it currently takes from 10 to 15 years for a new drug to make it all the way from research and development to market.

If a chemical with the desired activity is randomly discovered, only about one in 1000 may actually find its way into general use. Still, the process works. Many chemicals active against cancer and even AIDS (one has been isolated from the mulberry tree) are now in the pipeline for testing. There is some urgency in all of this. Not only are we anxious to cure specific diseases, but the tropical forests that contain the most diverse plants are disappearing at an alarming rate. In any case, nature is certainly our most important chemical laboratory.

At this time, most of the drugs that originated from synthetic or natural sources are considered cases of "serendipity." We are now moving more toward the concept of "rational drug design." Here, the goal is to identify the active sites on the molecules of diseases such as viruses, tumors, or bacteria. The next step is to deliberately synthesize a drug that attaches to that active site and either destroys or otherwise alters the disease molecules. This sounds easy, but it is not. It requires that we know more about the structure and geometry of these disease molecules. We can then advance hypotheses as to how designed molecules would interact. This is the direction in which pharmaceutical chemists are heading, however.

The scientific method has produced cures for many diseases that have plagued the human race for thousands of years. Eventually, it may lead to a cure or vaccine for AIDS. Our modern scientific methods also produce materials for space travel, all sorts of plastics and synthetic fibers, microchips for computers, and processes for genetic engineering. Just a century ago, everything was made out of stone, wood, glass, metal, or natural fibers (wool, cotton, and silk). Our modern society could hardly function on those materials alone.



CHAPTER

1

# Measurements in Chemistry

To help fly and land this large aircraft safely, a huge number of dials and gauges are displayed in the cockpit. Ground speed, temperature, cabin pressure, altitude, and location are just a few of the measurements that must be continually available to the experienced pilot. To a large degree, the study of nature in general and chemistry in particular is based on observations. But there is much more. We require reproducible, quantitative measurements. How measurements in chemistry are expressed and manipulated are the subjects of this chapter.



**PART A**  
**THE NUMBERS USED IN**  
**CHEMISTRY**

**1-1** The Numerical Value of a  
Measurement

**1-2** Significant Figures and  
Mathematical Operations



**MAKING IT REAL**

*Ted Williams and Significant Figures*

**1-3** Expressing Large and Small  
Numbers: Scientific Notation

**PART B**  
**THE MEASUREMENTS USED**  
**IN CHEMISTRY**

**1-4** Measurement of Mass, Length,  
and Volume



**MAKING IT REAL**

*Worlds from the Small to the Distant—Picometers  
to Terameters*

**1-5** Conversion of Units by the  
Factor-Label Method

**1-6** Measurement of Temperature

**SETTING THE STAGE** Before we were even aware of our own existence, we were being subjected to measurements. Within the first few minutes of our lives, we were placed on a scale and against a tape measure to provide our first weight and length. Years later, as adults, we now find ourselves immersed in a complex world that measures just about anything that lends itself to being measured. For example, it is hard to conceive of being able to operate a modern automobile without a speedometer as well as temperature and fuel gauges. The more expensive the car, the more measurements that are reported by more gauges and dials. If one pays enough, a global positioning satellite will even measure where you are and tell you how to get where you are going. Pilots, carpenters, artists, teachers, and most other professionals and skilled workers are usually involved in some type of measurement. So chemists are hardly unique in their reliance on measurements.

Chemistry is a science that requires us to deal with all the stuff that we see around us. This stuff, which we call matter, is subject to the laws of nature. Many of these laws originate from reproducible quantitative measurements. Measurements naturally contain numbers. The quality, meaning, magnitude, and manipulation of the numbers we use in chemistry form the beginning point of our study. Our journey into the actual concepts of chemistry begins in the next chapter.

If you are not in at least fair physical shape, playing a strenuous sport is not fun—it is exhausting and probably frustrating. Likewise, doing chemistry can be frustrating if you are not in at least fair mathematical shape. It is likely that most students need at least a bit of a mathematical workout to get into shape. For some, a simple review will do, and that is provided in the text. At appropriate points in this chapter, you will also be referred to a specific appendix in the back of the book for more extensive review. Review appendixes include basic arithmetical operations (Appendix A), basic algebra operations (Appendix B), and scientific notation (Appendix C). Also, Appendix E can aid you in the use of calculators for the mathematical operations found in the text. If you are worried about the math, you are not alone. Just remember that this text was written with your concerns in mind.

Measurements consist of two parts—a number and a specific unit. We will discuss these two parts separately. In Part A, we will address questions about the numerical quantity of a measurement. The units that are used in the measurement are then discussed in Part B.

## PART A THE NUMBERS USED IN CHEMISTRY

### SETTING A GOAL

- You will learn how to apply and manipulate measurements to produce scientifically meaningful outcomes.

### OBJECTIVES

- 1-1 (a)** Describe the difference between accuracy and precision. **(b)** Determine the number of significant figures in a measurement.
- 1-2** Perform arithmetic operations, rounding the answer to the appropriate number of significant figures.
- 1-3 (a)** Write very large or small measurements in scientific notation. **(b)** Perform arithmetic operations involving scientific notation.

### ▶ OBJECTIVES FOR SECTION 1-1

**(a)** Describe the difference between accuracy and precision. **(b)** Determine the number of significant figures in a measurement.

## 1-1 THE NUMERICAL VALUE OF A MEASUREMENT



**LOOKING AHEAD!** Much of science is based on numbers. How reliable are the numbers and what do they really tell us? In this section, we will evaluate the quality and reliability of the numbers that are part of a measurement. ■

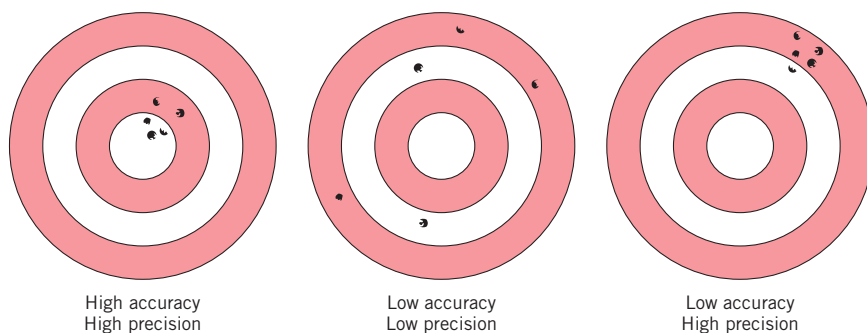
### 1-1.1 The Qualities of a Number

We will start this chapter with a formal definition of a measurement. A **measurement determines the quantity, dimensions, or extent of something, usually in comparison to a specific unit. A unit is a definite quantity adopted as a standard of measurement.** Thus, a measurement (e.g., 1.23 meters) consists of two parts: a numerical quantity (1.23) followed by a specific unit (meters).

First let's consider the numerical value of a measurement. Assume that the evening news informs us that 12,000 people gathered for a concert. Did they mean exactly 12,000? Not really—actually, it was just an estimate. Two other experts may have estimated the same crowd at 13,000 and 11,000, respectively. This means that the original estimate had an uncertainty of  $\pm 1000$ . Thus only the 1 and 2 are considered significant in this estimate. The three zeros simply tell us the magnitude of the number. In a measurement, a **significant figure is a digit that is either reliably known or closely estimated.** In the number 12,000, we can assume the 1 is reliable and reproducible from any number of estimates, but the 2 is estimated. The zeros are not significant since they actually have no specific numerical meaning. Thus, in our example, there are two significant figures: the 1 and the 2. The number of significant figures or digits in a measurement is simply the number of measured digits and refers to the precision of the measurement. **Precision relates to the degree of reproducibility or uncertainty of the measurement.** Indeed, all measured values have an uncertainty that is expressed in the last significant figure to the right.

Now assume the same crowd at the concert is seated in the bleachers of a stadium instead of milling about. In this case, a more precise estimate is possible since the exact capacity of the stadium is known. The crowd can now be estimated at between 12,400 and 12,600, or an average of 12,500. This is a measurement with three significant figures. The 1 and 2 are now reliable, but the third significant figure, the 5, is estimated. The extra significant figure means that the uncertainty is now reduced to  $\pm 100$ . The more significant figures in a measurement, the more precise it is. If the crowd went through a turnstile before entering the stadium, an even more precise number could be given. Notice that the significant figure farthest to the right in a measurement is estimated.

Participants in the sport of riflery (target shooting) are judged on two points: how close the bullet holes are to each other (the pattern) and how close the pattern is to the center of the target known as the bull's-eye. The precision of the contestant's shooting is measured by the tightness of the pattern. How close the pattern is to the bull's-eye is a measure of the shooter's accuracy. **Accuracy in a measurement refers to how close the measurement is to the true value.** Usually, the more precise the measurement, the more accurate it is—but not always. In our example, if a certain competitor has a faulty sight on the rifle, the shots may be close together (precise) but off center (inaccurate). (See Figure 1-1.)



**FIGURE 1-1 Precision and Accuracy** High precision does not necessarily mean high accuracy.

Accuracy in measurements depends on how carefully the instrument of measurement has been calibrated (compared to a reliable standard). For example, what if we attempted to measure length with a plastic ruler that became warped after being left in the hot sun? We obviously would not obtain accurate readings. We would need to recalibrate the ruler by comparing its length divisions to a reliable standard.

### 1-1.2 Zero as a Significant Figure

It would be easy to determine the number of significant figures in a measurement if it were not for the number zero. Unfortunately, zero serves two functions: as a reliable or estimated digit, or simply as a marker to locate the decimal point (such as the three zeros in the estimated crowd of 12,000 people). Since the zeros look alike in both cases, it is important for us to know whether a zero is significant or is there simply to locate the decimal point. The following rules can be used to tell us about zero. Digits that are underlined are significant.

1. When a zero is between other nonzero digits, it is significant. 709 has three significant figures. Zeros between two nonzero digits are always significant.
2. Zeros to the right of a nonzero digit and to the right of the decimal point are significant. 8.0 has two significant figures, just as 7.9 and 8.1 do. 7.900 has four significant figures. There is no value difference between 8.0 and just 8. Why, then, is the zero added? Quite simply because it is an estimated digit and should be included.
3. Zeros to the left of the first nonzero digit are not significant. 0.0078 and 0.45 both have two significant figures; 0.04060 has four significant figures. In this case, the zeros to the left of the digit are simply showing the decimal place and are not measured or estimated digits. Therefore, they are not significant.
4. Zeros to the left of an implied decimal point may or may not be significant. In most cases, they are not. The crowd of 12,000 has two significant figures, as does 6600. Just as in the above case, the zeros to the left are decimal place holders, not actual measurements. What if the zero in a number such as 890 is actually an estimated digit and thus significant? This is a tough question. Some texts use a line over the zero to indicate that it is significant (e.g., 890), and others simply place a decimal point after the zero (e.g., 890.). As we will see in Section 1-3, there is a solution to this dilemma.

In most problems used in this text, measurements are expressed to three significant figures. Therefore, in calculations where other numbers have three significant figures, we will assume that numbers such as 890 also have three significant figures.

**EXAMPLE 1-1****Evaluating Zero as a Significant Figure**

How many significant figures are in the following measurements? What is the uncertainty in each of the measurements?

- (a) 1508 cm    (b) 300.0 ft    (c) 20.003 lb    (d) 0.00705 gal

**PROCEDURE**

To determine the number of significant figures, refer to the rules regarding zero that were listed. Since these numbers all involve measurements, the last significant figure to the right is estimated. This digit indicates the uncertainty of the measurement.

**SOLUTION**

- (a) The zero between the two nonzero digits is significant. There are four significant figures. The uncertainty is in the last digit to the right, so is  $\pm 1$  cm.
- (b) The zero to the right of the decimal point is significant because it is displayed. Therefore, the other two zeros are also significant because they lie between significant figures. There are four significant figures. The uncertainty is in the last zero to the right, so is  $\pm 0.1$  ft.
- (c) All the zeros are between nonzero digits, so they are all significant. There are five significant figures. The uncertainty is in the last digit to the right, so is  $\pm 0.001$  lb.
- (d) The three zeros to the left of the first nonzero digit are not significant. The zero between the two nonzero digits is significant. Thus, there are three significant figures. The uncertainty is in the last digit to the right, so is  $\pm 0.00001$  gal.

**ANALYSIS**

Be certain not to confuse the concept of “significant” with the idea of “important.” In the measurement 0.00705 gallons, the two zeros immediately following the decimal are most assuredly important to the value of the number. Without them, the value changes. But *significant* refers to a measurement. In that particular example, the measurement doesn’t start until you reach the 7. Therefore, the zeros, while necessary, are not significant.

**SYNTHESIS**

The more significant figures there are in a measurement, the more precise it is. The closest the Earth and sun ever get to one another is 147,098,000 km. The uncertainty is  $\pm 1000$  km. The distance between New York and Philadelphia is 127 km, known with a precision to the nearest kilometer. One would assume that knowing a distance to a kilometer would be more precise than to the nearest 1000 kilometers. And yet, because the measured distance to the sun has six significant figures in it, it is 1000 times more precise than the measured driving distance between the two cities. Which of the four measurements in the problem is the most precise? 20.003 lb. It has more significant figures than any of the others.

**ASSESSING THE OBJECTIVES FOR SECTION 1-1**

**EXERCISE 1-1(a) KNOWLEDGE:** Students in different class sections attempted to measure the mass of a 100.0-gram object. Describe the series of measurements as precise, precise and accurate, or neither.

- (a) class 1: 94.2 g, 93.8 g, 94.4 g, 94.0 g  
 (b) class 2: 94.3 g, 89.7 g, 102.4 g, 97.8 g  
 (c) class 3: 100.2 g, 100.0 g, 99.8 g, 99.8 g

**EXERCISE 1-1(b) SYNTHESIS:** You are determining the boiling point of an unknown compound in degrees Celsius. On three successive attempts, you record 145.5°C, 145.8°C, and 146.0°C. Are your data precise? Are your data accurate? Is there extra information needed to make either of those claims?

**EXERCISE 1-1(c) ANALYSIS:** Determine the number of significant figures in the following measurements:

- (a) 45.00 oz    (b) 0.045 lbs    (c) 45000 s    (d) 0.450 in.

**EXERCISE 1-1(d) SYNTHESIS:** Two models of analytical balance are available for purchase. The first measures to  $\pm 0.01$  gram. The second is more



expensive, but measures to  $\pm 0.0001$  gram. How many significant figures will each give when measuring the mass of an object of about 25 grams? What considerations would you include in determining which model to buy?

(Throughout the text, answers to all Assessing the Objectives exercises can be found at the end of each chapter.)

For additional practice, work chapter problems 1-1, 1-3, 1-4, and 1-6.

## 1-2 SIGNIFICANT FIGURES AND MATHEMATICAL OPERATIONS



**LOOKING AHEAD!** In science we are continually adding, multiplying, or performing other calculations involving various measurements. Often these measurements involve different degrees of precision, so we need to understand how to report the results of such calculations. ■

For under \$10 we can own a small calculator that can almost instantly carry out any calculation we may encounter in general chemistry. This device is truly phenomenal, especially to older scientists, who years ago had to carry out these calculations using a slide rule. (This was a simple but effective device that performed many of the calculations found on an electronic calculator but not as quickly or as precisely.) The use of the calculator does have one serious drawback, however. It does not necessarily report the answer to a calculation involving measurements to the proper precision or number of significant figures. For example, 7.8 divided by 2.3 reads 3.3913043 on a standard eight-digit display. However, if the numbers represented measurements known to only two significant figures (e.g., 7.8 lb and 2.3 qt), then the calculator has created the illusion that these numbers were known to a much greater precision. Since the calculator does not express the answer to the calculation with the proper precision, we must know how to prune the answer so that the reported value is honest and appropriate.



The calculator does not give the answer to the proper number of decimal places or significant figures.

### 1-2.1 Rules for Addition and Subtraction and Rounding Off

There are two sets of rules for properly expressing the result of a mathematical operation: one applies to addition and subtraction and the other applies to multiplication and division. We will discuss the rule for addition and subtraction first.

When numbers are added or subtracted, the answer is expressed to the same number of decimal places as the measurement with the fewest decimal places. Or, in other words, the summation must have the same degree of **uncertainty** as the measurement with the most uncertainty (e.g.,  $\pm 100$  has more uncertainty than  $\pm 10$  and  $\pm 0.1$  more than  $\pm 0.01$ ). This is illustrated by the following summation.

$$\begin{array}{r} 10.6871 \quad (\text{four decimal places, or uncertainty of } \pm 0.0001) \\ \underline{1.42} \quad (\text{two decimal places, or uncertainty of } \pm 0.01) \\ 12.1071 = \underline{\underline{12.11}} \quad (\text{two decimal places, or uncertainty of } \pm 0.01) \end{array}$$

Notice that 1.42 and the answer have the same uncertainty. Therefore, expressing the 71 in the summation has no meaning and cannot be included except for rounding-off purposes. The calculator does not give the answer to the proper number of decimal places.

The rules for rounding off a number are as follows (the examples are all to be rounded off to three significant figures).

1. If the digit to be dropped is less than 5, simply drop that digit (e.g., 12.44 is rounded down to 12.4).

2. If the digit to be dropped is 5 or greater, increase the preceding digit by one (e.g., 0.3568 is rounded up to 0.357, and 13.65 is rounded up to 13.7). Note that the number 12.448 is rounded up to 12.45 if it is to be expressed to four significant figures or two decimal places, and down to 12.4 if it is to be expressed to three significant figures or one decimal place.

Recall our original example of a concert crowd estimated at 12,000 people. In cases like this where a decimal point is not shown, we must be careful how we add or subtract numbers from zeros that are not significant. The answer must still show the same precision as before (e.g.,  $\pm 1000$ ). For example, if we tried to subtract 8 or 80 from 12,000, it would not change our estimate, since the resulting numbers must still be rounded off to 12,000. Subtracting 800, however, would affect the result, since we can now round off the number to 11,000. These three operations are illustrated as follows.

$$\begin{array}{r} 12,000 \\ - \quad 8 \\ \hline 11,992 = \underline{\underline{12,000}} \end{array} \qquad \begin{array}{r} 12,000 \\ - \quad 80 \\ \hline 11,920 = \underline{\underline{12,000}} \end{array} \qquad \begin{array}{r} 12,000 \\ - \quad 800 \\ \hline 11,200 = \underline{\underline{11,000}} \end{array}$$

**EXAMPLE 1-2****Expressing Summations and Subtractions to the Proper Decimal Place**

Carry out the following calculations, rounding off the answer to the proper decimal place.

$$\begin{array}{lll} \text{(a)} & \begin{array}{r} 7.56 \\ 0.375 \\ +14.2203 \\ \hline \end{array} & \text{(b)} \begin{array}{r} 14,000 \\ 580 \\ +75 \\ \hline \end{array} & \text{(c)} \begin{array}{r} 0.0327 \\ -0.00068 \\ \hline \end{array} \end{array}$$

**PROCEDURE**

Refer to the rules on addition. In **(a)** the answer should be rounded off to two decimal places since the uncertainty is  $\pm 0.01$ , as in 7.56. In **(b)**, the zeros are all to be considered nonsignificant, so the answer should be rounded off to  $\pm 1000$ , which is the implied uncertainty in 14,000. In **(c)**, the answer should have an uncertainty of  $\pm 0.0001$ , as in 0.0327.

**SOLUTION**

- (a)** 22.16 (Round off 22.1553 to two decimal places.)  
**(b)** 15,000 (Round off 14,655 to thousands.)  
**(c)** 0.032 (Round off 0.03202 to three decimal places.)

**ANALYSIS**

Make certain to distinguish between the answer to a calculation and a measurement made in a lab setting. Calculations need to be rounded according to the rules in order to make sense. Measurements themselves should be made as precisely as the measuring device allows; they are never rounded.

**SYNTHESIS**

These are not just rules to be applied, but common sense ways of dealing with measurements. If you had two friends who lived in a town 450 miles away, and one lived a mile farther down the road than the other, you wouldn't say that the one was 450 miles from you and the other was 451 miles. You'd describe both friends as living 450 miles from you. Compared to the uncertainty in the larger measurement, which may be several miles, that extra mile really makes no difference to the total distance.

**1-2.2 Rules for Multiplication and Division**

In multiplication and division, we consider the number of significant figures in the answer rather than the number of decimal places. The answer is expressed with the same number of significant figures as the multiplier, dividend, or divisor with the least number of significant figures. In other words, the answer can be only as precise as the least precise part of the calculation (i.e., the chain is only as strong as its weakest link). We must be careful with this rule, however. If one of the multipliers represents a whole-

number count, rather than a measurement, then the multiplication is essentially a shortcut to addition. In this case, the rules for addition are appropriate. For example, if one cheeseburger weighs 352.4 grams, then three cheeseburgers weigh 1057.2 grams [i.e.,  $3 \text{ (exact)} \times 352.4 = 1057.2 \text{ grams}$ ]. In this case, because the multiplication of 352.4 by 3 is the same calculation as  $352.4 + 352.4 + 352.4$ , the answer should be expressed to one decimal place. This can be a confusing wrinkle to that rule, but we will remind you of this exception when it shows up in some future exercises. Just remember that in addition and subtraction we are concerned with the decimal point, but in multiplication and division we are concerned with the number of significant figures.

**EXAMPLE 1-3****Expressing Multiplications and Divisions to the Proper Number of Significant Figures**

Carry out the following calculations. Assume the numbers represent measurements; so the answer should be rounded off to the proper number of significant figures or decimal places.

(a)  $2.34 \times 3.225$

(b)  $\frac{11.688}{4.0}$

(c)  $(0.56 \times 11.73) + 22.34$

**PROCEDURE**

Refer to the rules on multiplication and division. The answer should have the same number of significant figures as the number in the calculation with the least.

**SOLUTION**

- (a) The answer on the calculator reads 7.5465. Since the first multiplier has three significant figures and the second has four, the answer should be expressed to three significant figures. The answer is rounded off to 7.55.
- (b) The answer shown on the calculator is 2.922 but should be rounded off to two significant figures because 4.0 has two significant figures. The answer is 2.9.
- (c) In cases where we must use both rules, carry out the exercise in parentheses first, round off to the proper number of significant figures, and then add and finally round off to the proper decimal place.

$$(0.56 \times 11.73) = 6.6 \quad 6.6 + 22.34 = \underline{28.9}$$

**ANALYSIS**

Numbers in chemistry are fundamentally different from numbers in math. In math, a 6 is a 6 and nothing else. In chemistry, if you measure something to be 6°C, it may actually only be 5.8°C. Every measurement has a degree of uncertainty in it. As such, any time calculations are done with measured values, there is uncertainty in the calculations. When numbers are multiplied, the uncertainties are multiplied, too. Small errors in several measurements that are to be multiplied can lead to very large uncertainties in the final values. Therefore, we always strive to make our measurements as accurate as we possibly can.

Consider another example of the difference between math and science: in math  $6 \times 6 = 36$ , but in science,  $6 \text{ in.} \times 6 \text{ in.} = 40 \text{ in.}^2$ . Do you understand why?

**SYNTHESIS**

Smaller measuring devices like graduated cylinders are generally more accurate than larger ones. Large devices hold more. What's a good rule of thumb when using measuring equipment as regards which one to choose? Pick the smallest cylinder that will hold what it is that you're trying to measure. Make only one measurement. The smallest device will give you the most precise reading, but it defeats the purpose if you have to refill it several times.

**ASSESSING THE OBJECTIVE FOR SECTION 1-2**

**EXERCISE 1-2(a) KNOWLEDGE:** To how many significant figures should the following calculations be rounded, assuming that the numbers are all measurements?

(a)  $45.0 \times 1.43$       (b)  $0.0034 \times 143.7$       (c)  $50 \times 138$

**EXERCISE 1-2(b) KNOWLEDGE:** To what decimal place should the following calculations be rounded, assuming that the numbers are all measurements?

(a)  $15.9 + 0.27$     (b)  $420 + 38.34$     (c)  $0.04 + 0.26$

**EXERCISE 1-2(c) ANALYSIS:** Perform the following calculations and round your answer to the appropriate number of significant figures.

(a)  $19.63 + 0.366$     (b)  $0.200 \times 12.765$     (c)  $(12.45 - 11.65) \times 2.68$

**EXERCISE 1-2(d) SYNTHESIS:** Which calculation is more precise, one made from many very precise measurements and a single less precise one, or one made from several modestly precise measurements?

*For additional practice, work chapter problems 1-8, 1-12, 1-14, and 1-22.*

MAKING

IT

REAL

### Ted Williams and Significant Figures



Ted Williams, a baseball legend.

Ted Williams was possibly the best hitter that baseball has ever known. He played from 1939 to 1960, interrupted by service as a fighter pilot in World War II and again in the Korean War. He was a true American hero. The “Splendid Splinter,” as he was known, passed away on July 5, 2002, at age 83.

So what does Ted Williams have to do with chemistry? Not much, actually. But his most important record has a lot to do with significant figures and how numbers are rounded off. Among

many other records that he set, Williams was the last major leaguer to hit the magical “400” in a season. In 1941, Williams, of the Boston Red Sox, had 185 hits in 456 at-bats. Baseball averages are computed by dividing the number of hits by the number of at-bats, expressed as

a decimal fraction rounded off to three significant figures. Thus his official final average was 406 (i.e., 0.406).

But there is more to this story. With one final day of baseball remaining, Williams had 179 hits in 448 at-bats for an average of 0.39955, which would officially round off to 0.400. If he had had only one fewer hit for the entire season, his average would have been 0.397—great but still not 400. The Boston manager, Joe Cronin, offered to let Ted sit out the final day’s games (a double-header) and preserve his 400 average for the record books. Ted was a true professional, however, so he put his 400 average at risk and played both games. If he got only three hits out of eight at-bats for the day, his average would drop to 0.39912, which now rounds off to 0.399. He would have to go four for eight or at least three for seven to preserve his average. Williams ended the day with a home run, a double, and four singles out of eight at-bats, which brought his average up to 0.4057 for an official average of 0.406.

The great Ted Williams did not want to settle for a record that had to be “rounded off.”

#### ▶ OBJECTIVES FOR SECTION 1-3

- (a) Write very large or small measurements in scientific notation.  
 (b) Perform arithmetic operations involving scientific notation.

## 1-3 EXPRESSING LARGE AND SMALL NUMBERS: SCIENTIFIC NOTATION



**LOOKING AHEAD!** The study of chemistry requires that we deal with some extremely large or small numbers. Keeping track of five or more nonsignificant zeros in these numbers is close to impossible. So how can we express the numbers in a more compact and readable form? That is the subject we review in this section, with further information and exercises in Appendix C. ■

### 1-3.1 Changing Numbers into Scientific Notation

It takes more than a quick glance at a number such as 0.0000078 in. to have any idea of its magnitude. However, if the number is written as  $7.8 \times 10^{-6}$  in., one can immediately gauge its value. When numbers require the use of many nonsignificant zeros, we express these numbers in scientific notation. In **scientific notation**, a given value is expressed as a number written with one nonzero digit to the left of the decimal point and all other digits to the right of it. This number is then multiplied by 10 raised to a given power, called the exponent. The **exponent** indicates the magnitude of the number. Following are some powers of 10 and their equivalent numbers.

$$\begin{array}{ll} 10^0 = 1 & 10^{-1} = \frac{1}{10^1} = 0.1 \\ 10^1 = 10 & 10^{-2} = \frac{1}{10^2} = 0.01 \\ 10^2 = 10 \times 10 = 100 & 10^{-3} = \frac{1}{10^3} = 0.001 \\ 10^3 = 10 \times 10 \times 10 = 1000 & 10^{-4} = \frac{1}{10^4} = 0.0001 \\ 10^4 = 10 \times 10 \times 10 \times 10 = 10,000 & \text{etc.} \\ \text{etc.} & \end{array}$$

A huge number that we will soon deal with is 602,200,000,000,000,000,000. The way it is expressed, however, is in a much more readable form as follows.

$$6.022 \times 10^{23} \leftarrow \text{Exponent}$$

Notice that the number (6.022, known as the **coefficient**) expresses the proper precision of four significant figures. This expression means that 6.022 is multiplied by  $10^{23}$  (which is 1 followed by 23 zeros).

### 1-3.2 Mathematical Manipulation of Scientific Notation

In the following exercises, we will give examples of how numbers are expressed in scientific notation and how scientific notation is handled in multiplication and division. These examples can serve as a brief review, but if further practice is needed, see Appendix C for additional discussion on adding, squaring, and taking square roots of numbers in scientific notation. Appendix E includes discussion of manipulation of scientific notation with calculators. Before we consider the examples, we can see how scientific notation can remove the ambiguity of numbers such as 12,000, where the zeros may or may not be significant. Notice that by expressing the number in scientific notation, we can make it clear whether one or more of the zeros are actually significant.

$$\begin{array}{l} 1.2 \times 10^4 \text{ has two significant figures} \\ 1.20 \times 10^4 \text{ has three significant figures} \\ 1.200 \times 10^4 \text{ has four significant figures} \end{array}$$

#### EXAMPLE 1-4

#### Changing Ordinary Numbers to Scientific Notation

Express each of the following numbers in scientific notation.

- (a) 47,500    (b) 5,030,000    (c) 0.0023    (d) 0.0000470

#### PROCEDURE

A practical way to convert ordinary numbers to scientific notation is to count places from the original decimal point to where you wish to move the decimal point. In scientific notation we seek a number between 1 and 10 multiplied by  $10^x$ . For



numbers greater than one, the decimal (which may not be shown) is on the right of the number. Count in from the original decimal point to the point where the new one should be. The number of places the decimal is moved to the left will be the positive exponent of ten. For numbers less than one, count in from the original decimal on the left to where the new one should be. The number of places that the decimal is moved to the right will be the negative exponent of ten.

### SOLUTION

(a) The number 47,500 can be factored as  $4.75 \times 10,000$ . Since  $10,000 = 10^4$ , the number can be expressed as

$$\underline{\underline{4.75 \times 10^4}}$$

We can also obtain this result by moving the decimal point four places to the left.

$$\begin{array}{cccc} & 4 & 3 & 2 & 1 \\ & 4 & 7 & 5 & 0 & 0 \\ & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow \\ & 4 & 7 & 5 & 0 & 0 \end{array} = 4.75 \times 10^4$$

(b) The decimal will be moved six places to the left so the exponent will be six.

$$\begin{array}{cccccc} & 6 & 5 & 4 & 3 & 2 & 1 \\ & 5 & 0 & 3 & 0 & 0 & 0 & 0 \\ & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow \\ & 5 & 0 & 3 & 0 & 0 & 0 & 0 \end{array} = \underline{\underline{5.03 \times 10^6}}$$

(c) The number 0.0023 can be factored into  $2.3 \times 0.001$ . Since  $0.001 = 10^{-3}$ , the number can be expressed as

$$\underline{\underline{2.3 \times 10^{-3}}}$$

Or, we can move the decimal point three spaces to the right.

$$\begin{array}{ccc} & 1 & 2 & 3 \\ & 0 & 0 & 0 & 2 & 3 \\ & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow \\ & 0 & 0 & 0 & 2 & 3 \end{array} = 2.3 \times 10^{-3}$$

(d) The decimal point is moved five places to the right.

$$\begin{array}{cccccc} & 1 & 2 & 3 & 4 & 5 \\ & 0 & 0 & 0 & 0 & 4 & 7 & 0 \\ & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow \\ & 0 & 0 & 0 & 0 & 4 & 7 & 0 \end{array} = \underline{\underline{4.70 \times 10^{-5}}}$$

### ANALYSIS

You may find a need to go back and forth between scientific notation and a number's long form. Don't get lost when considering how many places to move the decimal point and in which direction. Quite simply, the exponent tells you the number of spaces to move the decimal point from where it is in the number to where it needs to be for the correct notation format, or vice versa. In regards to whether to move it to the right or to the left, simply realize that positive exponents are for numbers larger than 1 and negative exponents are for numbers smaller than 1, and adjust accordingly. Some may find it is easier to imagine moving the exponent up or down rather than right or left. Consider Example C-2 in Appendix C.

### SYNTHESIS

When should a number be written in scientific notation? When it has become so large or so small that its magnitude is difficult to see at a glance. Alternately, when it has so many zeros in it that it becomes more convenient to use scientific notation. What is 60.4 written in scientific notation?  $6.04 \times 10^1$ . Clearly, scientific notation is not the appropriate choice here. On the other hand, 1,240,000,000 is much more conveniently stated as  $1.24 \times 10^9$ . What's the cutoff? That's generally an issue of personal preference.

## EXAMPLE 1-5

### Multiplying and Dividing Numbers Expressed in Scientific Notation

(Consult Appendix E, Section 3, on how to express exponents of 10 on a calculator.)

Carry out the following operations. Express the answer to the proper number of significant figures.

(a)  $(8.25 \times 10^{-5}) \times (5.442 \times 10^{-3})$       (b)  $(4.68 \times 10^{16}) \div (9.1 \times 10^{-5})$

### PROCEDURE

In both (a) and (b), group the digits and the powers of 10. In (a), carry out the multiplication of the digits and round off the answer to three significant figures. Add the exponents. Change the number to scientific notation. In (b), group the digits and carry out the division; express the answer to two significant figures. Change the number to scientific notation.

**SOLUTION**

$$\begin{aligned} \text{(a)} \quad (8.25 \times 5.442) \times (10^{-5} \times 10^{-3}) &= 44.9 \times 10^{-8} \\ &= \underline{4.49 \times 10^{-7}} \text{ (three significant figures)} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \frac{4.68 \times 10^{16}}{9.1 \times 10^{-5}} &= \frac{4.68}{9.1} \times \frac{10^{16}}{10^{-5}} \\ &= 0.51 \times 10^{16-(-5)} \\ &= 0.51 \times 10^{21} \\ &= 5.1 \times 10^{20} \text{ (two significant figures)} \end{aligned}$$

**ANALYSIS**

One of the advantages to scientific notation is that, because of the format, you can tell instantly how many significant figures are in a given measurement. It's always just the number of digits in the coefficient. By rule 2 in Section 1-1.2, any zeros found in correctly written scientific notation are automatically significant.

**SYNTHESIS**

Scientific notation can be used when there is no other convenient way to express the answer. Consider this tricky little problem:  $15.6 \times 64.1 = \text{????}$ . When entered into a calculator, 999.96 is the answer returned. By the rules of significant figures, the answer should have three digits, but nines round up, so then the answer rounds to 1000. As written, though, there's no way to know the number of significant figures. Only scientific notation can clearly illustrate the three significant digits. What, then, is the best expression of the answer?  $1.00 \times 10^3$

**ASSESSING THE OBJECTIVES FOR SECTION 1-3**

**EXERCISE 1-3(a) KNOWLEDGE:** Write the following numbers in scientific notation:

(a) 34,500      (b) 0.00000540      (c) 0.2

**EXERCISE 1-3(b) KNOWLEDGE:** Convert the following numbers to decimal form:

(a)  $9.854 \times 10^8$       (b)  $1.400 \times 10^{-3}$       (c)  $5.4 \times 10^0$

**EXERCISE 1-3(c) ANALYSIS:** With the aid of a calculator, perform the following calculations, rounding your answer as appropriate:

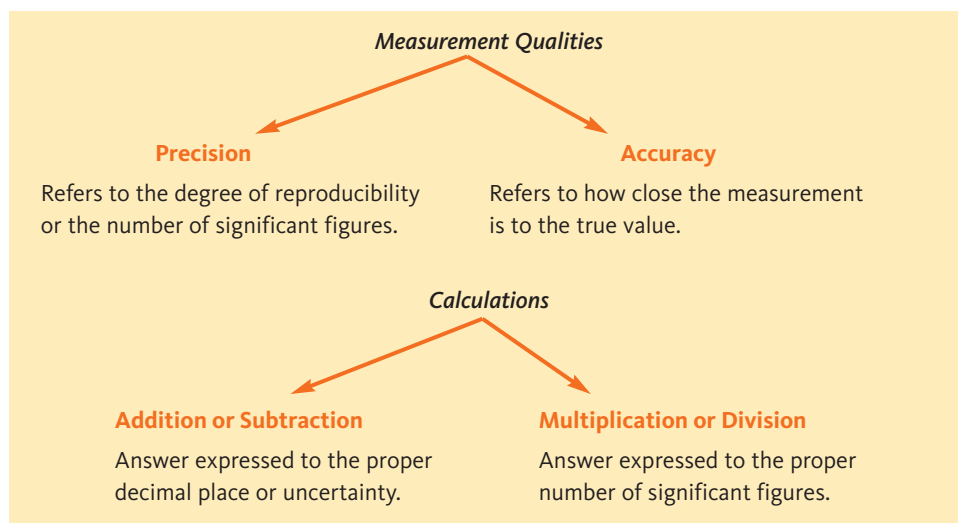
(a)  $(9.41 \times 10^{12}) \times (2.7722 \times 10^{-5})$       (b)  $\frac{4.856 \times 10^{10}}{2.0 \times 10^4}$

*For additional practice, work chapter problems 1-30, 1-32, 1-34, and 1-36.*

**PART A SUMMARY****KEY TERMS**

- 1-1.1 A **measurement** contains a numerical value and a specific **unit**. p. 16
- 1-1.1 The number of **significant figures** in a measurement is the number of measured or estimated digits. p. 16
- 1-1.1 The **precision** of a measurement relates to the number of significant figures, while the **accuracy** of a measurement relates to how close it is to the actual value. pp. 16–17
- 1-2.1 The precision of a measurement relates to its **uncertainty**. p. 19
- 1-3.1 Very large and very small numbers are conveniently expressed in **scientific notation**. p. 23
- 1-3.1 In scientific notation, the power of 10 is known as the **exponent**, while the number with one digit to the left of the decimal point is the **coefficient**. p. 23

## SUMMARY CHARTS



**PART B**  
THE MEASUREMENTS USED  
IN CHEMISTRY

## SETTING A GOAL

- You will learn how to manipulate the units of measurement for the purposes of problem solving.

## OBJECTIVES

- 1-4** List several fundamental and derived units of measurement in the metric (SI) system.
- 1-5** Interconvert measurements by the factor-label method.
- 1-6** Identify several key points on the Celsius and Kelvin temperature scales.

▶ **OBJECTIVE FOR SECTION 1-4**

List several fundamental and derived units of measurement in the metric (SI) system.

## 1-4 MEASUREMENT OF MASS, LENGTH, AND VOLUME



**LOOKING AHEAD!** Now that we have examined the numerical part of a measurement, we are ready to examine the other part—the units that are expressed in the measurement. We will consider some of the units used in chemistry and how they are defined. ■

### 1-4.1 The English System of Measurements

In the United States, we use a measurement of length called the foot. The standard for this unit was not particularly scientific, as it referred to the length of a certain English king's foot (Henry VIII). Another disadvantage of the English system is that it can be awkward. For example, a trophy bass out of a midwestern lake tips the scale at 9 lb 6 oz. An eagerly recruited basketball player for a men's college team tops out at 6 ft 11 in. Thus, we often need to use two units (e.g., feet and inches) to report only one measurement. A third major problem with these units is that they lack any systematic relationship between units (see Table 1-1). The monetary system in the United States is an exception because it is based on the decimal system. Therefore, only one unit (dollars and decimal fractions of dollars) is needed to show a typical student's dismal financial condition (e.g., \$11.98). The British system was decimalized in 1971. Before that time, it had 12 pence to the shilling and 20 shillings to the pound.

**TABLE 1-1** Relationships Among English Units

| LENGTH                        | VOLUME                      | MASS                          |
|-------------------------------|-----------------------------|-------------------------------|
| 12 inches (in.) = 1 foot (ft) | 2 pints (pt) = 1 quart (qt) | 16 ounces (oz) = 1 pound (lb) |
| 3 ft = 1 yard (yd)            | 4 qt = 1 gallon (gal)       | 2000 lb = 1 ton               |
| 1760 yd = 1 mile (mi)         | 42 gal = 1 barrel (bbl)     |                               |

### 1-4.2 The Metric System of Measurements

Most of the world and the sciences use the **metric system** of measurement for length, volume, and mass. The principal metric unit for length is the **meter**. **Volume** is the space that a sample of matter occupies and its principal metric unit is the **liter**. **Mass** is the quantity of matter that a sample contains. The principal metric unit for mass is the **gram**. (See Figure 1-2.) Since 1975, there have been plans to convert to the metric system in the United States, but there has been little progress toward this goal. However, most citizens are becoming more familiar with this system, such as purchasing soda in a 2-L plastic bottle. (See Figure 1-3.) Metric units also form the basis of the SI system, after the French *Système International* (International System). The fundamental SI units that will concern us are listed in Table 1-2. (Other SI units designate measurements that are not used in this text.) The fundamental units of the SI system have



(a)



(b)



(c)

**FIGURE 1-2** Length, Volume, and Mass These properties of a quantity of matter are measured with common laboratory equipment: (a) metric ruler; (b) graduated cylinders, burets, volumetric flasks, and pipet; (c) an electric balance.



**FIGURE 1-3** Metric Units The use of metric units in the United States is becoming common.

**TABLE 1-2** Fundamental SI Units

| MEASUREMENT | UNIT     | SYMBOL |
|-------------|----------|--------|
| Mass        | kilogram | kg     |
| Length      | meter    | m      |
| Time        | second   | s      |
| Temperature | kelvin   | K      |
| Quantity    | mole     | mol    |

very precisely defined standards based on certain known properties of matter and light. For example, the unit of one meter is defined as the distance light travels in a vacuum in  $1/299,792,458$ th of a second. (Originally, it was one-millionth of the distance between the North Pole and the equator on a meridian passing through Paris.) Obviously, the current standard is extremely precise, but when we are aiming a space ship at a planet billions of miles away (e.g., Neptune), we need a great deal of precision in our units. Although some English units were formerly based on a king's anatomy, in modern times many have been

redefined more precisely based on a corresponding metric unit. For example, one inch is now defined as exactly equal to 2.54 centimeters. The relationship between the familiar mile and the kilometer originated from a measurement, but 1 mile is now defined as exactly equal to 1.609344 km. For simplicity in our calculations, however, the relationship is rounded off to four significant figures. That is,  $1.000 \text{ mi} = 1.609 \text{ km}$ .

### 1-4.3 Fundamental Versus Derived Units

Of the many, many possible measurements that can be made, only seven are considered **fundamental**, which means that they cannot be described in terms of anything else. The five fundamental units listed in Table 1-2 can be combined in various useful and meaningful ways to make many other **derived** units. For example, the fundamental unit of distance can be divided by the fundamental unit of time to produce a derived unit called speed. In the English system, speed is measured in the familiar distance and time units of miles per hour. In the metric system, the unit for speed is the meter per second, or m/s. By combining two or more fundamental units through multiplication and division, we can produce all of the other measurements needed by scientists. In Table 1-3, three examples of common derived units are listed. Only volume will concern us at this point. Energy and pressure will be applied in later chapters.

**TABLE 1-3** Some Derived SI Units

| MEASUREMENT | UNIT   | SYMBOL | DERIVATION  |
|-------------|--------|--------|---|
| Volume      | liter  | L      | Length <sup>3</sup>                                     |
| Energy      | joule  | J      | Mass $\times$ Distance <sup>2</sup> / Time <sup>2</sup> |
| Pressure    | pascal | Pa     | Mass / (Time <sup>2</sup> $\times$ Distance)            |

### 1-4.4 The Prefixes Used in the Metric System

The metric system uses prefixes, which are exact multiples of 10 of the basic unit (e.g., meters, liters, or grams). Some of the prefixes refer to smaller portions of the basic unit (e.g., *centi-*, *milli-*, *nano-*) and others to larger portions (e.g., *deca-*, *kilo-*, *mega-*). (See Table 1-4.)

The most common prefixes used in chemistry are *milli-* and *kilo-*. *Centi-* is also commonly used in length (i.e., *cm*). In Making It Real, "Worlds From the Small to the Distant—Picometers to Terameters," we encounter the use of some of these prefixes as well as those expressing smaller and larger dimensions.

There is one other convenient feature of the metric system. There is an exact relationship between length and volume. The SI unit for volume is the cubic meter ( $\text{m}^3$ ). Since this is a rather large volume for typical laboratory situations, liter is used. One liter is defined as the exact volume of 1 cubic decimeter (i.e.,  $1 \text{ L} = 1 \text{ dm}^3$ ). On a smaller scale, 1 milliliter is the exact volume of 1 cubic centimeter ( $1 \text{ mL} = 1 \text{ cm}^3 = 1 \text{ cc}$ ). Thus the units milliliter and cubic centimeter can be used interchangeably when expressing volume. (See Figure 1-4.)



**TABLE 1-4** Prefixes Used in the Metric System

| PREFIX | SYMBOL | RELATION TO BASIC UNIT | PREFIX | SYMBOL  | RELATION TO BASIC UNIT |
|--------|--------|------------------------|--------|---------|------------------------|
| tera-  | T      | $10^{12}$              | deci-  | d       | $10^{-1}$              |
| giga-  | G      | $10^9$                 | centi- | c       | $10^{-2}$              |
| mega-  | M      | $10^6$                 | milli- | m       | $10^{-3}$              |
| kilo-  | k      | $10^3$                 | micro- | $\mu^a$ | $10^{-6}$              |
| hecto- | h      | $10^2$                 | nano-  | n       | $10^{-9}$              |
| deca-  | da     | $10^1$                 | pico-  | p       | $10^{-12}$             |

<sup>a</sup>A Greek letter, mu.

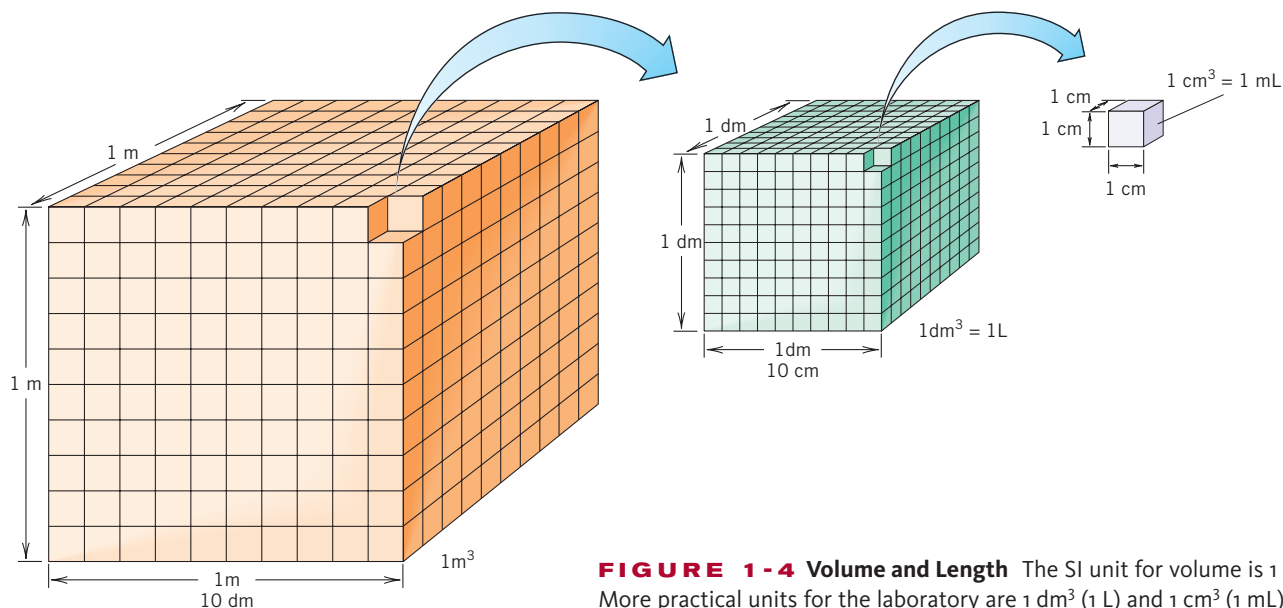
The basic metric unit of mass is the gram, but the SI unit is the kilogram (kg), which is equal to 1000 grams (g). The terms mass and weight are often used interchangeably, but they actually refer to different concepts. **Weight** is a measure of the attraction of gravity for the sample. An astronaut has the same mass on the moon as on Earth. Mass is the same anywhere in the universe. An astronaut who weighs 170 lb on Earth, however, weighs only about 29 lb on the moon. In earth orbit, where the effect of gravity is counteracted, the astronaut is “weightless” and floats free. You can lose all your weight by going into orbit, but obviously your body (mass) is still there. However, since our relevant universe is confined mostly to the surface of Earth, we often use weight as a measure of mass. In this text, we will use the term “mass,” as it is the more scientific term.

### 1-4.5 Relationships Between the Metric and English Systems

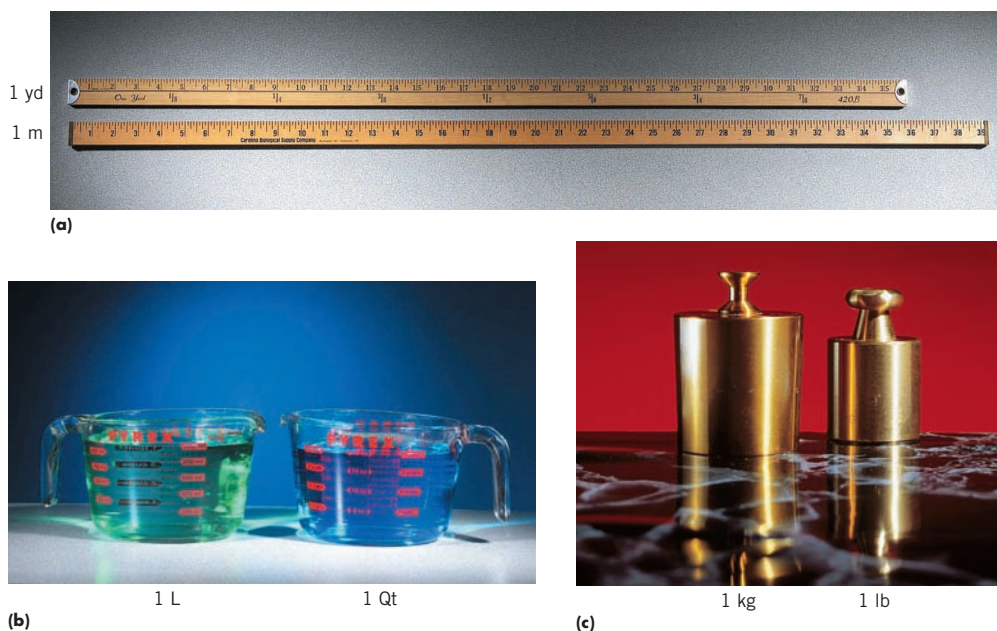
Several relationships between the metric and English systems are listed in Table 1-5. (See also Figure 1-5.) The relationships within systems (e.g., Tables 1-1 and 1-4) are always defined and exact numbers. Because most of the relationships between systems, however, are measured, they are not necessarily exact. Thus, they can be expressed to various degrees of precision. Most of the relationships shown in Table 1-5 are known to many more than the four significant figures given.

**TABLE 1-5** The Relationship Between English and Metric Units

|        | ENGLISH   | METRIC EQUIVALENT |
|--------|-----------|-------------------|
| Length | 1.000 in. | 2.540 cm (exact)  |
|        | 1.000 mi  | 1.609 km          |
| Mass   | 1.000 lb  | 453.6 g           |
|        | 2.205 lb  | 1.000 kg          |
| Volume | 1.057 qt  | 1.000 L           |
|        | 1.000 gal | 3.785 L           |
| Time   | 1.000 s   | 1.000 s           |



**FIGURE 1-4** Volume and Length The SI unit for volume is  $1 \text{ m}^3$ . More practical units for the laboratory are  $1 \text{ dm}^3$  (1 L) and  $1 \text{ cm}^3$  (1 mL).



**FIGURE 1-5**  
**Comparison of Metric and English Units** (a) 1 meter and 1 yard, (b) 1 quart and 1 liter, and (c) 1 kilogram and 1 pound.

### ASSESSING THE OBJECTIVE FOR SECTION 1-4

**EXERCISE 1-4(a) KNOWLEDGE:** List the metric units for the following.  
 (a) mass (b) volume (c) energy (d) temperature.

**EXERCISE 1-4(b) KNOWLEDGE:** What are the powers of 10 for the following metric prefixes?

(a) kilo- (b) centi- (c) milli- (d) Mega-

**EXERCISE 1-4(c) SYNTHESIS:** What are some of the advantages of using the metric system as compared to the English system? Are there any drawbacks?

*For additional practice, work chapter problems 1-47 and 1-48.*

### ▶ OBJECTIVE FOR SECTION 1-5

Interconvert measurements by the factor-label method.

## 1-5 CONVERSION OF UNITS BY THE FACTOR-LABEL METHOD



**LOOKING AHEAD!** When one learns a new language, the first goal is to be able to translate sentences from the new to the familiar. Likewise, to become comfortable with a different system of measurement, we need to convert from one to the other. Converting between systems can be accomplished with an important tool that we will introduce in this section. This will give us a chance to practice solving many of the types of problems that we will eventually encounter. ■

### 1-5.1 Relationships as Conversion Factors

In 1999, a rocket destined to land softly on the planet Mars apparently crashed into the surface instead. Apparently someone did not convert between English and metric units in programming the onboard computers that controlled the landing. This mistake cost about \$1 billion and disappointed a lot of scientists. In fact, we convert between one thing and another all the time. For example, electrical converters



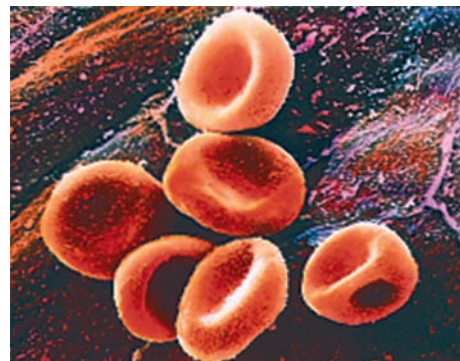
## Worlds from the Small to the Distant—Picometers to Terameters



Saturn is about 1 Tm from Earth.



2 meters tall



Blood cells are about 1  $\mu\text{m}$  in diameter.

The meter is just about right for the world of human beings. For example, our height may be a little less than 2 meters and the room may be about 7 square meters. If people were the size of ants, however, the meter would not be a very practical unit of length. Fortunately, the metric system allows us to venture into the far reaches of other worlds, either small or distant. All we need is a few prefixes to adjust the unit. First, let's shrink ourselves into the world of the small. Our first stop is the "milli" world ( $10^{-3}$  m), where normally small specks now appear large. Those little bugs called mites are of this size; if we lived in this world, it would look a lot more hostile than our world of the meter. When we go to the "micro" world ( $10^{-6}$  m), we are well into the invisible world of the tiny. Blood cells that circulate in our veins have these dimensions (i.e., 1  $\mu\text{m}$ ). Next, we descend to the "nano" world ( $10^{-9}$  m), where we encounter one of the tiniest forms of life, called viruses. Some of these nasty creatures measure 10 nm across. Our final stop is the "pico"

region ( $10^{-12}$  m), where we notice that the basic components of matter, atoms, appear as large spheres. The aluminum atom in a can of soda measures 125 pm in diameter.

Now we take ourselves out away from the surface of Earth and view our surroundings as we ascend into the sky. One km ( $10^3$  m) from the surface we are not that far up. We can still see cars and buildings. But if we ascend to one megameter ( $10^6$  m), we are certainly in outer space. In this region the artificial satellites drift silently by. Our planet still looms large in our vision, with a diameter of about 6 Mm. Now let's ascend to one gigameter ( $10^9$  m) from the surface. We find ourselves well past the moon, which would lie about halfway between us and Earth. Venus is still 32 Gm away. Finally, at one terameter ( $10^{12}$  m), we are nearly to the planet Saturn, which lies about 1.2 Tm from Earth at its closest approach.

The metric system obviously provides convenient units from the smallest to the largest or farthest. Even more units exist that take us to even smaller and farther regions.

change alternating current (AC) to direct current (DC) for devices such as electrical razors or to charge a cell phone battery. What we need is a mathematical converter to change measurements in one unit to those in another. In chemistry this mathematical converter is known as a conversion factor. A **conversion factor** is a relationship between two units or quantities expressed in fractional form. The **factor-label method** (also called **dimensional analysis**) converts a measurement in one unit to another by the use of conversion factors. For example, a conversion factor can be constructed from the exact relationship within the metric system.

$$10^3\text{m} = 1\text{km}$$

This equality can be converted to two fractions as shown below.

$$(1) \frac{1\text{km}}{10^3\text{m}} \quad \text{and} \quad (2) \frac{10^3\text{m}}{1\text{km}} \left( \text{or simply } \frac{10^3\text{m}}{\text{km}} \right)$$



To recharge this cell phone, AC current must be converted into DC current.

These fractional relationships read as “1 kilometer per  $10^3$  meters” and “ $10^3$  meters per 1 kilometer.” The latter fraction is usually simplified to “ $10^3$  meters per kilometer.” When just a unit (no number) is read or written in the denominator, it is assumed to be 1 of that unit. *Factors that relate a quantity in a certain unit to 1 of another unit are sometimes referred to as **unit factors**.* Unit factors are written without the 1 in the denominator in this text. It should be understood, however, that the 1 in the numerator or implied in the denominator can be considered exact in calculations.

Two other conversion factors can be constructed from an equality between English and metric units. For example, the exact relationship between inches (in.) and centimeters (cm) is

$$1 \text{ in.} = 2.54 \text{ cm}$$

which can be expressed in fractional form as

$$(3) \frac{1 \text{ in.}}{2.54 \text{ cm}} \quad \text{and} \quad (4) \frac{2.54 \text{ cm}}{1 \text{ in.}}$$

Each of the four fractions can be used to convert one unit into the other. The general procedure for a one-step conversion by the factor-label method is

$$(\text{what's given}) \times (\text{conversion factor}) = (\text{what's requested})$$

In most conversions, “what’s given” and “what’s requested” each have one unit. The conversion factor has two: the requested or new unit in the numerator and the given or old unit in the denominator. (In this scheme we are assuming that the new or requested unit is in the numerator.)

$$A (\text{given unit}) \times \frac{B (\text{requested unit})}{C (\text{given unit})} = D (\text{requested unit})$$

When combined in the calculation, the given units will appear in both the numerator and the denominator and thus cancel, just like any numerical quantity. The requested unit survives. This is illustrated as follows, where A, B, C, and D represent the numerical parts of the measurements or definitions.

$$\frac{A(\cancel{\text{given unit}}) \times B (\text{requested unit})}{C (\cancel{\text{given unit}})} = D (\text{requested unit})$$

Doing problems by this method is like taking a trip. The first two things we know about a trip are where we start and where we want to end up. The conversion factor is “how” we get from here to there. The key to using the factor-label method is to select the right conversion factor that relates the given and requested units. Recall that the units are to be treated like numerical quantities; that is, they are multiplied, divided, or canceled in the course of the calculation.

### 1-5.2 One-Step Conversions and Unit Maps

We will now give some examples of how the factor-label method is used in some one-step conversions. The first example (1-6) uses familiar units. The second example (1-7) will put to use one of the two conversion factors that we constructed within the metric system, and the next (Example 1-8) will use one of the two conversion factors between the English and metric systems. In the examples, we proceed carefully through four steps.

1. From what is given and what is requested, decide what the conversion factor must do (e.g., convert in. to cm). You can express the procedure in a shorthand method that we will refer to as the **unit map** in this text. (e.g.,  $\boxed{\text{in.}} \rightarrow \boxed{\text{cm}}$ ).
2. Find the proper relationship between units from a table (if necessary). Express the relationship as a conversion factor so that the new unit is in the numerator.

- Put the problem together, making sure that the proper unit cancels and your answer has the requested unit or units.
- Express your answer to the proper number of significant figures.

Be aware of conversion factors that are not the result of measurements but instead are exact definitions. The following relationships are examples of exact definitions

$$12 \text{ in.} = 1 \text{ ft} \quad 4 \text{ qt} = 1 \text{ gal} \quad 1 \text{ km} = 10^3 \text{ m}$$

That is, there are exactly 12 in. (12.0000 etc.) in 1 ft (1.0000 etc.) and so forth. Since exact relationships are considered to have unlimited precision in a calculation, they can be ignored in determining the number of significant figures in an answer. Exact definitions are generally relationships *within* a measurement system (e.g., in. and ft, km and m).

Measurements are never exact, so the number of significant figures shown reflects the precision of the instrument used to make the measurement. The use of exact relationships in calculations can be somewhat confusing at first, so we will remind you when one is being used in calculations in this chapter.

### EXAMPLE 1-6

#### Converting Hours to Days

Convert 129 hours to an equivalent number of days.

#### PROCEDURE

- The unit map for the conversion is



- The well-known relationship is that there are exactly 24 hours in one day. This exact relationship can be written as two conversion factors

$$\frac{24 \text{ hr}}{\text{day}} \quad \text{and} \quad \frac{1 \text{ day}}{24 \text{ hr}}$$

The latter is the appropriate factor since hr (the given unit) is in the denominator and day (the new requested unit) is in the numerator.

#### SOLUTION

$$129 \text{ hr} \times \frac{1 \text{ day}}{24 \text{ hr}} = \underline{\underline{5.38 \text{ day}}}$$

#### ANALYSIS

What would have happened if we had used the first conversion factor (i.e., 24 hr/day) by mistake? In that case, the strange units that result (i.e., hr<sup>2</sup>/day) would alert us that we made a mistake. Paying close attention to the units that cancel and those that don't will be a big help in correctly solving equivalent chemistry problems. Notice also that if we multiplied, the numerical answer would be 3096, which is not a reasonable value.

#### SYNTHESIS

Students sometimes have problems writing a proper conversion factor. For instance, if the conversion is between liters (L) and milliliters (mL), they recognize that there is a relationship of 1000 to 1 between the two. However, is it

$$\frac{1000 \text{ mL}}{\text{L}} \quad \text{or} \quad \frac{1000 \text{ L}}{\text{mL}} ?$$

Rarely would someone make that mistake with units that they're very familiar with, like feet and inches. We all know that it's

$$\frac{12 \text{ in.}}{\text{ft}} \quad \text{not} \quad \frac{12 \text{ ft}}{\text{in.}}$$

However, the concept here is worth noting. Notice that the larger numerical value goes with the smaller-sized unit. That is because the two units in a conversion factor are meant to be equivalent. Keeping that in mind will help prevent you from writing and using incorrect conversions like 100 m/cm.

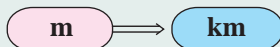


**EXAMPLE 1-7****Converting Meters to Kilometers**

Convert 0.468 m to (a) km and (b) mm.

**PROCEDURE (a)**

1. The unit map for the conversion in (a) is



2. From Table 1-4, we find the relationship is  $10^3 \text{ m} = 1 \text{ km}$ . When expressed as the proper conversion factor, km is in the numerator (requested) and m is in the denominator (given). The conversion factor is

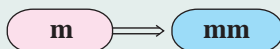
$$\frac{1 \text{ km}}{10^3 \text{ m}}$$

**SOLUTION (a)**

$$0.468 \text{ m} \times \frac{1 \text{ km}}{10^3 \text{ m}} = 0.468 \times 10^{-3} \text{ km} = \underline{\underline{4.68 \times 10^{-4} \text{ km}}}$$

**PROCEDURE (b)**

1. The unit map for the conversion in (b) is



2. From Table 1-4, we find the proper relationship is  $1 \text{ mm} = 10^{-3} \text{ m}$ . When shown as the proper conversion factor, mm is in the numerator (requested) and m is in the denominator (given). The conversion factor is

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

**SOLUTION (b)**

$$0.468 \text{ m} \times \frac{1 \text{ mm}}{10^{-3} \text{ m}} = 0.468 \times 10^3 \text{ mm} = \underline{\underline{468 \text{ mm}}}$$

**ANALYSIS**

Notice that both conversion factors are exact definitions, so do not limit the number of significant figures in the answers. We would expect (a) to be a smaller number than the given number, since the new unit is larger, and (b) to be larger, since the new unit is smaller.

**SYNTHESIS**

How might you convert from mm and km? This could be done as a two-step conversion, as discussed in the next section: millimeters  $\rightarrow$  meters  $\rightarrow$  kilometers, with each step having its own conversion factor.

$$\text{mm} \times \frac{10^{-3} \text{ m}}{\text{mm}} \times \frac{1 \text{ km}}{10^3 \text{ m}}$$

Alternately, you can realize that it is six powers of 10 from milli to kilo, and write a single conversion factor:

$$\frac{1 \text{ km}}{10^6 \text{ mm}}$$

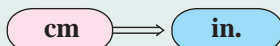
Use the strategy that makes the most sense to you.

**EXAMPLE 1-8****Converting Centimeters to Inches**

Convert 825 cm to in.

**PROCEDURE**

1. The unit map for the conversion is



2. From Table 1-5, we find that the proper relationship is 1 in. = 2.54 cm. Expressed as a conversion factor, in. is in the numerator (requested) and cm is in the denominator (given). The conversion factor is

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

### SOLUTION

$$825 \text{ cm} \times \frac{1 \text{ in.}}{2.54 \text{ cm}} = \underline{\underline{325 \text{ in.}}}$$

### ANALYSIS

Notice that the answer is reasonable, since we expect there to be fewer inches than cm.

### SYNTHESIS

When it comes to having conversion factors at your fingertips, we assume that you are familiar with most English system conversions, like 3 ft per yd, or 16 oz. per lb. Conversions within the metric system are all based on factors of 10: 100, 1000, 0.01, etc. Learn these as quickly as possible. It would also be helpful to memorize one conversion from the English to the metric system for mass, length, and volume. Then you will be able to convert from any given measurement to any other without need for reference, by employing the multistep conversions discussed in the next section.

In conversions between the metric and English systems, we will use a conversion factor with four significant figures. (Recall that the relationship between inches and centimeters, used in Example 1-8, is exact, however.) Since most of the measurements are given to three significant figures, this means that the conversion factor does not limit the precision of the answer. The answer should then be expressed to the same number of significant figures as the original measurement.

### 1-5.3 Multistep Conversions

A one-step conversion like those that have been worked so far is analogous to a direct, nonstop airline flight between your home city and your destination. A multistep conversion is analogous to the situation in which a nonstop flight is not available and you have to make two or more intervening stops before reaching your destination. Each stop in the flight is a separate journey, but it gets you closer to your ultimate destination. When one plans such a journey, one must carefully plan each step, perhaps with the help of a map. Many of our conversion problems also require more than one step and must be carefully planned. In multistep conversion problems, each step along the way requires a separate conversion factor which will be illustrated by the unit map.

For example, let's consider a problem requiring a conversion between two possible units of quantity—number of apples and boxes of apples. Let's assume we know that exactly six apples can be placed in each sack and exactly four sacks make up one box. The problem is, "How many boxes of apples can be prepared with 254 apples?" Since we don't have a direct relationship between apples and boxes, we need a "game plan," which is our unit map. First, we can convert number of apples to number of sacks (conversion a) and then number of sacks to number of boxes (conversion b). The problem and the unit map are set up and completed as follows.

$$\begin{array}{c}
 \text{apples} \xrightarrow{(a)} \text{sacks} \xrightarrow{(b)} \text{boxes} \\
 254 \text{ apples} \times \frac{1 \text{ sack}}{6 \text{ apples}} \times \frac{1 \text{ box}}{4 \text{ sacks}} = \frac{254}{6 \times 4} \text{ boxes} = 10.6 \text{ boxes}
 \end{array}$$

Notice that the two conversion factors represent exact relationships, so they do not affect the number of significant figures in the answer.

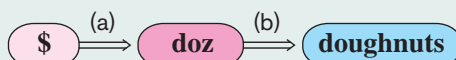
We are now ready to work through some real multistep conversions between units of measurement.

**EXAMPLE 1-9****Converting Dollars to Doughnuts**

How many doughnuts can one purchase for \$123 if doughnuts cost \$3.25 per dozen?

**PROCEDURE**

1. A conversion factor between dollars and individual doughnuts is not directly given. We can solve this problem by making a two-step conversion by (a) converting dollars (\$) to dozen (doz) and then (b) converting dozen to number of doughnuts. The unit map for the conversions is shown as



2. The conversion factors arise from the two relationships: \$3.25 per dozen and 12 doughnuts per dozen (an exact relationship). In conversion factor (a), \$ must be in the denominator to convert to doz. In conversion factor (b) doz [the new unit from the conversion in (a)] must be in the denominator to convert to doughnuts. The two conversion factors are

$$(a) \frac{1 \text{ doz.}}{\$3.25} \quad \text{and} \quad (b) \frac{12 \text{ doughnuts}}{\text{doz.}}$$

**SOLUTION**

$$\$123 \times \frac{(a) \ 1 \text{ doz.}}{\$3.25} \times \frac{(b) \ 12 \text{ doughnuts}}{\text{doz.}} = \underline{\underline{454 \text{ doughnuts}}}$$

**ANALYSIS**

As you are writing conversion factors for a problem, realize that it's not critical to put it in the exact form needed in the problem immediately. Once you have all the factors that you need, you can tell what unit needs to go into the numerator and what needs to be in the denominator, based on the units you are converting. You can enter them correctly when you're setting up the problem.

**SYNTHESIS**

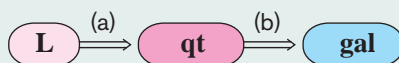
It's always wise to estimate your answer to see if what's calculated is at least reasonable. A quick estimate tells us that at about \$3.00 a dozen, about \$120 will buy us about 40 dozen:  $40 \times 12 = 480$ , which means that our answer is reasonable.

**EXAMPLE 1-10****Converting Liters to Gallons**

Convert 9.85 L to gal.

**PROCEDURE**

1. A two-step conversion is needed. L can be converted into qt (a) and qt then converted into gal (b). The unit map for the conversions is expressed as



2. The two relationships needed are  $1.057 \text{ qt} = 1.000 \text{ L}$  (from Table 1-5) for conversion (a) and  $4 \text{ qt} = 1 \text{ gal}$  (from Table 1-1) for conversion (b). The two relationships properly expressed as conversion factors are

$$(a) \frac{1.057 \text{ qt}}{\text{L}} \quad \text{and} \quad (b) \frac{1 \text{ gal}}{4 \text{ qt}}$$

**SOLUTION**

$$9.85 \text{ L} \times \frac{(a) \ 1.057 \text{ qt}}{\text{L}} \times \frac{(b) \ 1 \text{ gal}}{4 \text{ qt}} = \underline{\underline{2.60 \text{ gal}}}$$

**ANALYSIS**

Remember that the relationship between quarts and gallons is exact, since it is within the English system. We start with about 10 L, which is about 10 qt. Ten quarts is 2.5 gal, so our answer is reasonable.

**SYNTHESIS**

There is not always just one way to do a multistep problem. Suppose you knew that there were 3785 mL in 1 gallon. What conversion factors would be useful in solving the problem with this information? The unit map would be L → mL → gal, and the conversion factors necessary would be:

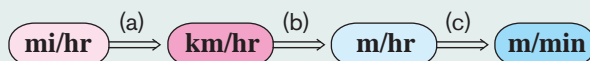
$$\frac{1000 \text{ mL}}{1 \text{ L}} \quad \text{and} \quad \frac{1 \text{ gal}}{3785 \text{ mL}}$$

**EXAMPLE 1-11****Converting Miles per Hour to Meters per Minute**

Convert 55 mi/hr to m/min.

**PROCEDURE**

- In this case, we can convert mi/hr to km/hr (a) and then km/hr to m/hr (b). It is then necessary to change the units of the denominator from hr to min (c). The unit map for the conversions is expressed as



- The needed relationships are 1.000 mi = 1.609 km (from Table 1-5),  $10^3 \text{ m} = 1 \text{ km}$  (from Table 1-4), and 60 min = 1 hr. The relationships expressed as conversion factors are

$$(a) \frac{1.609 \text{ km}}{\text{mi}} \quad (b) \frac{10^3 \text{ m}}{\text{km}} \quad (c) \frac{1 \text{ hr}}{60 \text{ min}}$$

Notice that factor (c) has the requested unit (minutes) in the denominator and the given unit (hours) in the numerator. This is different from all the previous examples because we are changing a denominator in the original unit.

**SOLUTION**

$$55 \frac{\text{mi}}{\text{hr}} \times \frac{1.609 \text{ km}}{\text{mi}} \times \frac{10^3 \text{ m}}{\text{km}} \times \frac{1 \text{ hr}}{60 \text{ min}} = \underline{1.5 \times 10^3 \text{ m/min}}$$

**ANALYSIS**

Recall that the relationships between meters and kilometers and between hours and minutes are exact. Thus the answer should be expressed to two significant figures because of the two digits in the original measurement (55).

**SYNTHESIS**

Though this text uses a single continuous calculation to solve most problems, many students prefer to break problems like this down into two individual problems. First, you can convert the units of distance, miles into meters, and then you can convert the units of time, hours into minutes. Finally, you can take those answers and divide the converted distance by the converted time to arrive at the same answer.

**ASSESSING THE OBJECTIVE FOR SECTION 1-5**

**EXERCISE 1-5(a) KNOWLEDGE:** What are the conversion factors necessary to perform the following conversions?

- (a) g into kg    (b) hr into s    (c) in. into yd    (d) m into cm

**EXERCISE 1-5(b) KNOWLEDGE:** What are the two conversion factors necessary to perform the following conversions?

- (a) oz into kg    (b) cm into ft    (c) mL into qt

**EXERCISE 1-5(c) ANALYSIS:** How many miles are in 25.0 km?

**EXERCISE 1-5(d) ANALYSIS:** A certain size of nail costs \$1.25/lb. What is the cost of 3.25 kg of these nails?

**EXERCISE 1-5(e) SYNTHESIS:** Estimate how many times your heart beats in one day. In one year.

**EXERCISE 1-5(f) SYNTHESIS:** A 2.0-L bottle of cola cost \$1.09. A six-pack of 12-oz cans costs \$1.89. There are 355 mL in 12 oz. What is the cost per ounce of the 2.0-L bottle and the cost per ounce of the cans? Which is the better deal?

*For additional practice, work chapter problems 1-53, 1-54, 1-57, 1-58, 1-64, 1-69, and 1-78.*

► **OBJECTIVE FOR SECTION 1-6**

Identify several key points on the Celsius and Kelvin temperature scales.

## 1-6 MEASUREMENT OF TEMPERATURE



**LOOKING AHEAD!** The final measurement we will consider in this chapter is temperature. Once again, those who grew up in the United States are at a disadvantage. The scale we are most familiar with is not the same as that used by science and most of the rest of the world. We will become more familiar with two other temperature scales in this section.

When someone says an item is “hot,” we can interpret this in several ways. It could mean that this item is something we should have, that it looks great, or that it has a somewhat higher temperature than “warm.” In this section, we will be concerned with the last concept. “Hot” in science refers to temperature. **Temperature** is a measure of the heat energy of a substance. (We will have more to say about the meaning of heat energy in Chapter 3.) A **thermometer** is a device that measures temperature.

### 1-6.1 Thermometer Scales

The thermometer scale with which we are most familiar in the United States is the **Fahrenheit** scale ( $^{\circ}\text{F}$ ), but the **Celsius** scale ( $^{\circ}\text{C}$ ) is commonly used elsewhere and in science. Many U.S. television news shows once broadcast the temperature in both scales, but, unfortunately, this practice has been mostly discontinued. Thermometer scales are established by reference to the freezing point and boiling point of pure water. These two temperatures are constant and unchanging (under constant air pressure). Also, when pure water is freezing or boiling, the temperature remains constant. We can take advantage of these facts to compare the two temperature scales and establish a relationship between them. In Figure 1-6, the temperature of an ice and water mixture is shown to be exactly  $0^{\circ}\text{C}$ . This temperature was originally established by definition and corresponds to exactly  $32^{\circ}\text{F}$  on the Fahrenheit thermometer. The boiling point of pure water is exactly  $100^{\circ}\text{C}$ , which corresponds to  $212^{\circ}\text{F}$ .

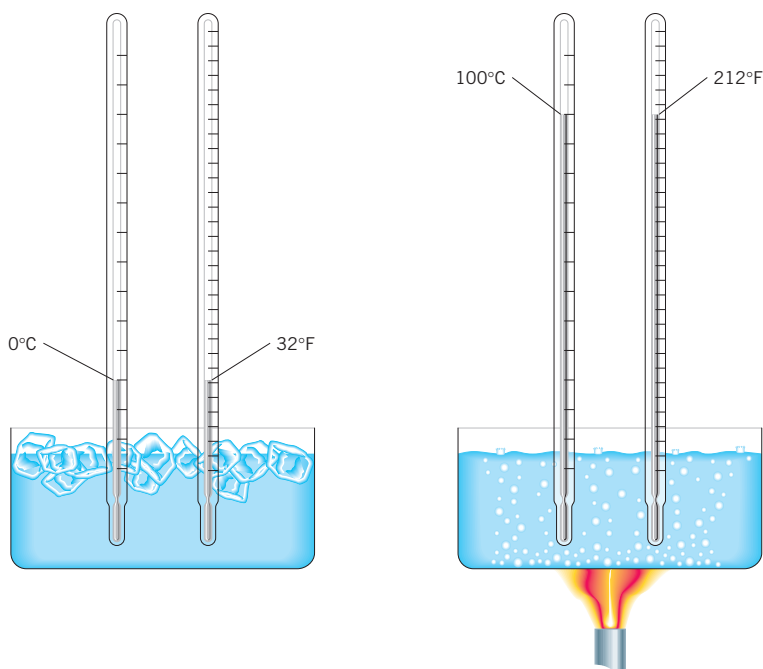
### 1-6.2 Relationships Between Scales

On the Celsius scale, there are 100 equal divisions (div.) between these two temperatures, whereas on the Fahrenheit scale, there are  $212 - 32 = 180$  equal divisions (div.) between the two temperatures. Thus, we have the following relationship between the scale divisions:

$$100 \text{ C div.} = 180 \text{ F div.}$$

This relationship can be used to construct conversion factors between an equivalent number of Celsius and Fahrenheit degrees. The relationship results from





**FIGURE 1-6** The Temperature Scales The freezing and boiling points of water are used to calibrate the temperature scales.

exact definitions, so it does not affect the number of significant figures in the calculation.

$$\frac{100 \text{ C div.}}{180 \text{ F div.}} = \frac{1 \text{ C div.}}{1.8 \text{ F div.}} \quad \text{The inverse relationship is } \frac{1.8 \text{ F div.}}{\text{C div.}}$$

To convert the Celsius temperature [ $T(^{\circ}\text{C})$ ] to Fahrenheit temperature [ $T(^{\circ}\text{F})$ ]:

1. Multiply the Celsius temperature by the proper conversion factor ( $1.8^{\circ}\text{F}/1^{\circ}\text{C}$ ) to get the equivalent number of Fahrenheit degrees.
2. Add  $32^{\circ}\text{F}$  to this number so that both scales start at the same point (the freezing point of water).

$$T(^{\circ}\text{F}) = \left[ T(^{\circ}\text{C}) \times \frac{1.8^{\circ}\text{F}}{1^{\circ}\text{C}} \right] + 32^{\circ}\text{F} = [T(^{\circ}\text{C}) \times 1.8] + 32$$

To convert the Fahrenheit temperature to the Celsius temperature,

1. Subtract  $32^{\circ}\text{F}$  from the Fahrenheit temperature so that both scales start at the same point.
2. Multiply the number by the proper conversion factor ( $1^{\circ}\text{C}/1.8^{\circ}\text{F}$ ) to convert to the equivalent number of Celsius degrees.

$$T(^{\circ}\text{C}) = [T(^{\circ}\text{F}) - 32^{\circ}\text{F}] \times \frac{1^{\circ}\text{C}}{1.8^{\circ}\text{F}} = \frac{[T(^{\circ}\text{F}) - 32]}{1.8}$$

### EXAMPLE 1-12

#### Converting Between Fahrenheit and Celsius

A person with a cold has a fever of  $102^{\circ}\text{F}$ . What would be the reading on a Celsius thermometer?

#### PROCEDURE

Use the equation that converts  $^{\circ}\text{F}$  to  $^{\circ}\text{C}$ :  $T(^{\circ}\text{C}) = \frac{[T(^{\circ}\text{F})] - 32}{1.8}$

#### SOLUTION

$$T(^{\circ}\text{C}) = \frac{102 - 32}{1.8} = \underline{\underline{39^{\circ}\text{C}}}$$

**EXAMPLE 1-13****Converting Between Celsius and Fahrenheit**

On a cold winter day the temperature is  $-10.0^{\circ}\text{C}$ . What is the reading on the Fahrenheit scale?

**PROCEDURE**

Use the equation that converts  $^{\circ}\text{C}$  to  $^{\circ}\text{F}$ :  $T(^{\circ}\text{F}) = (1.8 \times ^{\circ}\text{C}) + 32$

**SOLUTION**

$$T(^{\circ}\text{F}) = (-10.0 \times 1.8) + 32 = \underline{\underline{14.0^{\circ}\text{F}}}$$

**ANALYSIS**

These two calculations represent one of the few times in this text that memorization of an equation is necessary. For most of the problems you'll be doing, the factor-label method is useful and strongly encouraged. In this way, relatively few things need to be committed to memory. In this case, however, because the two scales are offset by 32 degrees, the specific formula is the only way to convert them.

**SYNTHESIS**

Since both scales, Fahrenheit and Celsius, represent straight-line relationships, there is a point where both lines intersect. Said another way, there is a temperature that is the same value on both scales. Put an  $x$  into the equation for both  $^{\circ}\text{F}$  and  $^{\circ}\text{C}$ , and solve. What value do you calculate for  $x$ ? (See chapter problem 1-103.)

The SI temperature unit is called the kelvin (K). Notice that a degree symbol ( $^{\circ}$ ) is not shown with a kelvin temperature. The zero on the **Kelvin scale** is theoretically the lowest possible temperature (the temperature at which the heat energy is zero). This corresponds to  $-273^{\circ}\text{C}$  (or, more precisely,  $-273.15^{\circ}\text{C}$ ). Since the Kelvin scale also has exactly 100 divisions between the freezing point and the boiling point of water, the magnitude of a kelvin and a Celsius degree is the same. Thus we have the following simple relationship between the two scales. The temperature in kelvins is represented by  $T(\text{K})$ , and  $T(^{\circ}\text{C})$  represents the Celsius temperature.

$$T(\text{K}) = T(^{\circ}\text{C}) + 273$$

Thus, the freezing point of water is  $0^{\circ}\text{C}$  or 273 K, and the boiling point is  $100^{\circ}\text{C}$  or 373 K. We will use the Kelvin scale more in later chapters.

**ASSESSING THE OBJECTIVE FOR SECTION 1-6**

**EXERCISE 1-6(a) KNOWLEDGE:** Fill in the following table with appropriate temperatures

|                | FAHRENHEIT | CELSIUS | KELVIN |
|----------------|------------|---------|--------|
| Water boiling  |            |         |        |
| Water freezing |            |         |        |
| Absolute zero  |            |         |        |

**EXERCISE 1-6(b) ANALYSIS:** The temperature of cooking oil reaches  $248^{\circ}\text{F}$ . What is this on the Celsius and Kelvin scales?

**EXERCISE 1-6(c) SYNTHESIS:** Despite U.S. insistence on using the Fahrenheit scale, Celsius seems to make much more sense. It is divided into 100 equal parts and has obvious set points at  $100^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ . Why do you suppose Fahrenheit uses such odd numbers for boiling and freezing?

*For additional practice, work chapter problems 1-94, 1-95, 1-100, and 1-101.*

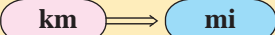
## KEY TERMS

- 1-4.2** Most measurements in chemistry are expressed using the **metric system**. p. 27
- 1-4.2** **Volume** is the space that a given sample of matter occupies and **mass** refers to the quantity of matter that the sample contains. p. 27
- 1-4.2** In the metric system, the principal unit for length is the **meter**, for volume it is the **liter**, and for mass it is the **gram**. p. 27
- 1-4.3** Five **fundamental** units can produce many **derived** units. p. 28
- 1-4.4** **Weight** refers to the attraction of gravity for a quantity of matter. p. 29
- 1-5.1** Converting from one unit of measurement to another requires the use of **conversion factors**. If the factor relates a quantity in one system to 1 in another system, is called a **unit factor**. p. 31
- 1-5.1** The procedure to convert from one measurement to another is the **factor-label** method. p. 31
- 1-5.2** An outline of a conversion procedure is expressed as a **unit map**. p. 32
- 1-6** The **temperature** is measured by a device called a **thermometer**. p. 38
- 1-6.1** The **Fahrenheit** scale is used in the United States, but the **Celsius** scale is used in science. p. 38
- 1-6.2** The **Kelvin scale** begins at absolute zero. p. 39

## SUMMARY CHART

## Sample Conversion

Problem: Convert 10.0 km to miles.

Unit map: 

Relationship: 1.609 km = 1.000 mi

Conversion factor:  $\frac{1 \text{ mi (requested)}}{1.609 \text{ km (given)}}$

Solution:  $10.0 \text{ km} \times \frac{1 \text{ mi}}{1.609 \text{ km}} = 6.22 \text{ mi}$

## CHAPTER SUMMARY

Chemistry, probably more than any other science, is a science of **measurements**. Certainly, that is not all there is—many other concepts are also central to the science—but handling measurements properly is of the highest priority. That is why we needed to address this subject very early in the text. A measurement consists of a number and a **unit**. Our first item of business was to examine the numerical part of a measurement as to the significance of the numbers that are reported. The numerical value has two qualities: **precision** (number of **significant figures** or **uncertainty**) and **accuracy**.

Perhaps a greater challenge than just understanding the precision of one measurement is to handle measurements of varying precision in mathematical operations. Addition and subtraction focus on the precision, or decimal place, in the answer, while multiplication and division are concerned with the number of significant figures.

We won't get too far into the text before we encounter some extremely small and extremely large numbers. Writing large numbers of zeros is cumbersome. **Scientific notation**, however, allows us to write a number in an easy-to-read manner, that is, as a number (the **coefficient**) between 1 and 10 multiplied by 10 raised to a power indicated by the **exponent**. Some of the ambiguities of zero as a significant figure are removed when the number is expressed in scientific notation. Remember, help is available in Appendix C if you are uneasy with scientific notation and using it in calculations.

Next, we turned our attention to units of measurements. Most of us have to become familiar with the SI system and the **metric system** on which it is based, specifically with regard to units of length (**meters**), **mass** or **weight** (**grams**), and volume (**liters**). Compared to the rather unsystematic English system, the metric system has the advantage of decimal relationships

between units. The most common prefixes are **milli**, **centi**, and **kilo**.

Because we need to convert between systems of measurement, we then introduced our main problem-solving technique—the **factor-label method**, also called dimensional analysis. In this, we change between units of measurement using **conversion factors** (usually **unit factors**), which are constructed from relationships between units. When a direct relationship is available between what's given and what's requested, conversion can be accomplished in a one-step calculation as shown in a **unit map**. If not, the calculation is more involved and requires a game plan that outlines step-by-step conversions from given to

requested. This problem-solving method is the language of this text. If you do not follow this method, it is hard to take full advantage of the worked-out examples in this and future chapters.

The final topic of this chapter concerned the measurement of **temperature** using **thermometers**. By comparing the number of divisions between the freezing point and boiling point of water, we can set up conversion factors between the two temperature scales, **Fahrenheit** ( $^{\circ}\text{F}$ ) and **Celsius** ( $^{\circ}\text{C}$ ). A third system, closely related to the Celsius scale, is the **Kelvin scale**. Using an algebraic approach, we are able to convert between Fahrenheit and Celsius as well as between Celsius and Kelvin temperatures.

| OBJECTIVES |  |                                |                        |  |
|------------|--|--------------------------------|------------------------|--|
| SECTION    | YOU SHOULD BE ABLE TO...   | EXAMPLES                       | EXERCISES              | CHAPTER PROBLEMS                       |
| 1-1        | Describe the difference between accuracy and precision.  |                                | 1a, 1b, 1d, 2d         | 1, 2, 3                                |
|            | Determine the number of significant figures in a measurement.  | 1-1                            | 1c                     | 4, 5                                   |
| 1-2        | Perform arithmetic operations, rounding the answer to the appropriate number of significant figures. | 1-2, 1-3                       | 2a, 2b, 2c             | 8, 9, 10, 14, 16, 18, 20, 24           |
| 1-3        | Write very large or small measurements in scientific notation.                                       | 1-4                            | 3a, 3b                 | 28, 30, 32, 34                         |
|            | Perform arithmetic operations involving scientific notation.   | 1-5                            | 3c                     | 38, 40, 42, 44                         |
| 1-4        | List several fundamental and derived units of measurement in the metric (SI) system.                 |                                | 4a, 4b, 4c             | 47, 48, 49                             |
| 1-5        | Interconvert measurements by the factor-label method.  | 1-6, 1-7, 1-8, 1-9, 1-10, 1-11 | 5a, 5b, 5c, 5d, 5e, 5f | 54, 56, 58, 60, 63, 66, 70, 74, 78, 83 |
| 1-6        | Identify several key points on the Celsius and Kelvin temperature scales.                            | 1-12, 1-13                     | 6a, 6b, 6c             | 100, 101, 102                          |

## ANSWERS TO ASSESSING THE OBJECTIVES

### PART A

#### EXERCISES

**1-1(a)** class 1—precise; class 2—neither; class 3—precise and accurate

**1-1(b)** The data are precise, based on the consistency of values. Without knowing what the chemical is and knowing its exact boiling point, it is impossible to say whether or not the data are accurate.

**1-1(c)** (a) four significant figures (b) two (c) two (d) three

**1-1(d)** The first balance would give four significant figures. The second balance would give six significant figures. Which one to buy really depends on the need for the extra preci-

sion versus the cost of the balance. In a teaching lab, it is probably reasonable to purchase the cheaper balance. In a research lab, the extra added precision is the more valuable commodity.

**1-2(a)** (a) three significant figures (b) two (c) just one

**1-2(b)** (a) rounded to the tenths place (b) tens place (c) hundredths place

**1-2(c)** (a) 20.00 (b) 2.55 (c) 2.1

**1-2(d)** One very large error destroys the accuracy of many precisely made measurements. The calculation with several modestly precise measurements will probably be more accurate.

**1-3(a)** (a)  $3.45 \times 10^4$  (b)  $5.40 \times 10^{-6}$  (c)  $2 \times 10^{-1}$

**1-3(b)** (a) 985,400,000 (b) 0.001400 (be sure to include the trailing zeroes to show the precision in the number)  
(c)  $5.4 (10^0 = 1)$

**1-3(c)** (a)  $2.61 \times 10^8$  (b)  $2.4 \times 10^6$

## PART B

### EXERCISES

**1-4(a)** (a) kilogram (b) liter (c) Joule (d) Kelvin

**1-4(b)** (a)  $10^3$  (b)  $10^{-2}$  (c)  $10^{-3}$  (d)  $10^6$

**1-4(c)** The metric system is accepted worldwide. Each prefix is 10 times larger or smaller than the one before it, so changing from one unit to another is as easy as moving a decimal. Each prefix can be applied to any unit, so less memorization is required. It can easily be scaled up or down as far as we need to go. The only real drawback might be our lack of familiarity with it. Full immersion would take care of this problem in a very short period of time.

**1-5(a)** (a) 1 kg/1000 g (b) 3600 s/hr (c) 1 yd/36 in.  
(d) 100 cm/m

**1-5(b)** (a) 1 lb/16 oz and 1 kg/2.205 lb (b) 1 in./2.54 cm and 1 ft/12 in. (c) 1 L/1000 mL and 1.057 qt/1 L

**1-5(c)** 15.5 mi

**1-5(d)** \$8.96

**1-5(e)** At 75 beats per minute;  $1.1 \times 10^5$  beats per day;  $3.9 \times 10^7$  beats per year. Adjust up or down for your particular heart rate.

**1-5(f)** For the 2.0-L bottle, the cost is 1.6¢/oz. For the six-pack, the cost is 2.6¢/oz. Buying soda in 2.0-L bottles is about 40% cheaper. Of course, the downside is that it goes flat faster, and cans are more convenient. Generally, as you know, people buy 2.0-L bottles for parties and cans for individual consumption.

**1-6(a)**

|                | Fahrenheit | Celsius | Kelvin |
|----------------|------------|---------|--------|
| Water boiling  | 212        | 100     | 373    |
| Water freezing | 32         | 0       | 273    |
| Absolute zero  | -460       | -273    | 0      |

**1-6(b)** 120°C; 393 K

**1-6(c)** The reason Fahrenheit has such odd numbers for boiling and freezing is that it wasn't based on those measurements. Instead, it was based on two other specific points. Is it a coincidence that body temperature is approximately 100°F? Consider checking Wikipedia for a number of possible sources.

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Significant Figures (SECTION 1-1)

**1-1.** Which of the following measurements is the most precise?

- (a) 75.2 gal (c) 75.22 gal  
(b) 74.212 gal (d) 75 gal

**1-2.** How can a measurement be precise but not accurate?

**1-3.** The actual length of a certain plank is 26.782 in. Which of the following measurements is the most precise and which is the most accurate?

- (a) 26.5 in. (c) 26.202 in.  
(b) 26.8 in. (d) 26.98 in.

**1-4.** How many significant figures are in each of the following measurements?

- (a) 7030 g (d) 0.01 ft (g) 8200 km  
(b) 4.0 kg (e) 4002 m (h) 0.00705 yd  
(c) 4.01 lb (f) 0.060 hr

**1-5.** How many significant figures are in each of the following measurements?

- (a) 0.045 in. (d) 21.0 m (g) 0.0080 in.  
(b) 405 ft (e) 7.060 qt (h) 2200 lb  
(c) 0.340 cm (f) 2.0010 yd

**1-6.** What is the uncertainty in each of the measurements in problem 1-4? Recall that the uncertainty is  $\pm 1$  expressed in the last significant figure to the right (e.g.,  $5670 = \pm 10$ ).

**1-7.** What is the uncertainty in each of the measurements in problem 1-5? Recall that the uncertainty is  $\pm 1$  expressed in the last significant figure to the right.

### Significant Figures in Mathematical Operations

(SECTION 1-2)

**1-8.** Round off each of the following numbers to three significant figures.

- (a) 15.9994 (e) 87,550  
(b) 1.0080 (f) 0.027225  
(c) 0.6654 (g) 301.4  
(d) 4885

**1-9.** Round off each of the following numbers to two significant figures.

- (a) 115 (f) 0.0396  
(b) 27.678 (g) 1,557,000  
(c) 37,500 (h) 321  
(d) 0.47322  
(e) 55.6



**1-10.** Express the following fractions in decimal form to three significant figures.

(a)  $\frac{1}{4}$       (b)  $\frac{4}{5}$       (c)  $\frac{5}{3}$       (d)  $\frac{7}{6}$

**1-11.** Express the following fractions in decimal form to three significant figures.

(a)  $\frac{2}{3}$       (b)  $\frac{2}{5}$       (c)  $\frac{5}{8}$       (d)  $\frac{13}{4}$

**1-12.** Without doing the calculation, determine the uncertainty in the answer (e.g., if the answer is to two decimal places, uncertainty =  $\pm 0.01$ ).

(a)  $12.34 + 0.003 + 1.2$       (c)  $45.66 + 12 + 0.002$   
 (b)  $26,000 + 450 + 132,500$       (d)  $0.055 + 13.43 + 1.202$

**1-13.** Without doing the calculation, determine the uncertainty in the answer.

(a)  $13,330 + 0.8 + 1554$       (c)  $14,230 + 34 + 1932$   
 (b)  $0.0002 + 0.164 + 0.00005$       (d)  $567 + 7 + 47$

**1-14.** Carry out each of the following operations. Assume that the numbers represent measurements, and express the answer to the proper decimal place.

(a)  $14.72 + 0.611 + 173$       (d)  $47 + 0.91 - 0.286$   
 (b)  $0.062 + 11.38 + 1.4578$       (e)  $0.125 + 0.71$   
 (c)  $1600 - 4 + 700$

**1-15.** Carry out each of the following operations. Assume that the numbers represent measurements and express the answer to the proper decimal place.

(a)  $0.013 + 0.7217 + 0.04$       (c)  $35.48 - 4 + 0.04$   
 (b)  $15.3 + 1.12 - 3.377$       (d)  $337 + 0.8 - 12.0$

**1-16.** A container holds 32.8 qt of water. The following portions of water are then added to the container: 0.12 qt, 3.7 qt, and 1.266 qt. What is the new volume of water?

**1-17.** A container holds 3760 lb (three significant figures) of sand. The following portions are added to the container: 1.8 lb, 32 lb, and 13.55 lb. What is the final mass of the sand?

**1-18.** Supply the missing measurements.

(a) 
$$\begin{array}{r} 6.03 \\ + (\quad) \\ \hline 13.0 \end{array}$$
      (d) 
$$\begin{array}{r} 0.5668 \\ - (\quad) \\ \hline 0.122 \end{array}$$
  
 (b) 
$$\begin{array}{r} (\quad) \\ + 0.9 \\ \hline 138 \end{array}$$
      (e) 
$$\begin{array}{r} 0.0468 \\ + (\quad) \\ \hline 3.25 \end{array}$$
  
 (c) 
$$\begin{array}{r} (\quad) \\ + 0.48 \\ \hline 192 \end{array}$$
      (f) 
$$\begin{array}{r} 47.9 \\ - (\quad) \\ \hline 45.0 \end{array}$$

**1-19.** Supply the missing measurements.

(a) 
$$\begin{array}{r} 98.732 \\ + (\quad) \\ \hline 98.780 \end{array}$$
      (d) 
$$\begin{array}{r} (\quad) \\ + 0.0468 \\ \hline 2.227 \end{array}$$
  
 (b) 
$$\begin{array}{r} 98.732 \\ + (\quad) \\ \hline 98.90 \end{array}$$
      (e) 
$$\begin{array}{r} 9.05 \\ + (\quad) \\ \hline 11.6 \end{array}$$
  
 (c) 
$$\begin{array}{r} 98.732 \\ + (\quad) \\ \hline 99.7 \end{array}$$
      (f) 
$$\begin{array}{r} 0.0377 \\ + (\quad) \\ \hline 0.16 \end{array}$$

**1-20.** Without doing the calculation, determine the number of significant figures in the answer from the following.

(a)  $0.59 \times 87 \times 23.0$       (c)  $\frac{176 \times 0.20}{33.45}$   
 (b)  $\frac{17.0}{2.334}$       (d)  $\frac{0.30 \times 22.42}{0.03}$

**1-21.** Without doing the calculation, determine the number of significant figures in the answer from the following.

(a)  $135,200 \times 0.330$       (c)  $\frac{0.4005 \times 1.2236}{0.0821 \times 298.5}$   
 (b)  $\frac{0.0303}{6.022}$       (d)  $\frac{23.44 \times 0.050}{0.006 \times 75}$

**1-22.** Supply the missing measurements.

(a)  $22.4 \times (\quad) = 136$       (e)  $878.8 / (\quad) = 221$   
 (b)  $22.400 \times (\quad) = 135.5$       (f)  $878.8 / (\quad) = 221.2$   
 (c)  $6.482 \times (\quad) = 55.9$       (g)  $0.7820 / (\quad) = 1.534$   
 (d)  $7 \times (\quad) = 50$

**1-23.** Supply the missing measurements.

(a)  $0.515 \times (\quad) = 1.65$       (d)  $(\quad) / 0.22 = 110$   
 (b)  $0.517 \times (\quad) = 0.04$       (e)  $25.1 / (\quad) = 114$   
 (c)  $6.482 \times (\quad) = 55.90$       (f)  $0.782 / (\quad) = 1.5$

**1-24.** Carry out the following calculations. Express your answer to the proper number of significant figures. Specify units.

(a)  $40.0 \text{ cm} \times 3.0 \text{ cm}$       (c)  $\frac{4.386 \text{ cm}^2}{2 \text{ cm}}$   
 (b)  $179 \text{ ft} \times 2.20 \text{ ft}$       (d)  $\frac{14.65 \text{ in.} \times 0.32 \text{ in.}}{2.00 \text{ in.}}$

**1-25.** Carry out the following calculations. Express your answer to the proper number of significant figures. Specify units.

(a)  $\frac{243 \text{ m}^2}{0.05 \text{ m}}$       (c)  $0.0575 \text{ in.} \times 21.0 \text{ in.}$   
 (b)  $3.0 \text{ ft} \times 472 \text{ ft}$       (d)  $\frac{1.84 \text{ yd} \times 42.8 \text{ yd}}{0.8 \text{ yd}}$

**\*1-26.** Carry out the following calculations. Express your answer to the proper number of significant figures or decimal places.

(a)  $\frac{146}{2.3} + 75.0$       (c)  $(12.688 - 10.0) \times (7.85 + 2.666)$

(b)  $(157 - 112) \times 25.6$

**1-27.** Carry out the following calculations. Express your answer to the proper number of significant figures or decimal places.

(a)  $(67.43 \times 0.44) - 23.456$

(b)  $(0.22 + 12.451 + 1.782) \times 0.876$

(c)  $(1.20 \times 0.8842) + (7.332 \times 0.0580)$

### Scientific Notation (SECTION 1-3)

**1-28.** Express the following numbers in scientific notation (one digit to the left of the decimal point).

- |   |                |
|---|----------------|
| (a) 157                                     | (e) 0.0349     |
| (b) 0.157                                   | (f) 32,000     |
| (c) 0.0300                                  | (g) 32 billion |
| (d) 40,000,000<br>(two significant figures) | (h) 0.000771   |
|   | (i) 2340       |

**1-29.** Express the following numbers in scientific notation (one digit to the left of the decimal point).

- |             |   |
|-------------|---|
| (a) 423,000 | (f) 82,000,000<br>(three significant figures) |
| (b) 433.8   | (g) 75 trillion                               |
| (c) 0.0020  | (h) 0.0000106                                 |
| (d) 880     |   |
| (e) 0.00008 |   |

**1-30.** Using scientific notation, express the number 87,000,000 to (a) one significant figure, (b) two significant figures, and (c) three significant figures.

**1-31.** Using scientific notation, express the number 23,600 to (a) one significant figure, (b) two significant figures, (c) three significant figures, and (d) four significant figures.

**1-32.** Express the following as ordinary decimal numbers.

- |                           |                             |
|---------------------------|-----------------------------|
| (a) $4.76 \times 10^{-4}$ | (d) $0.489 \times 10^6$     |
| (b) $6.55 \times 10^3$    | (e) $475 \times 10^{-2}$    |
| (c) $788 \times 10^{-5}$  | (f) $0.0034 \times 10^{-3}$ |

**1-33.** Express the following as ordinary decimal numbers.

- |                         |                            |
|-------------------------|----------------------------|
| (a) $64 \times 10^{-3}$ | (c) $0.022 \times 10^4$    |
| (b) $8.34 \times 10^3$  | (d) $0.342 \times 10^{-2}$ |

**1-34.** Change the following numbers to scientific notation (one digit to the left of the decimal point).

- |                            |                            |
|----------------------------|----------------------------|
| (a) $489 \times 10^{-6}$   | (d) $571 \times 10^{-4}$   |
| (b) $0.456 \times 10^{-4}$ | (e) $4975 \times 10^5$     |
| (c) $0.0078 \times 10^6$   | (f) $0.030 \times 10^{-2}$ |

**1-35.** Change the following numbers to scientific notation.

- |                             |                                |
|-----------------------------|--------------------------------|
| (a) $0.078 \times 10^{-8}$  | (d) $280.0 \times 10^8$        |
| (b) $72,000 \times 10^{-5}$ | (e) $0.000690 \times 10^{-10}$ |
| (c) $3450 \times 10^{16}$   | (f) $0.0023 \times 10^6$       |

**1-36.** Order the following numbers from the smallest to the largest.

- |                            |                          |            |
|----------------------------|--------------------------|------------|
| (a) 12                     | (d) $0.084 \times 10^2$  | (g) 0.0022 |
| (b) $0.042 \times 10^{-3}$ | (e) $3.7 \times 10^6$    |            |
| (c) $48 \times 10^5$       | (f) $8.6 \times 10^{-5}$ |            |

**1-37.** Order the following numbers from smallest to largest.

- |                            |                       |                          |
|----------------------------|-----------------------|--------------------------|
| (a) $0.40 \times 10^2$     | (d) $4.8 \times 10^5$ | (g) $2.7 \times 10^{-4}$ |
| (b) $40 \times 10^4$       | (e) $510 \times 10^2$ |                          |
| (c) $0.077 \times 10^{-2}$ | (f) 8.9               |                          |

**1-38.** Carry out each of the following operations. Assume that the numbers represent measurements, so the answer should be expressed to the proper decimal place.

- (a)  $(1.82 \times 10^{-4}) + (0.037 \times 10^{-4}) + (14.11 \times 10^{-4})$   
 (b)  $(13.7 \times 10^6) - (2.31 \times 10^6) + (116.28 \times 10^5)$   
 (c)  $(0.61 \times 10^{-6}) + (0.11 \times 10^{-4}) + (0.0232 \times 10^{-3})$   
 (d)  $(372 \times 10^{12}) + (1200 \times 10^{10}) - (0.18 \times 10^{15})$

**1-39.** Carry out each of the following operations. Assume that the numbers represent measurements, so the answer should be expressed to the proper decimal place.

- (a)  $(1.42 \times 10^{-10}) + (0.17 \times 10^{-10}) - (0.009 \times 10^{-10})$   
 (b)  $(146 \times 10^8) + (0.723 \times 10^{10}) + (11 \times 10^8)$   
 (c)  $(1.48 \times 10^{-7}) + (2911 \times 10^{-9}) + (0.6318 \times 10^{-6})$   
 (d)  $(299 \times 10^{10}) + (823 \times 10^8) + (0.75 \times 10^{11})$

**1-40.** Carry out the following calculations.

- |                           |  |
|---------------------------|--|
| (a) $10^3 \times 10^4$    | (c) $\frac{10^{26}}{10^{-3}}$              |
| (b) $10^6 \times 10^{-6}$ | (d) $\frac{10^4 \times 10^{-8}}{10^{-13}}$ |

**1-41.** Carry out the following calculations.

- |  |  |
|--|--|
| (a) $\frac{10^8}{10^{-8}}$                               | (c) $\frac{10^{16} \times 10^{-12}}{10^4}$ |
| (b) $\frac{10^{22} \times 10^{-4}}{10^{17} \times 10^8}$ | (d) $10^{21} \times 10^{-28}$              |

**1-42.** Carry out each of the following operations. Assume that the numbers represent measurements, so the answer should be expressed to the proper number of significant figures.

- (a)  $(149 \times 10^6) \times (0.21 \times 10^3)$   
 (b)  $\frac{0.371 \times 10^{14}}{2 \times 10^4}$   
 (c)  $(6 \times 10^6) \times (6 \times 10^6)$   
 (d)  $(0.1186 \times 10^6) \times (12 \times 10^{-5})$   
 (e)  $\frac{18.21 \times 10^{-10}}{0.0712 \times 10^6}$

**1-43.** Carry out each of the following operations. Assume that the numbers represent measurements, so the answer should be expressed to the proper number of significant figures.

(a)  $(76.0 \times 10^7) \times (0.6 \times 10^8)$

(b)  $(7 \times 10^{-5}) \times (7.0 \times 10^{-5})$

(c)  $\frac{0.786 \times 10^{-7}}{0.47 \times 10^7}$

(d)  $\frac{3798 \times 10^{18}}{0.00301 \times 10^{12}}$

(e)  $(0.06000 \times 10^{18}) \times (84,921 \times 10^{-9})$

**1-44.** Supply the missing measurement. Express in scientific notation.

(a)  $(4.0 \times 10^{12}) / (\quad) = 2.0$

(b)  $(\quad) \times (5.18 \times 10^{-8}) = 1.9 \times 10^9$

(c)  $(6.0 \times 10^4) \times (\quad) = 3.6 \times 10^7$

(d)  $(4.0 \times 10^{12}) / (\quad) = 2 \times 10^{24}$

(e)  $(8.520 \times 10^{-8}) \times (\quad) = 16$

**1-45.** Supply the missing measurement. Express in scientific notation.

(a)  $(\quad) / (7.890 \times 10^6) = 1.552$

(b)  $(\quad) / (7.50 \times 10^4) = 1.20 \times 10^{-16}$

(c)  $(9.00 \times 10^{-12}) / (\quad) = 3.0 \times 10^{12}$

(d)  $(9.0 \times 10^4) \times (\quad) = 8 \times 10^9$

(e)  $(8.002 \times 10^{15}) / (\quad) = 8 \times 10^5$

**1-46.** Supply the missing measurement. Express in scientific notation.

(a)  $(\quad) / (5.32 \times 10^{10}) = 3.4 \times 10^8$

(b)  $(8.55 \times 10^{12}) / (\quad) = 2 \times 10^8$

(c)  $(8.55 \times 10^{12}) / (\quad) = 4.13$

(d)  $(9.00 \times 10^4) \times (\quad) = 8.1 \times 10^8$

## Length, Volume, and Mass in the Metric System

### (SECTION 1-4)

**1-47.** Write the proper prefix, unit, and symbol for the following. Refer to Tables 1-2, 1-3 and 1-4.

(a)  $10^{-3}$  L

(c)  $10^{-9}$  J

(e)  $10^{-6}$  g

(b)  $10^2$  g

(d)  $\frac{1}{100}$  m

(f)  $10^{-1}$  Pa

**1-48.** Write the proper prefix, unit, and symbol for the following. Refer to Tables 1-2, 1-3, and 1-4.

(a)  $10^3$  m

(c)  $\frac{1}{1000}$  L

(e)  $10^{-9}$  m

(b)  $10^{-3}$  g

(d)  $10^3$  s

(f)  $\frac{1}{1000}$  mol

**1-49.** Complete the following table.

|         | mm                | cm    | m     | km                    |
|---------|-------------------|-------|-------|-----------------------|
| Example | 108               | 10.8  | 0.108 | $1.08 \times 10^{-4}$ |
| (a)     | $7.2 \times 10^3$ | _____ | _____ | _____                 |
| (b)     | _____             | _____ | 56.4  | _____                 |
| (c)     | _____             | _____ | _____ | 0.250                 |

**1-50.** Complete the following table.

|     | mg                | G     | kg    |
|-----|-------------------|-------|-------|
| (a) | $8.9 \times 10^3$ | _____ | _____ |
| (b) | _____             | 25.7  | _____ |
| (c) | _____             | _____ | 1.25  |

**1-51.** Complete the following table.

|     | mL    | L     | kL    |
|-----|-------|-------|-------|
| (a) | _____ | _____ | 6.8   |
| (b) | _____ | 0.786 | _____ |
| (c) | 4452  | _____ | _____ |

## Conversions Between Units of Measurement

### (SECTION 1-5)

**1-52.** Which of the following are “exact” relationships?

(a)  $12 = 1$  doz

(d)  $1.06$  qt = 1 L

(b) 1 gal = 3.78 L

(e)  $10^3$  m = 1 km

(c) 3 ft = 1 yd

(f) 454 g = 1 lb

**1-53.** How many significant figures are in each of the following relationships? (If exact, the answer is “infinite.”)

(a)  $10^3$  m = 1 km

(d) 1.609 km = 1 mi

(b) 4 qt = 1 gal

(e) 1 gal = 3.8 L

(c) 28.38 g = 1 oz

(f) 2 pt = 1 qt

**1-54.** Write a relationship in factor form that would be used in making the following conversions. Refer to Table 1-4.

(a) mg to g

(c) cL to L

(b) m to km

(d) mm to km (two factors)

**1-55.** Write a relationship in factor form that would be used in making the following conversions. Refer to Table 1-4.

(a) kL to L

(c) kg to mg (two factors)

(b) mg to g

(d) cg to hg (two factors)

**1-56.** Write a relationship in factor form that would be used in making the following conversions. Refer to Tables 1-1 and 1-5.

(a) in. to ft

(d) L to qt

(b) in. to cm

(e) pt to L (two steps)

(c) mi to ft

**1-57.** Write a relationship in factor form that would be used in making the following conversions. Refer to Tables 1-1 and 1-5.

(a) qt to gal

(c) gal to L

(b) kg to lb

(d) ft to km (three steps)

**1-58.** Convert each of these measurement to a unit in the same system that will produce a number between 1 and 100 (e.g., 150 cm converts to 1.5 m).

(a)  $4.7 \times 10^4$  mL =

(e)  $9.2 \times 10^{10}$  nm =

(b)  $98 \times 10^{-5}$  km =

(f) 1725 qt =

(c) 9780 ft =

(g)  $32 \times 10^{12}$  mg =

**1-59.** Convert each of these measurements to a unit in the same system that will produce a number between 1 and 100.

- (a)  $9.5 \times 10^4$  oz =                      (e)  $49 \times 10^5$  cm =  
 (b) 1548 in. =                                (f)  $2.52 \times 10^2$  pt =  
 (c)  $8.22 \times 10^6$  mm =                      (g)  $1.5 \times 10^{-12}$  mg =  
 (d)  $652 \times 10^{-7}$  kL =

**1-60.** Complete the following table.

|     | mi    | ft                 | m                 | km    |
|-----|-------|--------------------|-------------------|-------|
| (a) | _____ | _____              | $7.8 \times 10^3$ | _____ |
| (b) | 0.450 | _____              | _____             | _____ |
| (c) | _____ | $8.98 \times 10^3$ | _____             | _____ |
| (d) | _____ | _____              | _____             | 6.78  |

**1-61.** Complete the following table.

|     | gal   | qt    | L                  |
|-----|-------|-------|--------------------|
| (a) | 6.78  | _____ | _____              |
| (b) | _____ | 670   | _____              |
| (c) | _____ | _____ | $7.68 \times 10^3$ |

**1-62.** Complete the following table.

|     | lb    | g     | kg    |
|-----|-------|-------|-------|
| (a) | _____ | _____ | 0.780 |
| (b) | _____ | 985   | _____ |
| (c) | 16.0  | _____ | _____ |

**1-63.** If a person has a mass of 122 lb, what is her mass in kilograms?

**1-64.** The moon is 238,700 miles from Earth. What is this distance in kilometers?

**1-65.** A punter on a professional football team averaged 28.0 m per kick. What is his average in yards? Should he be kept on the team?

**1-66.** A can of soda has a volume of 355 mL. What is this volume in quarts?

**1-67.** If a student drinks a 12-oz (0.375-qt) can of soda, what volume did she drink in liters?

**1-68.** The meat in a “quarter-pounder” should weigh 4.00 oz. What is its mass in grams?

**1-69.** A prospective basketball player is 6 ft  $10\frac{1}{2}$  in. tall and weighs 212 lb. What are his height in meters and his weight in kilograms?

**1-70.** Gasoline is sold by the liter in Europe. How many gallons does a 55.0-L gas tank hold?

**1-71.** If the length of a football field is changed from 100 yd to 100 m, will the field be longer or shorter than the current field? How many yards would a “first and ten” be on the metric field?

**1-72.** Bourbon used to be sold by the “fifth” (one-fifth of a gallon). A bottle now contains 750 mL. Which is greater?

**1-73.** A marathon runner must cover 26 mi 385 yd. How far is this in kilometers?

**1-74.** If the speed limit is 65.0 mi/hr, what is the speed limit in km/hr?

**1-75.** Mount Everest is 29,028 ft in elevation. How high is this in kilometers?

**1-76.** It is 525 mi from St. Louis to Detroit. How far is this in kilometers?

**1-77.** A small pizza has a diameter of 9.00 in. What is this length in millimeters?

**1-78.** Gasoline sold as low as \$0.899 per gallon in 2001. (That’s hard to believe.) What was the cost per liter? What did it cost to fill an 80.0-L tank in the good old days? In 2008, the price was \$3.759 per gallon. What did it cost to fill the 80.0-L tank in 2008?

**1-79.** At the price of gas in the preceding problem (in 2008), how much does it cost to drive 551 mi if your car averages 21.0 mi/gal? How much does it cost to drive 482 km?

**1-80.** Using the information from the two preceding problems, how many kilometers can you drive for \$75.00?

**1-81.** An aspirin contains 0.324 g (5.00 grains) of aspirin. How many pounds of aspirin are in a 500-aspirin bottle?

**1-82.** A hamburger in Canada sold for \$4.55 (Canadian dollars) in 2002. The exchange rate at that time was \$1.56 Canadian per one U.S. dollar. (In 2008, they were about even.) What was the cost in U.S. dollars?

**1-83.** A certain type of nail costs \$0.95/lb. If there are 145 nails per pound, how many nails can you purchase for \$2.50?

**1-84.** Another type of nail costs \$0.92/lb, and there are 185 nails per pound. What is the cost of 5670 nails?

**1-85.** If a hybrid automobile gets 38.5 mi/gal of gasoline and gasoline costs \$3.759/gal, what would it cost to drive 858 km? How much would it cost if the car is an SUV that gets only 18.5 mi/gal?

**1-86.** If a train travels at a speed of 85 mi/hr, how many hours does it take to travel 17,000 ft? How many yards can it travel in 37 min?

**1-87.** If grapes sell for \$2.15/lb and there are 255 grapes per pound, how many grapes can you buy for \$8.15?

**1-88.** A high-speed train in Europe travels 215 km/h. How long would it take for this train to travel nonstop from Boston to Washington, D.C., which is 442 miles?

**1-89.** The exchange rates among currencies vary from day to day and are usually expressed with up to five significant figures. The new currency in Europe since the beginning of 2002 is the Eurodollar (or simply the “euro”). It began trading at about 1.12 euros per U.S. dollar.

- (a) What was the cost in euros of a sandwich that would cost \$6.50 in the United States? (b) What was the cost in U.S. dollars of 1 liter of wine in France that sold for 12.65 euros? The exchange rate in 2008 was \$1.46/euro. (c) What is the cost in dollars for 1 liter of wine that now sells for 15.58 euros?

**1-90.** The traditional pound as well as the euro is used in Britain. The British pound traded for 0.592 pound per U.S. dollar in 2008. What is the current conversion rate between the pound and the euro using the conversion rate between the dollar and euro? If an automobile sells for 25,500 euros in Germany, how much would it cost in pounds?

**1-91.** In Mexico, the peso exchanged for 10.92 pesos per U.S. dollar in 2008. What is the cost in dollars for a Corona beer that sells for 25.0 pesos in Cancun? What would it cost in euros and in British pounds? (See the previous two problems.)

**\*1-92.** At a speed of 35 mi/hr, how many centimeters do you travel per second?

**\*1-93.** The planet Jupiter is about  $4.0 \times 10^8$  mi from Earth. If radio signals travel at the speed of light, which is  $3.0 \times 10^{10}$  cm/s, how long would it take a radio command from Earth to reach a spacecraft passing Jupiter?

### Temperature (SECTION 1-6)

**1-94.** The temperature of the water around a nuclear reactor core is about  $300^\circ\text{C}$ . What is this temperature in degrees Fahrenheit?

**1-95.** The temperature on a comfortable day is  $76^\circ\text{F}$ . What is this temperature in degrees Celsius?

**1-96.** The lowest possible temperature is  $-273^\circ\text{C}$  and is referred to as absolute zero. What is this temperature in degrees Fahrenheit?

**1-97.** Mercury thermometers cannot be used in cold arctic climates because mercury freezes at  $-39^\circ\text{C}$ . What is this temperature in degrees Fahrenheit?

**1-98.** The coldest temperature recorded on Earth was  $-110^\circ\text{F}$ . What is this temperature in degrees Celsius?

**1-99.** A hot day in the U.S. Midwest is  $35.0^\circ\text{C}$ . What is this in degrees Fahrenheit?

**1-100.** Convert the following Kelvin temperatures to degrees Celsius.

- |           |           |
|-----------|-----------|
| (a) 175 K | (d) 225 K |
| (b) 295 K | (e) 873 K |
| (c) 300 K |           |

**1-101.** Convert the following temperatures to the Kelvin scale.

- |                         |                         |
|-------------------------|-------------------------|
| (a) $47^\circ\text{C}$  | (d) $-12^\circ\text{C}$ |
| (b) $23^\circ\text{C}$  | (e) $65^\circ\text{F}$  |
| (c) $-73^\circ\text{C}$ | (f) $-20^\circ\text{F}$ |

**1-102.** Make the following temperature conversions.

- |                               |                               |
|-------------------------------|-------------------------------|
| (a) $37^\circ\text{C}$ to K   | (d) 127 K to $^\circ\text{F}$ |
| (b) $135^\circ\text{C}$ to K  | (e) $100^\circ\text{F}$ to K  |
| (c) 205 K to $^\circ\text{C}$ | (f) $-25^\circ\text{C}$ to K  |

**\*1-103.** At what temperature are the Celsius and Fahrenheit scales numerically equal?

### General Problems

**1-104.** Carry out the following calculations. Express the answer to the proper number of significant figures.

- (a)  $\frac{12.61 + 0.22 + 0.037}{0.04}$
- (b)  $0.333 \text{ g} \times (23.60 + 1.2) \text{ cm}$
- (c)  $\frac{6.286 \text{ g}}{(13.68 - 12.48) \text{ mL}}$
- (d)  $\frac{44.35 + 0.03 + 0.057}{22.35 - 20.018}$

**1-105.** Write in factor form the two relationships needed to convert the following.

- |              |              |
|--------------|--------------|
| (a) mg to lb | (c) hm to mi |
| (b) L to pt  | (d) cm to ft |

**1-106.** Convert  $5.34 \times 10^{10}$  ng to pounds.

**1-107.** Convert  $7.88 \times 10^{-4}$  mL to gallons.

**1-108.** If gold costs  $\$720/\text{oz}$ , what is the cost of 1.00 kg of gold? (Metals are traded as troy ounces. There are exactly 12 troy ounces per troy pound, and one troy pound is equal to 373 g, to three significant figures.)

**1-109.** Construct unit factors from the following information: A 82.3-dozen quantity of oranges weighs 247 lb.

- (a) What is the mass per dozen oranges?
- (b) How many dozen oranges are there per pound?

**1-110.** A unit of length in horse racing is the furlong. The height of a horse is measured in hands. There are exactly 8 furlongs per mile, and 1 hand is exactly 4 inches. How many hands are there in 12.0 furlongs? (Express the answer in standard scientific notation.)

**1-111.** The unit price of groceries is sometimes listed in cost per ounce. Which has the smaller cost per ounce: 16 oz of baked beans costing  $\$1.45$  or 26 oz costing  $\$2.10$ ?

**1-112.** A cigarette contains 11.0 mg of tar. How many packages of cigarettes (20 cigarettes per package) would have to be smoked to produce 0.500 lb of tar? If a person smoked two packs per day, how many years would it take to accumulate 0.500 lb of tar?

**1-113.** An automobile engine has a volume of  $306 \text{ in.}^3$ . What is this volume in liters?

**1-114.** A U.S. quarter has a mass of 5.70 g. How many dollars is 1 pound of quarters worth?

**1-115.** The surface of the sun is at a temperature of about  $3.0 \times 10^7^\circ\text{C}$ . What is this temperature in degrees Fahrenheit? In kelvins?

**1-116.** In Saudi Arabia, gasoline costs 30.0 hillala per liter. If there are exactly 100 hillalas in 1 ryal and 1 ryal exchanges for about 25.0 cents (U.S.), what is the cost in cents/gal?

**\*1-117.** If snow were piled up by 1.00 ft on a roof  $30.0 \text{ ft} \times 50.0 \text{ ft}$ , what would be the mass of snow on the roof in pounds and in tons? Assume that  $1 \text{ ft}^3$  of snow is equivalent to  $0.100 \text{ ft}^3$  of water and that  $1 \text{ ft}^3$  of water has a mass of 62.0 lb.

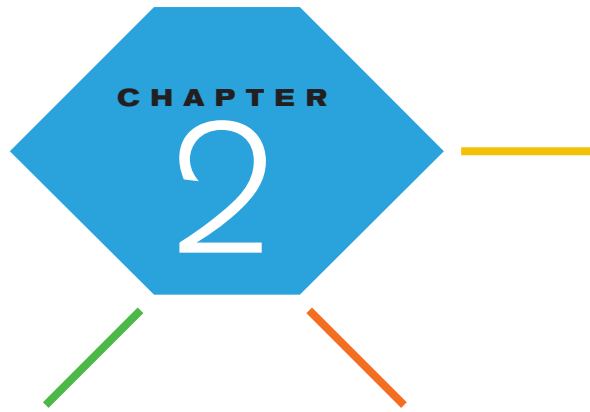


## Accuracy and Precision

**Purpose:** To make measurements that illustrate the difference between precision and accuracy. (Work in groups of three to five. Estimated time: 15 min.)

**Equipment:** 2 disposable pipettes per group. One small graduated cylinder per group.

1. Each person in the group counts the number of drops from one of the pipettes needed to fill the graduated cylinder to the 5.0-mL line. (If there are only three in a group, each person should do this twice.)
2. Determine how precise your four to six measurements are. If any value is dramatically different from the others, it should be discarded.
3. Use all the good measurements to determine the average volume per drop.
4. Calculate how many drops it would take to fill the graduated cylinder to 8.0 mL.
5. Perform the experiment twice, once with each pipette. Count out the number of drops that was calculated in (4). What is the measured volume? Was the calculation correct for the first pipette? Do the results for the second pipette indicate that most disposable pipettes deliver approximately the same volume per drop?
6. Calculate the number of drops in 1 oz.



# Elements and Compounds



**A** diamond is a pure form of an element carbon. It is composed of atoms arranged in a specific geometric arrangement.

## PART A THE ELEMENTS AND THEIR COMPOSITION

### 2-1 The Elements



#### MAKING IT REAL

*Iridium, the Missing Dinosaurs, and the Scientific Method*

### 2-2 The Composition of Elements: Atomic Theory

### 2-3 Composition of the Atom

### 2-4 Atomic Number, Mass Number, and Atomic Mass



#### MAKING IT REAL

*Isotopes and the History of Earth's Weather*

## PART B COMPOUNDS AND THEIR COMPOSITION

### 2-5 Molecular Compounds

### 2-6 Ionic Compounds



#### MAKING IT REAL

*Ionic Compounds and Essential Elements*

**SETTING THE STAGE** In early 2004, two small rovers named *Spirit* and *Opportunity* began their historic exploration on opposite sides of the dry, harsh surface of the planet Mars. Their primary mission was to explore this barren landscape for signs of the familiar substance we know as *water*. Apparently their mission was successful; photos and analysis of nearby rock formations did indeed indicate that water had at one time been present in the form of a lake or shallow ocean. At the time of this writing the journey of the rovers has continued in late 2008, sending back more and more important information. In fact, spacecraft sent to Mars decades ago relayed photos showing channels that must have been formed from a flowing liquid. Since then, we have wondered whether, at one time, conditions on Mars may have allowed liquid water to exist on its surface much like it does on Earth today. If so, then there is a reasonable chance that some elementary form of life may have existed on Mars and perhaps still does below the surface. Water is a necessary component for the formation of living creatures. It is the medium in which other substances can rearrange and combine into the most basic forms of living creatures.

Water is just one example of matter. *Matter is defined as anything that has mass and occupies space.* Mars, the moon, and all of the flickering stars in the night sky are all composed of the same kinds of matter that we find on Earth. The forms of matter that we see on Earth are often changing. Plants grow, die, and decay; rocks weather, crumble, and become part of the fertile soil of the plains or deposits in the oceans. These changes are also the domain of chemistry. *Chemistry can be defined as the study of matter and the changes it undergoes.*

There are basically two types of matter—elements and compounds. In Part A in this chapter we will discuss elements, which are the most basic form of visible matter. In Part B we will explore the more complex form of matter, compounds. In both parts we begin our discussion with the matter that we can see in front of us (the macroscopic) and then delve into the unseen world within the matter (the microscopic).

## PART A THE ELEMENTS AND THEIR COMPOSITION

### SETTING A GOAL

- You will become familiar with the basic components of matter and the properties that make each type of matter unique.

### OBJECTIVES

- 2-1 (a)** Distinguish between elements and compounds. **(b)** Match the names and symbols of common elements.
- 2-2** List the postulates of the atomic theory.
- 2-3** List the components of an atom and their relative masses, charges, and location in the atom.
- 2-4 (a)** Define the terms *atomic number*, *mass number*, and *isotope*. **(b)** Using the table of elements, determine the number of protons, neutrons, and electrons in any isotope of an element. **(c)** Demonstrate how the atomic mass of an element is determined from isotopes and their percent abundance

### ▶ OBJECTIVES FOR SECTION 2-1

- (a)** Distinguish between elements and compounds. **(b)** Match the names and symbols of common elements.

## 2-1 THE ELEMENTS



**LOOKING AHEAD!** Many of the most basic forms of matter—the elements—are familiar to us, but some are not. The names and symbolic representation of the elements are the first topics that we will discuss. ■

At first glance, the world around us seems so complex. However, we can simplify our understanding by organizing it into general classifications. Many sciences group their disciplines into categories. For example, biology is divided into the study of plants (the flora) and animals (the fauna.) Geology divides its study into the continents and the oceans. The matter we study in chemistry can also be placed into one of two categories.

All of the matter that we see around us from the contents of your room to the farthest stars in space is essentially composed of fewer than 90 unique substances called *elements*. Because it cannot be broken down into simpler substances, an **element** is the most basic form of matter that exists under ordinary conditions. The more complex forms of matter are known as compounds. A **compound** is a unique substance that is composed of two or more elements that are chemically combined. When we say chemically combined we do not mean merely a mixture of elements. Rather, the elements are intimately joined together into a unique form of matter that is distinct from the elements that compose the compound. We will return to a discussion of compounds in Part B.

### 2-1.1 Free Elements in Nature

Only a few elements are found around us in their free state; that is, they are not combined with any other element. The shiny gold in a ring, the life-supporting oxygen in air, and the carbon in a sparkling diamond are examples of free elements. (See Figure 2-1.)

Other free elements that we have put to use include the aluminum in a can and the iron in a bridge support. These elements were not originally found in the free state in nature but in compounds containing other elements. (A small amount of



**FIGURE 2-1 Some Elements Found in Nature** Three elements found in their free state are diamond (left), oxygen, and gold nuggets (right).

iron is found in the free state in certain meteorites.) In most cases, elements are extracted from their compounds by rigorous chemical processes.

### 2-1.2 The Names of Elements

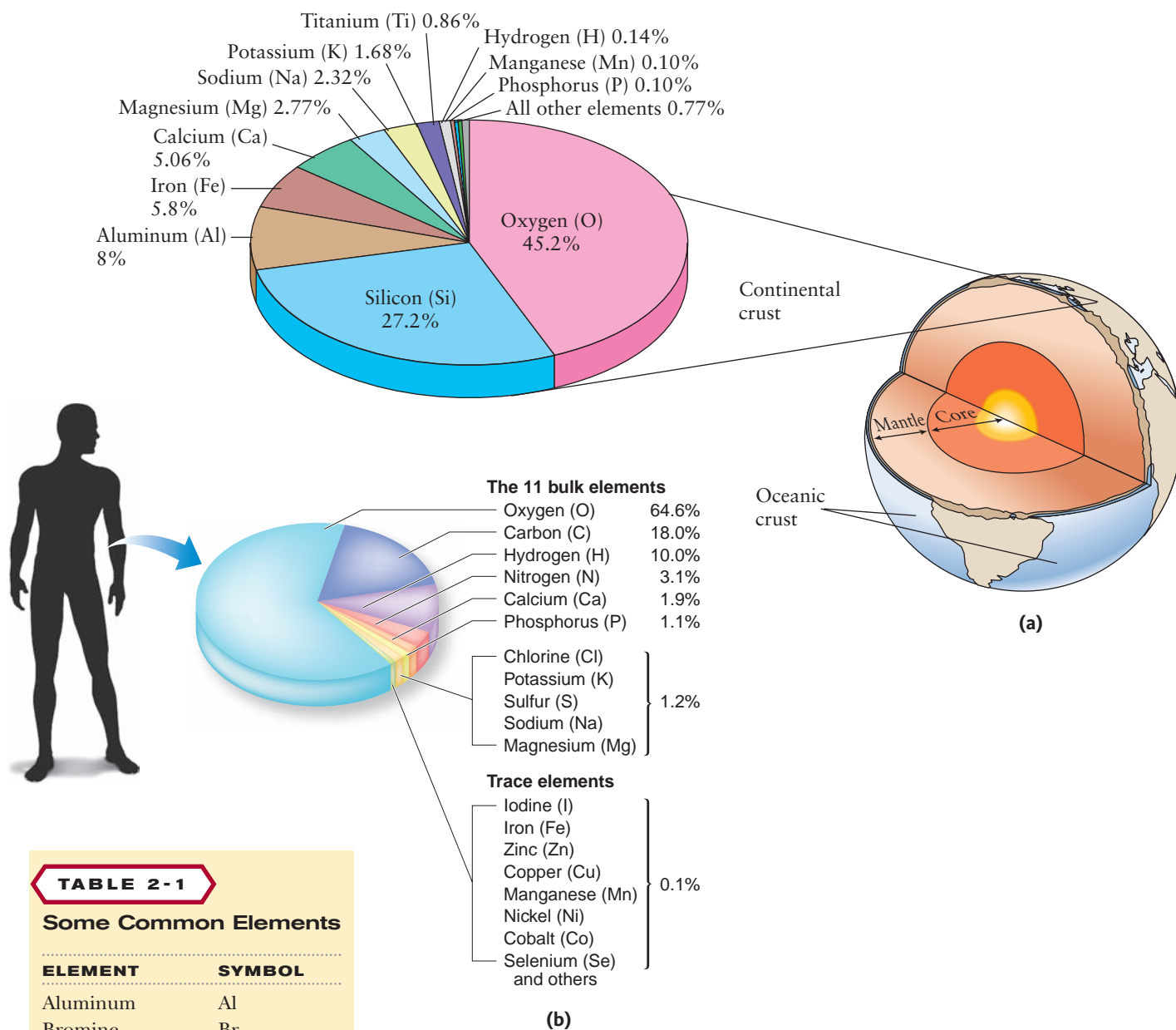
The names of elements come from many sources. Some are derived from Greek, Latin, or German words for colors—for example, bismuth (white mass), iridium (rainbow), rubidium (deep red), and chlorine (greenish-yellow). Some relate to the locality where the element was discovered (e.g., germanium, francium, and californium). Four elements (yttrium, erbium, terbium, and ytterbium) are all named after a town in Sweden (Ytterby) near where they were discovered. Other elements honor noted scientists (e.g., einsteinium, fermium, and curium) or mythological figures (e.g., plutonium, uranium, titanium, and mercury.) Many of the oldest known elements have names with obscure origins.

### 2-1.3 The Distribution of the Elements

In the Prologue, we traced the origins of the elements from the *big bang* to the current day on our comfortable planet, Earth. The original universe was composed of just three elements, hydrogen (90%), helium (10%), and just a trace of lithium. For the last 14 billion years, all the other elements have been produced from the original hydrogen in the cores of billions of stars and from the supernova explosions at the end of the stars' lives. Still, since the beginning of time, the abundances of the elements have changed little. In fact, all of this solar activity has converted only about 0.25% of the mass of the universe into elements heavier than helium. Fortunately, that was enough to form the solid earth on which we exist.

Earth and the other planets were formed 4.5 billion years ago from the debris of earlier stars. There is comparatively little hydrogen and helium on Earth, although these elements are predominant in the universe as a whole. Figure 2-2a shows the relative abundances of the elements present in Earth's crust in percent by weight. The crust is the outer few miles of the solid surface plus the oceans and atmosphere. Since the core of this planet is mostly iron and nickel, these two elements are more plentiful for Earth as a whole. However, the crust is the region from which we can most easily acquire all our natural resources. It is therefore more meaningful to us to evaluate the distribution of elements found there. Notice that of all the elements, just the top 10 constitute 99% of the mass of the crust. Similarly, consider the human body. Over 96% of the mass of our bodies is composed of only four elements: oxygen, carbon, nitrogen, and hydrogen. This is shown in Figure 2-2b.





**FIGURE 2-2** The Distribution of the Elements Most of Earth's crust is composed of surprisingly few elements. (a) The human body is composed mostly of just three elements. (b)

**TABLE 2-1**

### Some Common Elements

| ELEMENT    | SYMBOL |
|------------|--------|
| Aluminum   | Al     |
| Bromine    | Br     |
| Calcium    | Ca     |
| Carbon     | C      |
| Chlorine   | Cl     |
| Chromium   | Cr     |
| Fluorine   | F      |
| Helium     | He     |
| Hydrogen   | H      |
| Iodine     | I      |
| Magnesium  | Mg     |
| Nickel     | Ni     |
| Nitrogen   | N      |
| Oxygen     | O      |
| Phosphorus | P      |
| Silicon    | Si     |
| Sulfur     | S      |
| Zinc       | Zn     |

### 2-1.4 The Symbols of the Elements

An element can be conveniently identified by a symbol. A **symbol** is usually the first one or two letters of the element's English or Latin name. When an element has a two-letter symbol, the first is capitalized but the second is not. The table on the inside cover of the text includes a complete list of elements along with their symbols. Some common elements and their symbols are listed in Table 2-1. The symbols of some common elements are derived from their original Latin names (or, in the case of tungsten, its German name—Wolfram). The symbols of these elements are listed in Table 2-2.

**TABLE 2-2** Elements with Symbols from Earlier or Alternate Names

| ELEMENT   | SYMBOL | FORMER LATIN NAME |
|-----------|--------|-------------------|
| Antimony  | Sb     | Stibium           |
| Copper    | Cu     | Cuprum            |
| Gold      | Au     | Aurum             |
| Iron      | Fe     | Ferrum            |
| Lead      | Pb     | Plumbum           |
| Mercury   | Hg     | Hydragyrum        |
| Potassium | K      | Kalium            |
| Silver    | Ag     | Argentum          |
| Sodium    | Na     | Natrium           |
| Tin       | Sn     | Stannum           |
| Tungsten  | W      | Wolfram           |

MAKING

REAL

IT

### Iridium, the Missing Dinosaurs, and the Scientific Method



The dinosaurs such as the T-rex probably had a catastrophic end.

“It’s elementary, my dear Watson.” If Sherlock Holmes had been on the case of the missing dinosaurs, that statement would have been brilliant. The first major clue was indeed “elementary” or, more specifically, “elemental!” Iridium is a very rare element found on Earth’s surface. Four billion years ago the Earth was

molten, and most iridium (which is very dense) sank deep into the interior. However, matter from space including meteors, asteroids, and comets also contain comparatively high amounts of this element. The following application of the scientific method, as discussed in the Prologue, provides us with a theory of how the element iridium is connected to the extinction of the dinosaurs.

In 1979, American scientists discovered a thin layer of sediment in various locations around the world that was deposited about 65 million years ago, coincidentally the same time frame in which the dinosaurs became extinct. Indeed, there were dinosaur fossils below that layer but none above. Interestingly, that layer contained comparatively high amounts of iridium. Scientists proposed that this layer

contained the dust and debris from a collision of a huge asteroid or comet (about 6 miles in diameter) with Earth. They concluded that a large cloud of dust must have formed, encircling Earth and completely shutting out the sunlight. A bitter cold wave followed, and most animals and plants quickly died. A *hypothesis* (a tentative explanation of facts) was proposed that the dinosaurs must have been among the casualties. After many months the dust settled, forming a thin layer of sediment. Scientists further proposed that small mammals and some reptiles had survived and inherited the planet.

More information has since been discovered to support the original hypothesis. Perhaps most important was the discovery in 1991 of a huge impact crater near the Yucatan Peninsula in Mexico. The crater, 110 miles wide, is buried miles under the ocean surface and was formed about 65 million years ago, evidence that surely a huge asteroid or comet had collided with Earth. Since it landed in the ocean, huge tidal waves must have formed. Evidence of waves over 1 mile high has been found in North and Central America.

Based on all the evidence, most scientists have now embraced the originally proposed hypothesis as a plausible *theory* (a well-established hypothesis). Apparently, the end of the dinosaurs was sudden and dramatic. Now, instead of worrying about a nasty Tyrannosaurus Rex lurking in the forest, we can instead worry about collisions with asteroids!

**ASSESSING THE  
OBJECTIVES FOR  
SECTION 2-1**

**EXERCISE 2-1(a) KNOWLEDGE:** The following chemicals are either elements or compounds. Which are elements and which are compounds?

(a) tin (b) baking soda (c) water (d) quartz (e) mercury

**EXERCISE 2-1(b) KNOWLEDGE:** Provide the symbols for the following elements.

(a) copper (b) sulfur (c) calcium

**EXERCISE 2-1(c) KNOWLEDGE:** Provide the name of the element from its symbol.

(a) Pb (b) P (c) Na

**EXERCISE 2-1(d) ANALYSIS:** There are nearly 120 different elements. Would you expect the number of compounds to be roughly the same, slightly more, or significantly more than that?

**EXERCISE 2-1(e) SYNTHESIS:** What might you assume about the possibility of finding elements in their free state based on the name being of Latin origin?

**EXERCISE 2-1(f) SYNTHESIS:** How could you tell if an unknown substance was an element or a compound?

*For additional practice, work chapter problems 2-1, 2-5, 2-7, and 2-32.*

**▶ OBJECTIVE FOR  
SECTION 2-2**

List the postulates of the atomic theory.

## 2-2 THE COMPOSITION OF ELEMENTS: ATOMIC THEORY



**LOOKING AHEAD!** We are now ready to look deeper into the composition of the elements. We will see that they are composed of basic particles called atoms. ■

Our modern understanding of the particulate nature of matter actually had its beginning over 2000 years ago. A Greek philosopher named Democritus suggested that all matter is like grains of sand on a beach. In other words, he proposed that matter is composed of tiny indivisible particles that he called *atoms*. However, as recently as two centuries ago, the idea of matter being composed of atoms was not accepted. Most knowledgeable scientists thought that a sample of an element such as copper could be divided (theoretically) into infinitely smaller pieces without changing its nature. In other words, they believed that matter was continuous.

### 2-2.1 The Atomic Theory

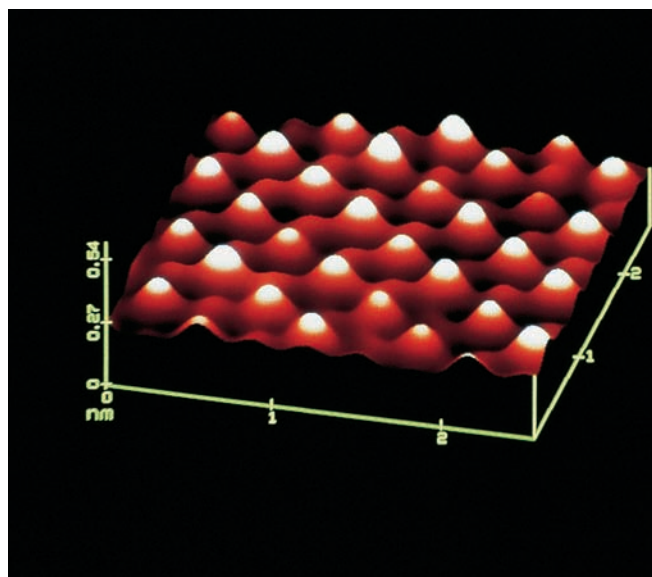
In 1803 an English scientist named John Dalton (1766–1844) proposed a theory of matter based on the original thoughts of Democritus. His ideas are now known as **atomic theory**. The major conclusions of atomic theory are as follows:

- Matter is composed of small, indivisible particles called atoms.
- Atoms of the same element are identical and have the same properties.
- Chemical compounds are composed of atoms of different elements combined in small whole-number ratios.
- Chemical reactions are merely the rearrangement of atoms into different combinations

The atomic theory is now universally accepted as our current view of matter. Thus, we may define an **atom** as the *smallest fundamental particle of an element that has the properties of that element*.

Democritus' proposal 2000 years ago was simply the product of his own rational thought. Dalton's theory was a brilliant and logical explanation of many experimental observations and laws that were known at the time but had not been explained. One of these laws, the law of conservation of mass, will be discussed in the next chapter.

Why are we so sure that Dalton was right? Besides the overwhelming amount of indirect experimental evidence, we now have direct proof. In recent years, a highly sophisticated instrument called the scanning tunneling microscope (STM) has produced images of atoms of several elements. Although these images are somewhat fuzzy, they indicate that an element such as gold is composed of spherical atoms packed closely together, just as you would find in a container of marbles all of the same size. (See Figure 2-3.)



**FIGURE 2-3** STM of the Atoms of an Element  
The atoms are shown in an orderly pattern.

### 2-2.2 The Size of an Atom

When we look at a small piece of copper wire, it is hard to imagine that it is not continuous. This is because it is so difficult to comprehend the small size of the atom. Since the diameter of a typical atom is on the order of  $0.00000001\text{ cm}$  ( $10^{-8}\text{ cm}$ ), it would take about 10 quadrillion atoms to appear as a tiny speck. The piece of copper wire is like a brick wall: from a distance it looks completely featureless, but up close we notice that it is actually composed of closely packed basic units.

#### ASSESSING THE OBJECTIVE FOR SECTION 2-2

**EXERCISE 2-2(a) KNOWLEDGE:** Fill in the blanks.

An \_\_\_\_\_ is composed of small, indivisible particles called \_\_\_\_\_.  
 Atoms of the same \_\_\_\_\_ are identical and have the same \_\_\_\_\_.  
 Chemical \_\_\_\_\_ are composed of atoms of different elements combined in small \_\_\_\_\_ ratios. Chemical \_\_\_\_\_ are rearrangements of \_\_\_\_\_ into different combinations.

**EXERCISE 2-2(b) ANALYSIS:** Are each of the following statements supported by any of Dalton's postulates?

- Any chemical experiment on an element should always yield the same result.
- Any two elements will always form the same compound.
- There is a limit to how far a substance can be divided.
- All atoms involved before a chemical reaction are there after the chemical reaction.

**EXERCISE 2-2(c) SYNTHESIS:** The ideas of Democritus and Dalton are very similar. Why, then, is Dalton considered the father of modern chemistry? Why is Dalton's statement of his ideas superior to that of Democritus?

*For additional practice, work chapter problem 2-8.*

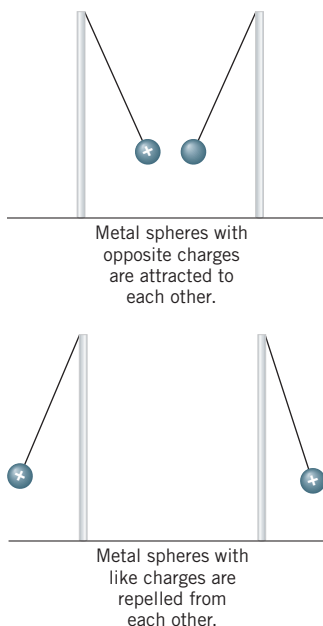
### ▶ OBJECTIVE FOR SECTION 2-3

List the components of an atom and their relative masses, charges, and location in the atom.

## 2-3 COMPOSITION OF THE ATOM

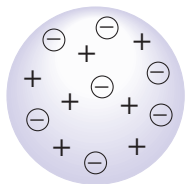


**LOOKING AHEAD!** We now look even deeper into the nature of matter—the structure of the atom itself. In this section, we will describe the contents of the atom as we journey into its tiny confines. ■



**FIGURE 2-4 Electrostatic Forces** Opposite charges attract; like charges repel.

**FIGURE 2-5 The Plum Pudding Model** Electrons were thought to be like tiny particles distributed in a positively charged medium.



Just over 100 years ago, scientists perceived the atom to be a hard, featureless sphere. However, beginning in the late 1880s and continuing today, the mysteries and complexities of the atom have been slowly discovered and understood. Ingenious experiments of brilliant scientists such as Thomson, Rutherford, Becquerel, Curie, and Roentgen, among others, contributed to the current model of the atom.

### 2-3.1 The Electron and Electrostatic Forces

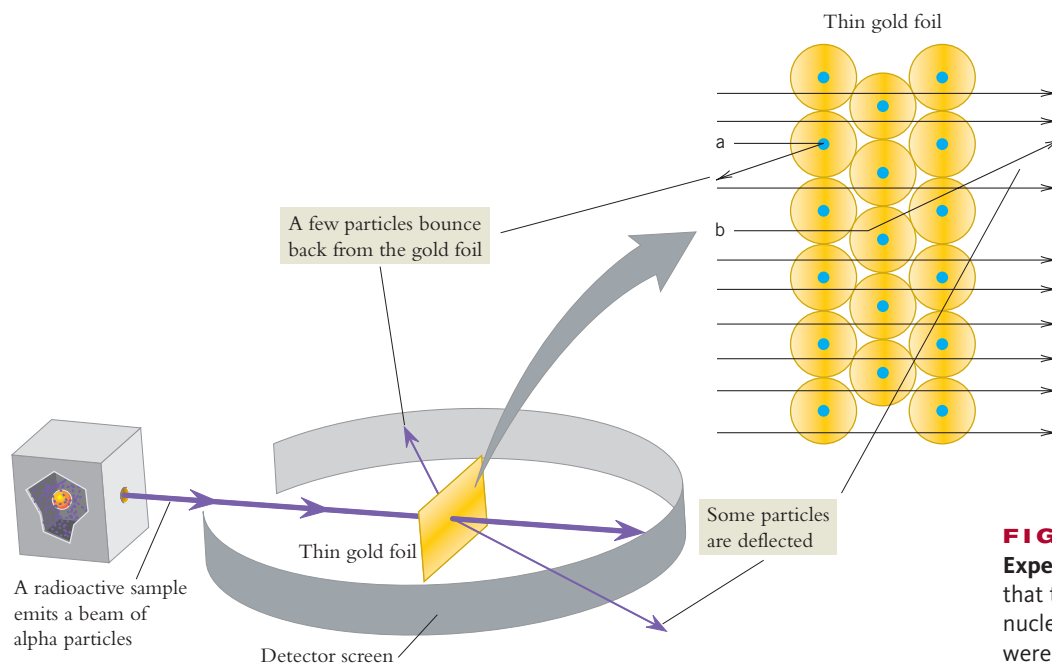
If we had a magical microscope that could peer into the atom, we would find that there are even more fundamental particles within. As we enter the confines of the atom, we would first encounter a relatively small particle (compared to the other particles in the atom) called an **electron**. The electron was the first subatomic particle to be identified. In 1897, J. J. Thomson characterized the electron by proving that it has a negative electrical charge (assigned a value of  $-1$ ) and is common to the atoms of all elements. The identification of electrons indicated that matter is electrical in nature and that electrostatic forces are at work within the confines of the atom. **Electrostatic forces** consist of forces of attraction between unlike charges and forces of repulsion between like charges. (See Figure 2-4.) Atoms themselves have no net electrical charge, so they must contain positive charges that counterbalance the negative charge of the electrons.

The first model of the atom based on this information was proposed by Thomson and was known as the plum pudding model of the atom (plum pudding was a popular English dessert). It was suggested that the positive charge would be diffuse and evenly distributed throughout the volume of the atom (analogous to pudding). This is logical—the like positive charges would tend to spread out as much as possible because of their mutual repulsion. The negative particles (electrons) would be embedded throughout the atom like raisins in the pudding. There would be enough electrons to balance the positive charge. Since few of us identify with plum pudding, a better analogy would be to picture the atom as a ball of cotton with tiny seeds (representing electrons) distributed throughout the cotton. (See Figure 2-5.)

### 2-3.2 The Nuclear Model of the Atom

The next major development in understanding the atom occurred in 1911. Ernest Rutherford in England conducted experiments that he fully expected would support the accepted model of Thomson. His results, however, suggested a radically different model. Radioactivity had recently been discovered, one form of which is called alpha radiation. It is composed of positively charged helium atoms that are spontaneously ejected at high velocities from certain heavy elements. When students in his laboratories bombarded a thin foil of gold with the small, fast-moving alpha particles, they expected that the alpha particles would pass right through the large atoms of gold with very little effect. The small, hard alpha particles should easily push the tiny electrons within the gold atoms aside and pass unaffected through the diffuse positive charge, similar to bullets through a bale of cotton. Instead, a small number of the alpha particles were deflected significantly from their path; a few even came straight back. Imagine shooting a volley of bullets into a thin bale of cotton and finding one or two bullets being ricocheted at a large angle. The conclusion would have





**FIGURE 2-6 Rutherford's Experiment** Rutherford suggested that the atom contains a small nucleus, since a few alpha particles were deflected or reflected back.

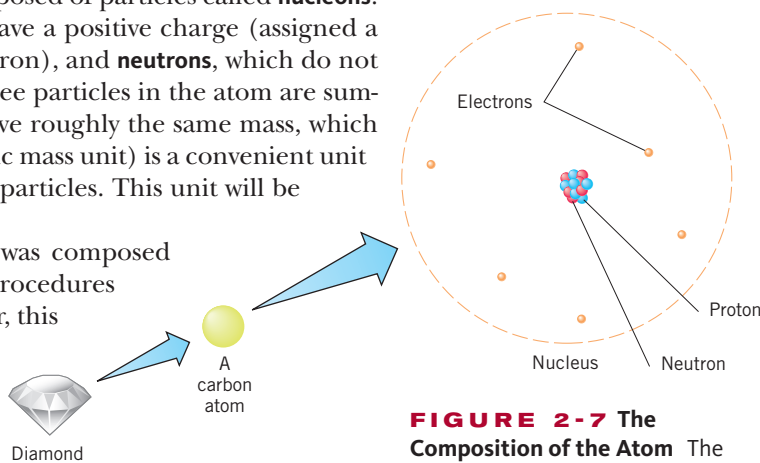
to be that something hard, like a rock, was embedded in the soft cotton. Likewise, Rutherford was forced to conclude that the gold atoms had a small, hard core containing most of the mass of the atom and all of the positive charge.

Rutherford's new model was needed to explain the experimental results. The close encounters between the alpha particles and core, or **nucleus**, would cause the alpha particles to be deflected because of the repulsion of like positive charges. Occasional "direct hits" onto the nucleus would reflect the alpha particle back toward the source. (See Figure 2-6.) The alpha particles that were unaffected indicated that most of the volume of the atom is actually empty space containing the very small electrons. At first scientists wondered why the electrons were not pulled into the nucleus. However, an explanation of this puzzle would eventually be advanced through modern theories. To get an idea about proportions of the atom, imagine a nucleus expanded to the size of a softball. In this case, the radius of the atom would extend for about 1 mile.

### 2-3.3 The Particles in the Nucleus

Later experiments showed that the nucleus is composed of particles called **nucleons**. There are two types of nucleons: **protons**, which have a positive charge (assigned a value of +1, equal and opposite to that of an electron), and **neutrons**, which do not carry a charge. (See Figure 2-7.) Data on these three particles in the atom are summarized in Table 2-3. The proton and neutron have roughly the same mass, which is about "1 amu" ( $1.67 \times 10^{-24}$  g). The amu (atomic mass unit) is a convenient unit for the masses of individual atoms and subatomic particles. This unit will be defined more precisely in the next section.

For some time, it was thought that the atom was composed of just these three particles. As experimental procedures became more elaborate and sophisticated, however, this model became outdated. It now appears that the proton and the neutron are themselves composed of various combinations of even more fundamental particles called quarks. Fortunately for us, the original three-particle model of the atom still meets the needs of the chemist.



**FIGURE 2-7 The Composition of the Atom** The atom is composed of electrons, neutrons, and protons.

**TABLE 2-3** Atomic Particles

| NAME     | SYMBOL   | ELECTRICAL CHARGE | MASS (amu) | MASS (g)                |
|----------|----------|-------------------|------------|-------------------------|
| Electron | <i>e</i> | -1                | 0.000549   | $9.110 \times 10^{-28}$ |
| Proton   | <i>p</i> | +1                | 1.00728    | $1.673 \times 10^{-24}$ |
| Neutron  | <i>n</i> | 0                 | 1.00867    | $1.675 \times 10^{-24}$ |

**ASSESSING THE OBJECTIVE FOR SECTION 2-3**

**EXERCISE 2-3(a) KNOWLEDGE:** Identify the specific subatomic particle(s).

- (a) smallest of the three
- (b) found in the nucleus
- (c) most massive
- (d) positive in charge

**EXERCISE 2-3(b) KNOWLEDGE:** Complete the following table.

| PARTICLE | MASS (amu) | CHARGE  | LOCATION           |
|----------|------------|---------|--------------------|
| Proton   |            |         |                    |
|          |            | Neutral |                    |
|          |            |         | Outside of nucleus |

**EXERCISE 2-3(c) ANALYSIS:** Answer the following questions.

- (a) Where is virtually all of the mass of an atom located?
- (b) What takes up most of the volume of an atom?
- (c) Historically, which was the first particle to be identified?

**EXERCISE 2-3(d) SYNTHESIS:** It has been proposed that neutrons are simply particles formed when protons and electrons are combined into one particle. What facts about neutrons suggest this might be the case?

*For additional practice, work chapter problems 2-9 and 2-10.*

**OBJECTIVES FOR SECTION 2-4**

(a) Define the terms *atomic number*, *mass number*, and *isotope*. (b) Using the table of elements, determine the number of protons, neutrons, and electrons in any isotope of an element. (c) Demonstrate how the atomic mass of an element is determined from isotopes and their percent abundance.

## 2-4 ATOMIC NUMBER, MASS NUMBER, AND ATOMIC MASS



**LOOKING AHEAD!** We are now ready to look into how protons, neutrons, and electrons define the atoms of a particular element. We will see in this section why not all atoms of an element are exactly the same and how the atoms of one element differ from another. ■

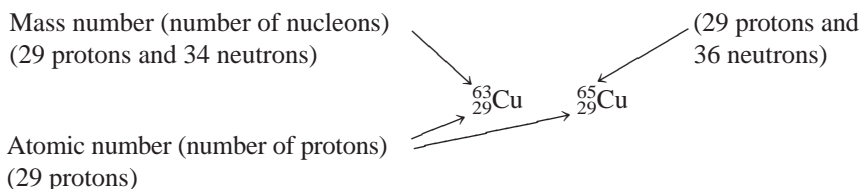
### 2-4.1 Atomic Number, Mass Number, and Isotopes

In Dalton's original atomic theory, he suggested that all atoms of an element are identical. But if we look at a number of atoms of most elements, we find that this statement is not exactly true. For example, consider the atoms of the element copper. Most atoms are composed of a nucleus containing a total of 63 nucleons, of which 29 are protons and 34 are neutrons. The atom also contains

29 electrons that exactly balance the positive charge of the protons, resulting in a neutral atom. *The number of protons in the nucleus (which is equal to the total positive charge) is referred to as the atom's **atomic number**. The total number of nucleons (protons and neutrons) is called the **mass number**.* Therefore, this particular copper atom has an atomic number of 29 and a mass number of 63. There are other copper atoms that are not exactly the same, however. These atoms of copper have a mass number of 65 rather than 63. This means that these atoms have 36 neutrons as well as 29 protons. *An atom of a specific element with a specific mass number is known as an **isotope**.* Isotopes of an element have the same atomic number but different mass numbers.

Most elements that are present in nature exist as a mixture of isotopes. *It is the atomic number, however, that distinguishes one element from another.* Any atom with an atomic number of 29, regardless of any other consideration, is an atom of copper. If the atomic number is 28, the element is nickel; if it is 30, the element is zinc.

Specific isotopes are written in a form known as *isotopic notation*. In isotopic notation, the mass number is written as a superscript to the left of the element. Sometimes, the atomic number is written as a subscript, also on the left. The indication of the atomic number is strictly a convenience. Since the atomic number determines the identity of the element, it can therefore be determined from the symbol. The isotopic notations for the two isotopes of copper are written as follows.



The convention for verbally naming specific isotopes is to use the element's name followed by its mass number. For example,  ${}^{63}\text{Cu}$  is called copper-63, and  ${}^{65}\text{Cu}$  is called copper-65. From either the written isotopic notation or the isotope name, we can determine the number of each type of particle in an isotope, as we will see in Example 2-1.

### EXAMPLE 2-1

#### Calculating the Number of Particles in an Isotope

How many protons, neutrons, and electrons are present in  ${}^{90}_{38}\text{Sr}$ ?

#### PROCEDURE

The subscript (and symbol) provide us information on protons. Since this is a neutral atom, the number of protons and electrons is the same. The superscript gives us the total number of protons and neutrons. The number of neutrons alone is the difference.

#### SOLUTION

$$\begin{aligned}\text{number of protons} &= \text{atomic number} = \underline{\underline{38}} \\ \text{number of neutrons} &= \text{mass number} - \text{number of protons} \quad 90 - 38 = \underline{\underline{52}} \\ \text{number of electrons} &= \text{number of protons} = \underline{\underline{38}}\end{aligned}$$

#### ANALYSIS

If you knew only the name of an element, which, if any, of the fundamental particles could you determine? Protons and electrons can be determined directly from the identity of the element, but the number of neutrons must be determined from the mass number. Knowing the specific isotope of an element allows you to determine the exact numbers of protons, neutrons, and electrons.

#### SYNTHESIS

What would happen in an atom if the number of protons and electrons were not exactly balanced? What if there was an extra electron? Or one too few? Would the positive and negative charges cancel out? Clearly not. If there was an extra electron, the atom would have an overall negative charge. If there was one too few, there would be an overall positive charge. This situation occurs and is explored later in this chapter.

In Chapter 6, we'll consider how the mass of one element compares to another. The mass of the electrons is extremely small compared to the masses of the protons and neutrons, so it is not included in the mass of an isotope. Thus, the mass number of an isotope is a convenient but rather imprecise measure of its mass. It is imprecise because electrons are not included and protons and neutrons do not have exactly the same mass.

### 2-4.2 Isotopic Mass and Atomic Mass

A more precise measure of the mass of one isotope relative to another is known as the isotopic mass. **Isotopic mass** is determined by comparison to a standard,  $^{12}\text{C}$ , which is defined as having a mass of exactly 12 atomic mass units. Therefore, one **atomic mass unit** (amu) is a mass of exactly  $1/12$  of the mass of  $^{12}\text{C}$ . For example, precise measurements show that the mass of  $^{10}\text{B}$  is 0.83442 times the mass of  $^{12}\text{C}$ , which means it has an isotopic mass of 10.013 amu. From similar calculations, we find that the atomic mass of  $^{11}\text{B}$  is 11.009 amu. Since boron, as well as most other naturally occurring elements, is found in nature as a mixture of isotopes, the atomic mass of the element reflects this mixture. The **atomic mass** of an element is obtained from the weighted average of the atomic masses of all isotopes present in nature. A weighted average relates the isotopic mass of each isotope present to its percent abundance. It can be considered as the isotopic mass of an "average atom," although an *average* atom does not itself exist. Example 2-2 illustrates how atomic mass relates to the distribution of isotopes.



### Isotopes and the History of Earth's Weather



Greenland.

Lately it seems like we are always hearing of some great storm or heat record. Is something strange going on, or are the media just doing a better job of reporting these events?

Actually, we are all anxious to know whether the climate is permanently changing and, if so, whether it is going to get

worse. The key to predicting the future, however, may lie in understanding the past. An ingenious key to past climates is found with the naturally occurring isotopes of oxygen and hydrogen. We will consider here how the isotopes of oxygen are put to use.

Oxygen is composed of 99.76%  $^{16}\text{O}$ , 0.04%  $^{17}\text{O}$ , and 0.20%  $^{18}\text{O}$ , which produces a weighted average of 15.9994. This means that only 24 out of 10,000 oxygen atoms are "heavy" oxygen atoms (i.e.,  $^{17}\text{O}$  or  $^{18}\text{O}$ ). When  $^{17}\text{O}$  or  $^{18}\text{O}$  is part of a water molecule, the properties are very slightly different from normal water ( $\text{H}_2\ ^{16}\text{O}$ ). For example, the heavier water evaporates just a little more slowly than normal water. The colder the temperature of the oceans, the less heavy oxygen ends up in the clouds.

This means that the amount of water with the heavier oxygen is slightly less in fresh water (which comes from precipitation of the evaporated water) than in the ocean. But even this can vary ever so slightly. When the climate is colder than normal, less water evaporates from the ocean and so the amount of heavy water in precipitation is less than normal.

Greenland and Antarctica are our natural weather-history laboratories. Greenland has been covered with ice for more than 100,000 years and Antarctica for almost 1 million years. In some areas of Greenland, the ice is now 2 miles deep. Year by year, the snow has been accumulating and has been pressed down into layers that resemble tree rings. Scientists have bored through the ice and analyzed the layers for their content of dust, trapped gases, and the ratio of oxygen isotopes. Results of isotope studies indicate that the Northern Hemisphere was a whopping  $20^\circ\text{C}$  (or  $36^\circ\text{F}$ ) colder during the last ice age (about 30,000 years ago) than it is now. More important, variations in the weather from then to now have also been determined. These studies will help us understand and perhaps predict what's going to happen to our weather in the future. Is our current warming a natural occurrence or a new phenomenon? Most evidence indicates that humans have a hand in the warming weather.

**EXAMPLE 2-2****Calculating the Atomic Mass of an Element from Percent Distribution of Isotopes**

In nature, the element boron occurs as 19.9%  $^{10}\text{B}$  and 80.1%  $^{11}\text{B}$ . If the isotopic mass of  $^{10}\text{B}$  is 10.013 and that of  $^{11}\text{B}$  is 11.009 amu, what is the atomic mass of boron?

**PROCEDURE**

Find the contribution of each isotope toward the atomic mass by multiplying the percent in decimal form by the isotopic mass. Recall that percent can be expressed as a normal fraction or a decimal fraction. (e.g., 25% =  $1/4$  = 0.25)

**SOLUTION**

$$^{10}\text{B} \ 0.199 \times 10.013 = 1.99 \text{ amu}$$

$$^{11}\text{B} \ 0.801 \times 11.009 = \underline{8.82 \text{ amu}}$$

$$\text{atomic mass of boron} = \underline{\underline{10.81}}$$

**ANALYSIS**

Based on the percentages of boron-10 and boron-11, does this answer seem reasonable? Since the atomic mass is a weighted average of the two isotopes, and they have mass numbers of 10 and 11, the answer should be between those values. It should be closer to the isotope with the higher percent abundance. The answer of 10.81 is between the two numbers and closer to the isotope of 80.1% abundance.

**SYNTHESIS**

The atomic mass of boron is approximately 80% of the way between the mass numbers of boron-10 and boron-11. What can you conclude about the percentages of various isotopes of an element whose atomic mass is very close to an integer? Consider carbon as an example. Its atomic mass is 12.011, just a little higher than 12 exactly. We would most likely conclude that the isotope with mass 12 is by far the most common (actually, more than 99%).

**ASSESSING THE OBJECTIVES FOR SECTION 2-4**

**EXERCISE 2-4(a) KNOWLEDGE:** Identify the following as atomic number, mass number, or isotopic mass.

- (a) always an integer value
- (b) the superscript in isotopic notation
- (c) the total mass of the atom
- (d) the number of protons
- (e) determines the number of protons and neutrons combined.

**EXERCISE 2-4(b) ANALYSIS:** Determine the number of protons, neutrons, and electrons in the following isotopes.

- (a)  $^{13}_6\text{C}$     (b)  $^1_1\text{H}$     (c)  $^{238}_{92}\text{U}$

**EXERCISE 2-4(c) ANALYSIS:** Write the isotopic notation for the following three species.

- (a) protons = 9, neutrons = 10, electrons = 9
- (b) protons = 35, neutrons = 44, electrons = 35
- (c) protons = 20, neutrons = 20, electrons = 20

**EXERCISE 2-4(d) ANALYSIS:** Antimony (Sb) has two naturally occurring isotopes:  $^{121}\text{Sb}$ , with a mass of 120.903 amu and a 57.3% abundance, and  $^{123}\text{Sb}$ , with a mass of 122.904 amu and a 42.7% abundance. Determine antimony's atomic mass.

**EXERCISE 2-4(e) ANALYSIS:** Lithium has two naturally occurring isotopes:  $^6\text{Li}$  has a mass of 6.015 and is 7.42% abundant;  $^7\text{Li}$  has a mass of 7.016 and is 92.58% abundant. Calculate the atomic mass of lithium.

**EXERCISE 2-4(f) SYNTHESIS:** All through the Middle Ages, alchemists searched for ways to turn base metals, such as lead, into gold. Why was this a chemically fruitless endeavor?



**EXERCISE 2-4(g) SYNTHESIS:** Bromine has two naturally occurring isotopes,  $^{79}\text{Br}$  and  $^{81}\text{Br}$ . From its atomic weight, estimate the percentage abundances of the two isotopes.

*For additional practice, work chapter problems 2-11, 2-13, 2-15, 2-26, and 2-28.*

## PART A SUMMARY

### KEY TERMS

- 2-1** All substances can be classified as either **elements** or **compounds**. p. 52
- 2-1.4** Each element is designated by a unique **symbol**. p. 54
- 2-2.1** According to **atomic theory**, the basic particle of an element is an **atom**. p. 56
- 2-3.1** The discovery of the **electron** proved the presence of **electrostatic forces** in the atom. p. 58
- 2-3.2** Experiments indicated that the atom contained a central positively charged core called a **nucleus**. p. 59
- 2-3.3** The nucleus consists of particles called **nucleons**, which are either **neutrons** or **protons**. p. 59
- 2-4.2** The number of protons in a nucleus is known as its **atomic number**, and the number of nucleons is known as its **mass number**. p. 61
- 2-4.1** Naturally occurring elements are composed of one or more **isotopes**. p. 61
- 2-4.2** The standard of mass is  $^{12}\text{C}$ , which is defined as exactly 12 **atomic mass units** (amu). The **isotopic mass** of an isotope is determined experimentally by comparison to this standard. p. 62
- 2-4.2** The **atomic mass** of an element is determined by its naturally occurring isotopes and their percent abundance. p. 62

### SUMMARY CHART

| <i>Two Common Elements</i>   |  |
|--|--|
| <b>Name: Chromium</b>  | <b>Name: Arsenic</b>                             |
| Symbol: <b>Cr</b>  | Symbol: <b>As</b>                                |
| Isotopic composition:<br>$^{50}\text{Cr}$ (4%), $^{52}\text{Cr}$ (84%),<br>$^{53}\text{Cr}$ (10%), $^{54}\text{Cr}$ (2%) | Isotopic composition:<br>$^{75}\text{As}$ (100%) |
| Atomic mass: 51.9961   | Atomic mass: 74.92159                            |

## PART B COMPOUNDS AND THEIR COMPOSITION

### SETTING A GOAL

- You will learn to distinguish between ionic and molecular compounds based on their chemical structure and general properties.

### OBJECTIVES

- 2-5 and 2-6** Describe the difference between a molecular and an ionic compound.
- 2-6** Write the formulas of simple ionic compounds given the charges on the ions.

### ▶ OBJECTIVES FOR SECTION 2-5 AND 2-6

Describe the difference between a molecular and an ionic compound.

## 2-5 MOLECULAR COMPOUNDS



**LOOKING AHEAD!** The atoms of elements are usually joined together with other atoms of the same element or other elements into a more complex form of particulate matter. In this section, we will examine one of the two principal forms of matter formed by the combined atoms. ■

Every element and compound has a unique set of properties. Properties *describe the particular characteristics or traits of a substance*. We will have more to say about specific properties in the next chapter. Elements and compounds can be referred to as pure substances. **Pure substances have definite compositions and definite, unchanging properties.** (See Figure 2-8.)

### 2-5.1 Recognizing the Names of Compounds

The names of the simplest compounds are usually based on the elements from which they are composed, and most contain two words. Carbon dioxide, sodium sulfite, and silver nitrate all refer to specific compounds. Notice that the second word ends in *-ide*, *-ite*, or *-ate*. A few compounds have three words, such as sodium hydrogen carbonate. A number of compounds have common names of one word, such as water, ammonia, lye, and methane. We will talk in more detail about how we determine the names of compounds in Chapter 4.

### 2-5.2 Molecules, Molecular Compounds, and Covalent Bonds

About three centuries ago, water was thought to be an element. When scientists were able to decompose water into hydrogen and oxygen, it became apparent that water is a compound. Just as the basic particles of most elements are atoms, the basic particles of a particular type of compound are known as molecules. **A molecule is formed by the chemical combination of two or more atoms. Molecules composed of different atoms are the basic particles of molecular compounds. The atoms in a molecule are joined and held together by a force called the covalent bond.** (The nature of the covalent bond will be examined in more detail in Chapter 9.) If it were possible to magnify a droplet of water and visualize its basic particles, we would see that it is an example of a molecular compound. Each molecule of water is composed of two atoms of hydrogen joined by covalent bonds to one atom of oxygen. (See Figure 2-9.) Molecules can contain as few as two atoms or, in the case of the complex molecules on which life is based, millions of atoms. We will concentrate on molecular compounds in the remainder of this section. In the next section we will discuss a second category of compounds known as ionic compounds.

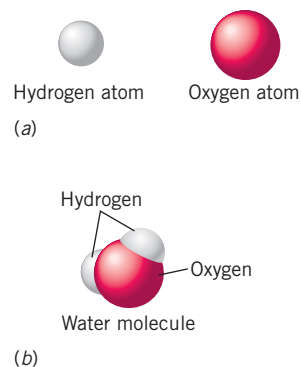
### 2-5.3 The Formulas of Molecular Compounds

A compound is represented by the symbols of the elements of which it is composed. This is called the **formula of the compound**. The familiar formula for water is therefore  $\text{H}_2\text{O}$ . Note that the 2 is written as a subscript, indicating that the molecule has two hydrogen atoms. When there is only one atom of a given element present (e.g., oxygen), a subscript of “1” is assumed but not shown.

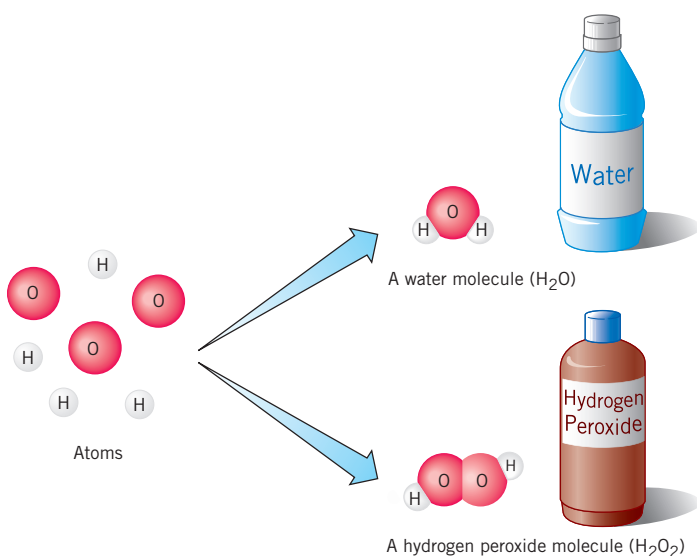
What makes one molecular compound different from another? The answer is that each chemical compound has a unique formula or arrangement of atoms in its molecules. For example, there is another compound composed of just hydrogen and oxygen, but it has the formula  $\text{H}_2\text{O}_2$ . Its name is hydrogen peroxide, and its properties are distinctly different from those of water ( $\text{H}_2\text{O}$ ). Figure 2-10 illustrates how the *atoms* of hydrogen and oxygen combine to form the *molecules* of two different compounds. The formulas of other well-known compounds are  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (sucrose, which we know as table sugar),  $\text{C}_9\text{H}_8\text{O}_4$  (aspirin),  $\text{NH}_3$  (ammonia), and  $\text{CH}_4$  (methane).



**FIGURE 2-8 Some Familiar Compounds** These products all contain one compound. Notice their common names do not indicate the elements in the compounds.



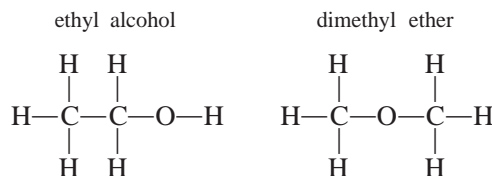
**FIGURE 2-9 Molecules of Water** A molecule of water is composed of one atom of oxygen and two atoms of hydrogen.



**FIGURE 2-10 Atoms and Molecules** Atoms of hydrogen and atoms of oxygen can combine to form molecules of two different compounds.

Sometimes two or more compounds may share the same chemical formula. What, then, makes them unique? In this case, their difference stems from the sequence of the atoms within the molecule. For example, ethyl alcohol and dimethyl ether are two distinct compounds, but both have the formula C<sub>2</sub>H<sub>6</sub>O. The difference in the two compounds lies in the order of the bonded atoms.

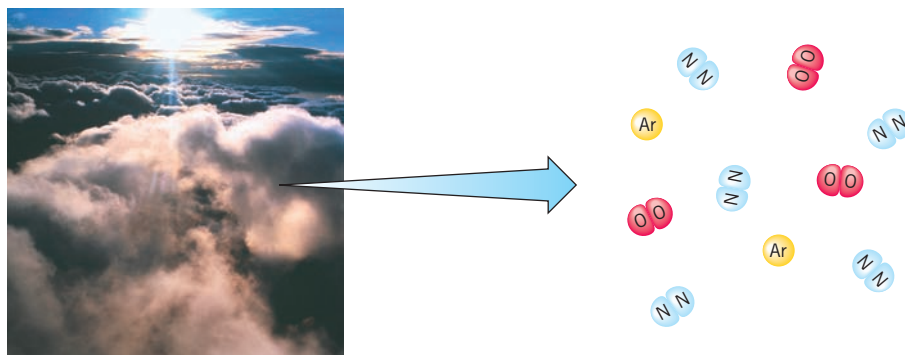
Notice that in ethyl alcohol the order of bonds is C—C—O and in ether the order is C—O—C. (The dashes between atoms represent covalent chemical bonds, which hold the atoms together.) The difference in the arrangement has a profound effect on the properties of these two compounds. Ingestion of alcohol causes intoxication, while a similar amount of ether may cause death. *Formulas that show the order and arrangement of specific atoms are known as structural formulas.*



### 2-5.4 Molecular Elements

Each breath of fresh air that we inhale is primarily just three elements—nitrogen (78%), oxygen (21%), and argon (less than 1%), although there are traces of other gases as well. What would we see if we could magnify a sample of air so that the atoms of these three elements could become visible? The most noticeable difference among these elements is that argon exists as solitary atoms, but atoms of nitrogen and oxygen are joined together in pairs to form molecules. (See Figure 2-11.)

Hydrogen, fluorine, chlorine, bromine, and iodine in their elemental form also exist as diatomic (two-atom) molecules under normal temperature conditions. A form of elemental phosphorus consists of molecules composed of four atoms, and a form of sulfur consists of molecules composed of eight atoms. There is also a second form of elemental oxygen, known as ozone, which is composed of three atoms of oxygen. Molecules composed of two or more atoms of the same element are also referred to by formulas such as I<sub>2</sub> (iodine), O<sub>2</sub> (oxygen), O<sub>3</sub> (ozone), and P<sub>4</sub> (phosphorus).



**FIGURE 2-11 The Composition of the Atmosphere** Our atmosphere is composed mostly of nitrogen and oxygen molecules with a small amount of argon atoms.

## 2-6 IONIC COMPOUNDS

### OBJECTIVE FOR SECTION 2-6

Write the formulas of simple ionic compounds given the charges on the ions.



**LOOKING AHEAD!** There is a second classification of compounds known as ionic compounds. You may have noticed that molecular compounds are often found as gases or liquids. Ionic compounds are always solids at normal temperatures. We will discuss ionic compounds next. ■

### 2-6.1 Cations and Anions

When you scrape your stocking feet along a carpet in a dry room, you often pick up a charge of static electricity that discharges when you touch something metallic, resulting in an unpleasant shock. Atoms can also achieve an electrostatic charge. *When atoms have an electrostatic charge, they are known as ions. Positively charged ions are known as cations, and negatively charged ions are called anions.* Ordinary table salt is a compound named sodium chloride. In sodium chloride, the sodium exists as a cation with a single positive charge and the chlorine exists as an anion with a single negative charge. This is illustrated with a + or - as a superscript to the right of the symbol of the element as follows.

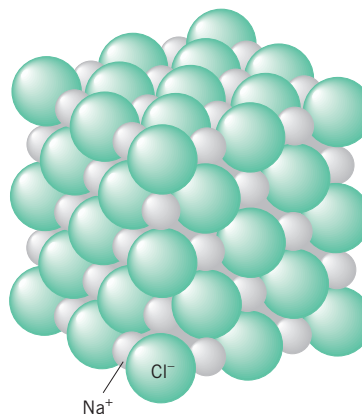


### 2-6.2 The Origin of the Charge on Ions

To understand why the  $\text{Na}^+$  cation has a positive charge, we must look at its basic particles and how an atom of Na differs from a  $\text{Na}^+$  cation. A cation contains fewer electrons than the number of protons found in a neutral atom. An anion contains more electrons than there are protons in a neutral atom. *In both cases, it is the electrons that are out of balance, not the protons.* A +1 charge on a cation indicates that it has one *less* electron than its number of protons (its atomic number), and a +2 charge indicates that the cation has two *fewer* electrons than its atomic number. For example, the  $\text{Na}^+$  cation has 11 protons (the atomic number of Na) and 10 electrons. The +1 charge arises from this imbalance [i.e.,  $(11\text{p} \times +1) + (10\text{e} \times -1) = +1$ ]. An anion with a -1 charge has one *more* electron than the atomic number of the element, and a -2 charge indicates two *more* electrons than its atomic number. For example, the  $\text{S}^{2-}$  ion has 16 protons in its nucleus and 18 electrons. The -2 charge arises from the two extra electrons [i.e.,  $(16\text{p} \times +1) + (18\text{e} \times -1) = -2$ ].

### 2-6.3 The Formulas of Ionic Compounds

Since the sodium cations and the chlorine anions are oppositely charged, the ions are held together by electrostatic forces of attraction. In Figure 2-12 the ions in sodium chloride are shown as they would appear if sufficient magnification were possible. Note that each cation (one of the smaller spheres) is attached to more than one anion. In fact, each ion

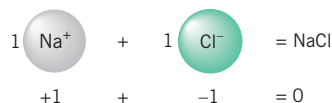


**FIGURE 2-12**  
**The Ions in Sodium Chloride** A solid ionic compound such as sodium chloride exists as an arrangement of ions.

is surrounded by six oppositely charged ions. The reason that cations are usually small compared to anions will be discussed in Chapter 8. Bonding in these compounds is much different from that of the previously discussed molecular compounds, in which atoms bond together to form discrete entities (molecules.)

Compounds consisting of ions are known as **ionic compounds**. The electrostatic forces holding the ions together are known as **ionic bonds**. The ions in ionic compounds are locked tightly in their positions by the strong electrostatic attractions. This results in solid compounds that are almost all hard and rigid. They are the material of most rocks and minerals.

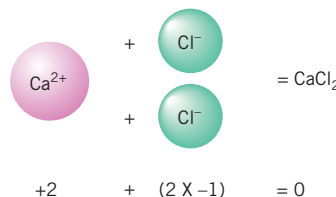
The formula of sodium chloride is



This represents the simplest ratio of cations to anions present (in this case, one to one). This ratio reflects the fact that the two ions have equal and opposite charges and that *in any ionic compound, the anions and cations exist together in a ratio such that the negative charge balances the positive charge* [e.g.,  $+1 + (-1) = 0$ ]. Notice that the charges are not displayed in the formula. *The simplest whole-number ratio of ions in an ionic compound is referred to as a formula unit.*

Ions may also have charges greater than 1. In these cases, the ratio of ions in the formula may not be simply one-to-one.

Calcium chloride is a compound composed of  $\text{Ca}^{2+}$  cations and  $\text{Cl}^-$  anions. Two chlorine anions are needed to balance the  $+2$  charge on the calcium [ $+2 + (2 \times -1) = 0$ ]. Thus the formula is



### EXAMPLE 2-3

#### Determining the Formula of an Ionic Compound

What is the formula unit of an ionic compound formed from the  $\text{Al}^{3+}$  cation and the  $\text{S}^{2-}$  anion?

#### PROCEDURE

In an ionic compound, the total positive charge of all cations and the total negative charge of all anions must be the same absolute value. We need to determine how many  $+3$ 's will cancel with how many  $-2$ 's. Look for the least common multiple of the charges.

#### SOLUTION

The least common multiple of 2 and 3 is 6:

$$2 \times (+3) = +6$$

$$3 \times (-2) = -6$$

$(+6) + (-6) = 0$ , a neutral compound. It will take **2**  $\text{Al}^{3+}$  and **3**  $\text{S}^{2-}$  to form an ionic compound. The formula is written  **$\text{Al}_2\text{S}_3$** .

#### ANALYSIS

Do you notice a pattern between the charges on the ions and the subscripts? The absolute value of the charge on the sulfur, 2, becomes the subscript for the aluminum. Similarly, the charge on the aluminum, 3, becomes the subscript for the sulfur. This works in most cases, but don't lose sight of the fact that we do this to *balance the charge*. Do not write  $\text{Mg}_2\text{S}_2$ , even though the charges on the ions are  $+2$  and  $-2$  respectively. It is sufficient to have one of each to balance the charge:  $\text{MgS}$ .



## SYNTHESIS

A positive charge means a loss of electrons. What happened to these electrons? A negative charge means a gain of electrons. Where did they come from? It becomes clear that the electrons lost by one atom in a compound were gained by the other. It now makes all the more sense that charges have to balance. As electrons shift from one atom to another, there must always be the same number of electrons lost as gained.

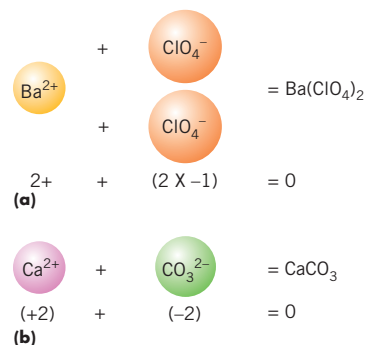
### 2-6.4 The Formulas of Compounds Containing Polyatomic Ions

Groups of atoms that are covalently bonded to each other may as a whole also be cations or anions. They are known as **polyatomic ions**. Examples include the nitrate anion ( $\text{NO}_3^-$ ), the perchlorate anion ( $\text{ClO}_4^-$ ), and the ammonium cation ( $\text{NH}_4^+$ ). When more than one polyatomic ion is in a formula unit, parentheses and a subscript are used. When there is only one polyatomic ion, no parentheses are used. Barium perchlorate (a compound containing one  $\text{Ba}^{2+}$  ion and two  $\text{ClO}_4^-$  ions) is represented in margin in (a), and calcium carbonate (a compound containing one  $\text{Ca}^{2+}$  ion and one  $\text{CO}_3^{2-}$  ion) is represented in (b).

Sometimes the formulas of molecular compounds are confused with those of ions. (See Figure 2-13.) For example,  $\text{NO}_2$  is the formula of a molecular compound known as nitrogen dioxide. The  $\text{NO}_2$  molecules are neutral entities. It is a brownish gas responsible for some air pollution. Notice that no charge is shown by the formula. The  $\text{NO}_2^-$  species (known as the nitrite ion) contains a negative charge, which means that it is a polyatomic ion. It exists only with a cation as part of an ionic compound (e.g.,  $\text{NaNO}_2$ , sodium nitrite). Remember that cations and anions do not normally exist alone but only as the two oppositely charged parts of an ionic compound. We will spend more time writing and naming ionic compounds in Chapter 4.

The charge on polyatomic ions also arises from an imbalance of electrons. For example, the  $\text{CO}_3^{2-}$  ion has a total of 30 protons in the four nuclei [i.e.,  $6(\text{C}) + (3 \times 8)(\text{O}) = 30$ ]. The presence of a  $-2$  charge indicates that 32 negatively charged electrons are present.

In the next chapter we will see how the properties of molecular and ionic compounds differ. In a later chapter, we will discuss why specific atoms tend to acquire positive charges while others tend to acquire negative charges.



**FIGURE 2-13 Molecules and Ions**  $\text{NO}_2$  is a gaseous compound composed of discrete neutral molecules, whereas the  $\text{NO}_2^-$  (nitrite) ion is part of a solid, ionic compound.

### EXAMPLE 2-4

#### Determining the Formula of an Ionic Compound Containing a Polyatomic Ion

What is the formula unit of an ionic compound formed from the  $\text{Fe}^{3+}$  cation and the  $\text{NO}_3^-$  anion?

#### PROCEDURE

Again, the total positive charge of all cations and the total negative charge of all anions must be the same absolute value. Determine the least common multiple of the two charges, and then use the necessary numbers as subscripts to get a neutral entity.

**SOLUTION**

The least common multiple of 3 and 1 is 3:

$$1 \times (+3) = +3$$

$$3 \times (-1) = -3$$

$(+3) + (-3) = 0$ , a neutral compound. It will take **1**  $\text{Fe}^{3+}$  and **3**  $\text{NO}_3^-$  to form an ionic compound with no net charge (neutral). Remember to include parentheses around the  $\text{NO}_3^-$  ion with “3” as a subscript to indicate three  $\text{NO}_3^-$  ions along with the one  $\text{Fe}^{3+}$  ion:  **$\text{Fe}(\text{NO}_3)_3$** .

**ANALYSIS**

How many atoms of each type—Fe, N and O—are present in one formula unit of  $\text{Fe}(\text{NO}_3)_3$ ? When the subscript is “1,” as in the case of iron, it is understood to be present. Subscripts apply only to what they immediately follow. The interior “3,” next to oxygen, applies only to the oxygen. The exterior “3,” by the parenthesis, applies to everything within the parenthesis. The formula unit therefore consists of one Fe atom, three N atoms, and nine O atoms.

**SYNTHESIS**

Is it possible to form an ionic compound composed of only two anions or of only two cations? If we again think of charges as resulting from the gain or loss of electrons, we realize that a theoretical substance made from two anions would have a total number of electrons greater than the number of protons. The substance would not be neutral and therefore not stable. The same argument applies to theoretical substances made entirely of cations. You must always match a cation with an anion to generate a neutral compound.

**ASSESSING THE  
OBJECTIVES FOR  
SECTIONS  
2-5 AND 2-6**

**EXERCISE 2-6(a) KNOWLEDGE:** Determine whether the following statements apply to molecular compounds, ionic compounds, or both.

- (a) composed of charged particles
- (b) have properties different than their constituent elements
- (c) consist of individual molecules
- (d) have an overall neutral charge
- (e) formula written as the smallest whole-number ratio of elements
- (f) held together by a covalent bond

**EXERCISE 2-6(b) ANALYSIS:** What is the formula of the ionic compounds formed by combining the following?

- (a)  $\text{Mg}^{2+}$  and  $\text{I}^-$       (b)  $\text{Li}^+$  and  $\text{SO}_4^{2-}$       (c)  $\text{Al}^{3+}$  and  $\text{Se}^{2-}$

**EXERCISE 2-6(c) ANALYSIS:** Complete the table by writing the chemical formula for ionic compounds formed from the corresponding cations and anions:

|                    | $\text{Cs}^+$ | $\text{Zn}^{2+}$ | $\text{Fe}^{3+}$ |
|--------------------|---------------|------------------|------------------|
| $\text{ClO}_3^-$   |               |                  |                  |
| $\text{O}^{2-}$    |               |                  |                  |
| $\text{PO}_4^{3-}$ |               |                  |                  |

**EXERCISE 2-6(d) SYNTHESIS:** If you saw that the formula of a compound was  $\text{C}_6\text{H}_{12}\text{O}_6$  and were asked whether the compound was ionic or molecular, which would you answer, and what evidence would you cite?

**EXERCISE 2-6(e) SYNTHESIS:** You are a research scientist analyzing athletes' blood for a particular illegal chemical whose formula is  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}$ . You found a chemical with that exact formula in one of the athlete's blood sample. Is that enough evidence to indict the athlete?

*For additional practice, work chapter problems 2-36, 2-42, 2-45, 2-46, and 2-56.*



## Ionic Compounds and Essential Elements

As our bodies age, it becomes more important that we include adequate amounts of trace elements in our diets. Some of these elements include boron, calcium, chromium, copper, iodine, iron, magnesium, phosphorus, potassium, and zinc. This is not an all-inclusive list—there are several others. In fact, we are learning more all the time about the role of other trace elements in our body chemistry. As a result, the list will only grow. Deficiencies of any of these elements can cause serious health effects. For example, one of the most widespread maladies is *anemia*. Anemia is caused by a shortage of red blood cells, which are involved in the transport of oxygen from the lungs to the tissues. Iron plays a key role in the action of the hemoglobin in red blood cells. If there is too little iron in the body, anemia results; on the other hand, too much iron in the body can also cause serious problems. Genetic problems can cause some individuals to accumulate excess iron in certain organs, resulting in a condition known as *hemochromatosis*. The victims of such “iron overload” can also be very sick indeed. This condition is usually treated by periodically removing blood from the individual. However, iron deficiency is the more common malady.

Of course, we all hear on television of the need for older individuals to take plenty of calcium supplements. As we age, bones may become brittle, especially among women. This condition is known as *osteoporosis*. It is important to take calcium supplements so as to slow or even stop this degenerative process.

The best way to make sure our bodies get all the necessary elements is to eat a balanced diet. This includes green leafy

vegetables as well as the usual meats, vegetables, dairy products, and carbohydrates. If that isn't enough, we may include a multivitamin on a daily basis. A typical multivitamin includes (besides vitamins) all of the trace elements, usually referred to as minerals, that we need. Actually, the minerals are not present as free elements but rather as components of a compound. For example, the most common calcium supplement is actually calcium carbonate ( $\text{CaCO}_3$ ). In nature,  $\text{CaCO}_3$  is known as limestone, chalk, or marble.

The essential element, the name of the compound containing the element, and its formula are shown in the accompanying table. Except for boric acid, all of the compounds shown are ionic. All are solid compounds that can be included in a solid pill.

| ELEMENT        | NAME OF COMPOUND  | FORMULA OF COMPOUND                              |
|----------------|-------------------|--|
| Boron (B)      | boric acid        | $\text{H}_3\text{BO}_3$                          |
| Calcium (Ca)   | calcium carbonate | $\text{CaCO}_3$                                  |
|                | calcium citrate   | $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$  |
| Chromium (Cr)  | chromic chloride  | $\text{CrCl}_3$                                  |
| Copper (Cu)    | cupric sulfate    | $\text{CuSO}_4$                                  |
|                | cupric gluconate  | $\text{Cu}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ |
| Iodine (I)     | sodium iodide     | $\text{NaI}$                                     |
| Iron (Fe)      | ferrous sulfate   | $\text{FeSO}_4$                                  |
|                | ferrous fumarate  | $\text{FeC}_4\text{H}_2\text{O}_4$               |
|                | ferrous gluconate | $\text{Fe}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ |
| Magnesium (Mg) | magnesium oxide   | $\text{MgO}$                                     |
| Phosphorus (P) | calcium phosphate | $\text{Ca}_3(\text{PO}_4)_2$                     |

Refer to Student Workshop at the end of the chapter.

### KEY TERMS

- 2-5** A sample of a particular element or compound is known as a **pure substance**. p. 65
- 2-5.2** **Molecular compounds** are composed of discrete **molecules**. p. 65
- 2-5.2** The atoms in molecules are held together by **covalent bonds**. p. 65
- 2-5.3** The **formula** of a molecular compound indicates the number of atoms of each element in one molecule. p. 65
- 2-5.3** The **structural formula** of a compound shows the position of the atoms relative to each other. p. 66
- 2-6.1** **Ions** are charged species that are either **cations** (positive) or **anions** (negative). p. 67
- 2-6.3** **Ionic compounds** are held together by **ionic bonds**, which are electrostatic interactions between positive and negative ions. p. 68
- 2-6.3** A **formula unit** of an ionic compound contains the simplest whole-number ratio of ions that balances the positive and negative charge. p. 68
- 2-6.4** Ionic compounds may contain **polyatomic ions**, which are groups of atoms that are held together by covalent bonds but that have a positive or negative charge. p. 69

### PART B SUMMARY

## SUMMARY CHART

| Compounds  |   |
|--|---|
| Molecular  | Ionic   |
| Composition: discrete neutral molecules  | Composition: cations (+) and anions (–)               |
| Example formula: NH <sub>3</sub> (ammonia)   | Example formula: Na <sub>2</sub> S (sodium sulfide)   |
| One formula unit:  | One formula unit:                                     |
| $\begin{array}{c} \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$ molecules | 2Na <sup>+</sup> S <sup>2-</sup> ions                 |
| Binding force: covalent bonds between atoms  | Binding force: ionic bonds between cations and anions |

## CHAPTER SUMMARY

All of the various forms of nature around us, from the simple elements in the air to the complex **compounds** of living systems, are composed of only a few basic forms of matter called **elements**. Each element has a name and a unique one- or two-letter **symbol**.

A little more than 200 years ago, John Dalton's **atomic theory** introduced the concept that elements are composed of fundamental particles called **atoms**. It has been about 30 years since we have been able to produce images of these atoms with a special microscope.

The atom is the smallest unique particle that characterizes an element. It is composed of more basic particles called **electrons** and **nucleons**. There are two types of nucleons, **protons** and **neutrons**. The relative charges and masses of these three particles are summarized in Table 2-3. The proton and electron are attracted to each other by **electrostatic forces**.

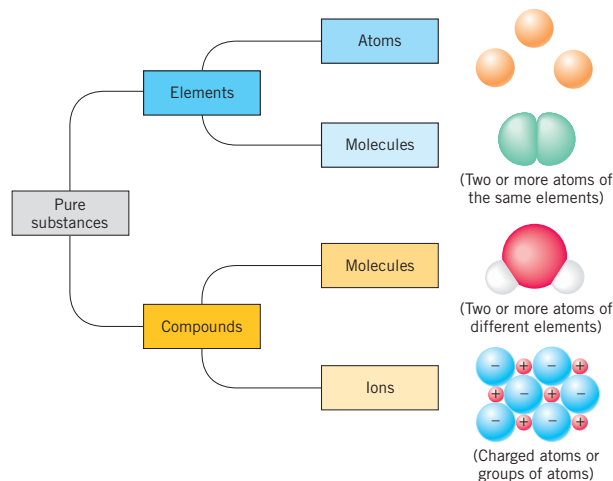
Rather than being a hard sphere, an atom is mostly empty space containing the negatively charged electrons. The protons and neutrons are located in a small dense core called the **nucleus**. The number of protons in an atom is known as its **atomic number**, which distinguishes the atoms of one element from those of another. The total number of nucleons in an atom is known as its **mass number**. Atoms of the same element may have different mass numbers and are known as **isotopes** of that element. An atom is neutral because it has the same number of electrons as protons.

Since protons and neutrons do not have exactly the same mass, the mass number is not an exact measure of the comparative masses of isotopes. A more precise measure of mass is the **isotopic mass**. This is obtained by comparing the mass of the particular isotope with the mass of <sup>12</sup>C, which is defined as having a mass of exactly 12 **atomic mass units** (amu). The **atomic mass** of an element is the weighted average of all of the naturally occurring isotopes found in nature.

Most elements are present in nature as aggregates of individual atoms. In some elements, however, two or

more atoms are combined by **covalent bonds** to produce basic units called **molecules**. **Molecular compounds** are also composed of molecules, although, in this case, the atoms of at least two different elements are involved. The **formula** of a molecular compound represents the actual number of atoms of each element contained in a molecular unit. Each compound has a unique arrangement of atoms in the molecular unit. These are sometimes conveniently represented by **structural formulas**.

There is another type of compound, however. Atoms can become electrically charged to form **ions**. An atom can have a net positive charge if there are fewer electrons than protons in the nucleus or a net negative charge when there are more electrons than protons. Groups of atoms that are covalently bonded together can also have a net charge and are known as **polyatomic ions**. An **ionic compound** is composed of **cations** (positive ions) and **anions** (negative ions). The interactions of cations and anions are known as **ionic bonds**. The formula of an ionic compound shows the type and number of ions in a **formula unit**. A formula unit represents the smallest whole-number ratio of cations and anions, which reflects the fact that the positive charge is balanced by the negative charge. The four most common ways that we find atoms in nature are summarized as follows:



| SECTION     | YOU SHOULD BE ABLE TO...  | EXAMPLES | OBJECTIVES     |                    |
|-------------|---|----------|----------------|--------------------|
|             |   |          | EXERCISES      | CHAPTER PROBLEMS   |
| 2-1         | Distinguish between elements and compounds.   |          | 1a, 1b, 1e, 1g | 31, 32, 34         |
|             | Match the names and symbols of common elements.   |          | 1c, 1d, 1f     | 1, 5, 6, 7         |
| 2-2         | List the postulates of the atomic theory.   |          | 2a, 2b, 2c     | 8                  |
| 2-3         | List the components of an atom, and their relative masses, charges, and location in the atom.                       |          | 3a, 3b, 3c, 3d | 9, 10              |
| 2-4         | Define the terms <i>atomic number</i> , <i>mass number</i> , and <i>isotope</i> .                                   |          | 4a, 4f         | 14, 18, 19         |
|             | Using the table of elements, determine the number of protons, neutrons, and electrons in any isotope of an element. | 2-1      | 4b, 4c         | 11, 13, 22         |
|             | Demonstrate how the atomic mass of an element is determined from isotopes and their percent abundance.              | 2-2      | 4d, 4e, 4g     | 26, 27, 28         |
| 2-5 and 2-6 | Describe the difference between a molecular and an ionic compound.  |          |                | 44, 45, 56, 63     |
| 2-6         | Write the formulas of simple ionic compounds given the charges on the ions.   | 2-3, 2-4 | 6a, 6d, 6e     | 39, 41, 43, 46, 50 |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**2-1(a)** Look at the table of elements inside the front cover. If the substance is present, it is an element. (a) element (b) compound (made from Na, C, H, and O) (c) compound (made from H and O) (d) compound (made from Si and O) (e) element

**2-1(b)** (a) Cu (b) S (c) Ca

**2-1(c)** (a) lead (b) phosphorus (c) sodium

**2-1(d)** Compounds are combinations of elements. How many different ways can 120 objects be combined? Theoretically, there are an infinite number of combinations. The actual number is in the tens of millions, with new ones created every day.

**2-1(e)** The elements with Latin roots for their names and symbols were likely discovered in ancient times (like gold). Since technology was not as advanced back then, it stands to reason that those elements must be the most stable and the most easily found in their free state.

**2-1(f)** You would have to run some sort of chemical test on it to see if it could be broken down any further. If test after test failed to break the substance down any further, you might begin to assume that the unknown substance was an element.

**2-2(a)** An *element* is composed of small, indivisible particles called *atoms*. Atoms of the same *element* are identical and have the same *properties*. Chemical *compounds* are composed of atoms of different elements combined in small *whole-number ratios*. Chemical *reactions* are rearrangements of *atoms* into different combinations.

**2-2(b)** (a) True. If all atoms of an element are identical, then an experiment should always yield the same result. (b) False. Even though compounds have specific whole number ratios of atoms, nothing prohibits them from combining in different numbers to form a different compound. (c) True. Indivisible means indivisible, at least as far as chemical properties are concerned. (d) True. The rearrangement that occurs in a chemical reaction ensures that no atoms disappear, nor are any atoms formed, in the reaction.

**2-2(c)** Democritus, the philosopher, based his ideas on nothing more than rational thought. Dalton used experimental evidence to support his conclusions. These conclusions have stood up to 200 years of scrutiny.

**2-3(a)** (a) electron (b) proton and neutron (c) neutron (just barely) (d) proton

**2-3(b)**

| Particle | Mass (amu) | Charge  | Location        |
|----------|------------|---------|-----------------|
| Proton   | 1          | +1      | Nucleus         |
| Neutron  | 1          | Neutral | Nucleus         |
| Electron | 0          | -1      | Outside nucleus |

**2-3(c)** (a) Virtually all of the mass is in the nucleus with the protons and neutrons. (b) The electrons take up most of the volume. (c) The electron was first to be identified by Thompson in 1897. Its existence implied the proton. The neutron was the last identified.



**2-3(d)** Neutrons are neutrally charged, which is what would happen if a positive proton and negative electron combined into one particle. Also, the mass of the neutron is just a little more than the combined mass of the proton and the electron.

**2-4(a)** (a) atomic number and mass number (b) mass number (c) isotopic mass (d) atomic number (e) mass number

**2-4(b)** The protons are determined by matching an elemental symbol to its atomic number. The number of electrons in these neutral species are the same. The number of neutrons is equal to the difference between the atomic number and the mass number. (a) protons = 6, neutrons = 7, electrons = 6 (b) protons = 1, neutrons = 0, electrons = 1 (c) protons = 92, neutrons = 146, electrons = 92

**2-4(c)** (a)  $^{19}\text{F}$  (b)  $^{79}\text{Br}$  (c)  $^{40}\text{Ca}$

**2-4(d)**  $120.903 \times 0.573 + 122.904 \times 0.427 = 122$

**2-4(e)**  $6.015 \times 0.0742 + 7.016 \times 0.9258 = 6.94$ . Compare this answer to lithium's atomic mass on the periodic table. It's a match.

**2-4(f)** Lead and gold are both elements with their own sets of protons, neutrons, and electrons. To convert one element to another, these three particles, and specifically the number of protons, would have to change. There is no chemical way to add or subtract protons from the nucleus of an atom.

**2-4(g)** The weighted average (atomic mass) of the two isotopes is 79.9, or almost 80. This is halfway between the

two isotopes. It stands to reason that each isotope contributes roughly evenly to the mass number. Therefore the percentage abundance of each is nearly 50%.

## PART B

### EXERCISES

**2-6(a)** (a) ionic (b) both (c) molecular (d) both (e) ionic (f) molecular

**2-6(b)** (a)  $\text{MgI}_2$  (b)  $\text{Li}_2\text{SO}_4$  (c)  $\text{Al}_2\text{Se}_3$

**2-6(c)**

|                    |                          |                              |                             |
|--------------------|--------------------------|------------------------------|-----------------------------|
|                    | $\text{Cs}^+$            | $\text{Zn}^{2+}$             | $\text{Fe}^{3+}$            |
| $\text{ClO}_3^-$   | $\text{CsClO}_3$         | $\text{Zn}(\text{ClO}_3)_2$  | $\text{Fe}(\text{ClO}_3)_3$ |
| $\text{O}^{2-}$    | $\text{Cs}_2\text{O}$    | $\text{ZnO}$                 | $\text{Fe}_2\text{O}_3$     |
| $\text{PO}_4^{3-}$ | $\text{Cs}_3\text{PO}_4$ | $\text{Zn}_3(\text{PO}_4)_2$ | $\text{FePO}_4$             |

**2-6(d)** In ionic compounds, atoms are present in the smallest whole-number ratio. If this were an ionic compound, the formula would be  $\text{CH}_2\text{O}$ . Since the formula is six times bigger, it must be molecular.

**2-6(e)** No, not nearly. Two or more compounds can share the same formula, but the order of their bonds might be quite different. Further tests would be required to establish the identity of the substance beyond a reasonable doubt.

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Names and Symbols of the Elements (SECTION 2-1)

**2-1.** Write the symbols of the following elements. Try to do this without referring to a table of elements.

- (a) bromine (c) lead (e) sodium  
(b) oxygen (d) tin (f) sulfur

**2-2.** The following elements all have symbols that begin with the letter C: cadmium, calcium, californium, carbon, cerium, cesium, chlorine, chromium, cobalt, copper, and curium. The symbols are C, Ca, Cd, Ce, Cf, Cl, Cm, Co, Cr, Cs, and Cu. Match each symbol with an element and then check with the table of elements inside the front cover.

**2-3.** The names of seven elements begin with the letter B. What are their names and symbols?

**2-4.** The names of nine elements begin with the letter S. What are their names and symbols?

**2-5.** Using the table inside the front cover, write the symbols for the following elements.

- (a) barium (c) cesium (e) manganese  
(b) neon (d) platinum (f) tungsten

**2-6.** Name the elements corresponding to the following symbols. Try to do this without reference to a table of the elements.

- (a) S (c) Fe (e) Mg  
(b) K (d) N (f) Al

**2-7.** Using the table, name the elements corresponding to the following symbols.

- (a) B (c) Ge (e) Cl (g) Be  
(b) Bi (d) U (f) Hg (h) As

### Composition of the Atom (SECTIONS 2-2 AND 2-3)

**2-8.** Which of the following were not part of Dalton's atomic theory?

- (a) Atoms are the basic building blocks of nature.  
(b) Atoms are composed of electrons, neutrons, and protons.  
(c) Atoms are reshuffled in chemical reactions.  
(d) The atoms of an element are identical.  
(e) Different isotopes can exist for the same element.

**2-9.** Which of the following describes a neutron?

- (a) +1 charge, mass 1 amu (c) 0 charge, mass 1 amu  
(b) +1 charge, mass 0 amu (d) -1 charge, mass 0 amu

**2-10.** Which of the following describes an electron?

- (a) +1 charge, mass 1 amu (c) -1 charge, mass 1 amu  
(b) +1 charge, mass 0 amu (d) -1 charge, mass 0 amu

**2-11.** Give the mass numbers and atomic numbers of the following isotopes. Refer to the table of the elements inside the front cover.

- (a)  $^{193}\text{Au}$  (b)  $^{132}\text{Te}$  (c)  $^{118}\text{I}$  (d)  $^{39}\text{Cl}$

**2-12.** Give the numbers of protons, neutrons, and electrons in each of the following isotopes. Refer to the table of the elements inside the front cover.

(a)  $^{45}\text{Sc}$  (b)  $^{232}\text{Th}$  (c)  $^{223}\text{Fr}$  (d)  $^{90}\text{Sr}$

**2-13.** Three isotopes of uranium are  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ . How many protons, neutrons, and electrons are in each isotope?

**2-14.** Using the table of elements inside the front cover, complete the following table for neutral isotopes.

| Isotope        | Isotopic Notation     | Atomic Number | Mass Number | Subatomic Particles |          |           |
|----------------|-----------------------|---------------|-------------|---------------------|----------|-----------|
|                |                       |               |             | Protons             | Neutrons | Electrons |
| molybdenum-96  | $^{96}_{42}\text{Mo}$ | 42            | 96          | 42                  | 54       | 42        |
| (a)            | $^?_{?}\text{Ag}$     |               |             |                     | 61       |           |
| (b)            |                       | 14            |             |                     | 14       |           |
| (c)            |                       |               | 39          |                     | 20       |           |
| (d) cerium-140 |                       |               |             |                     |          |           |
| (e)            |                       |               |             | 26                  | 30       |           |
| (f)            |                       | 50            | 110         |                     |          |           |
| (g)            | $^{181}_{?}\text{I}$  |               |             |                     |          |           |
| (h) mercury-?  |                       |               |             |                     | 116      |           |

**2-15.** Using the table of elements inside the front cover, complete the following table for neutral isotopes.

| Isotope        | Isotopic Notation     | Atomic Number | Mass Number | Subatomic Particles |          |           |
|----------------|-----------------------|---------------|-------------|---------------------|----------|-----------|
|                |                       |               |             | Protons             | Neutrons | Electrons |
| (a) tungsten-? |                       |               | 184         |                     |          |           |
| (b)            |                       |               |             |                     | 12       | 11        |
| (c)            | $^{200}_{?}\text{At}$ |               |             |                     |          |           |
| (d)            | $^?_{?}\text{Pm}$     |               |             |                     | 87       |           |
| (e)            |                       |               | 109         | 46                  |          |           |
| (f)            |                       |               | 48          |                     |          | 23        |
| (g)            |                       | 21            |             |                     | 29       |           |

**2-16.** Write the isotopic notation for an isotope of cobalt that has the same number of neutrons as  $^{60}\text{Ni}$ .

**2-17.** Write the isotopic notation for an isotope of uranium that has the same number of neutrons as  $^{240}\text{Pu}$ .

### Atomic Number and Mass (SECTION 2-4)

**2-18.** How do the following concepts relate and differ?

- element and atomic number
- atomic mass and atomic number
- mass number and atomic mass
- isotopes and number of protons
- isotopes and number of neutrons

**2-19.** Determine the atomic number and the atomic mass of each of the following elements. Use the table inside the front cover.

(a) Re (b) Co (c) Br (d) Si

**2-20.** About 75% of a U.S. “nickel” is an element with an atomic mass of 63.546 amu. What is the element?

**2-21.** White gold is a mixture of gold containing an element with an atomic mass of 106.4 amu. What is the element?

**2-22.** The elements O, N, Si, and Ca are among several that are composed *primarily* of one isotope. Using the table inside the front cover, write the atomic number and mass number of the principal isotope of each of these elements.

**2-23.** The atomic mass of hydrogen is given inside the front cover as 1.00794. The three isotopes of hydrogen are  $^1\text{H}$ ,  $^2\text{H}$ , and  $^3\text{H}$ . What does the atomic mass tell us about the relative abundances of the three isotopes?

**2-24.** A given element has a mass 5.81 times that of  $^{12}\text{C}$ . What is the atomic mass of the element? What is the element?

**2-25.** The atomic mass of a given element is about 3.13 times that of  $^{12}\text{C}$ . Give the atomic mass, the name, and the symbol of the element.

**2-26.** Bromine is composed of 50.5%  $^{79}\text{Br}$  and 49.5%  $^{81}\text{Br}$ . The isotopic mass of  $^{79}\text{Br}$  is 78.92 amu and that of  $^{81}\text{Br}$  is 80.92 amu. What is the atomic mass of the element?

**2-27.** Silicon occurs in nature as a mixture of three isotopes:  $^{28}\text{Si}$  (27.98 amu),  $^{29}\text{Si}$  (28.98 amu), and  $^{30}\text{Si}$  (29.97 amu). The mixture is 92.21%  $^{28}\text{Si}$ , 4.70%  $^{29}\text{Si}$ , and 3.09%  $^{30}\text{Si}$ . Calculate the atomic mass of naturally occurring silicon.

**2-28.** Naturally occurring Cu is 69.09%  $^{63}\text{Cu}$  (63.96 amu). The only other isotope is  $^{65}\text{Cu}$  (64.96 amu). What is the atomic mass of copper?

**\*2-29.** Chlorine occurs in nature as a mixture of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ . If the isotopic mass of  $^{35}\text{Cl}$  is approximately 35.0 amu and that of  $^{37}\text{Cl}$  is 37.0 amu, and the atomic mass of the mixture as it occurs in nature is 35.5 amu, what is the proportion of the two isotopes?

**\*2-30.** The atomic mass of the element gallium is 69.72 amu. If it is composed of two isotopes,  $^{69}\text{Ga}$  (68.926 amu) and  $^{71}\text{Ga}$  (70.925 amu), what is the percent of  $^{69}\text{Ga}$ ?

### Molecular Compounds and Formulas (SECTION 2-5)

**2-31.** How do the following concepts relate and differ?

- a molecule and an atom
- a molecule and a compound
- an element and a compound
- a molecular element and a monatomic element

**2-32.** Which of the following are formulas of elements rather than compounds?

- $\text{P}_4\text{O}_{10}$
- $\text{Br}_2$
- $\text{F}_2\text{O}$
- $\text{S}_8$
- $\text{MgO}$
- $\text{P}_4$

**2-33.** Name the elements in the previous problem.

**2-34.** What is the difference between Hf and HF?

**2-35.** What is the difference between NO and No?

**2-36.** Which of the following is the formula of a diatomic element? Which is the formula of a diatomic compound?

- $\text{NO}_2$
- $\text{CO}$
- $\text{K}_2\text{O}$
- $(\text{NH}_4)_2\text{S}$
- $\text{N}_2$
- $\text{CO}_2$

**2-37.** Give the name and number of atoms of each element in the formulas of the following compounds.

- $\text{H}_2\text{SeO}_3$
- $\text{Na}_4\text{SiO}_4$
- $\text{NI}_3$
- $\text{NiI}_2$
- $\text{Ba}(\text{BrO}_3)_2$
- $\text{B}_3\text{N}_3(\text{CH}_3)_6$

**2-38.** What is the total number of atoms in each formula unit for the compounds in problem 2-37?

**2-39.** Determine the number of atoms of each element in the formulas of the following compounds.

- (a)  $C_6H_4Cl_2$   
 (b)  $C_2H_5OH$  (ethyl alcohol)  
 (c)  $CuSO_4 \cdot 9H_2O$  ( $H_2O$ 's are part of a single formula unit)  
 (d)  $C_9H_8O_4$  (aspirin)  
 (e)  $Al_2(SO_4)_3$   
 (f)  $(NH_4)_2CO_3$

**2-40.** What is the total number of atoms in each molecule or formula unit for the compounds listed in problem 2-39?

**2-41.** How many carbon atoms are in each molecule or formula unit of the following compounds?

- (a)  $C_8H_{18}$  (octane in gasoline)      (c)  $Fe(C_2O_4)_2$   
 (b)  $NaC_7H_4O_3NS$  (saccharin)      (d)  $Al_2(CO_3)_3$

**2-42.** Write the formulas of the following molecular compounds.

- (a) sulfur dioxide (one sulfur and two oxygen atoms)  
 (b) carbon dioxide (one carbon and two oxygen atoms)  
 (c) sulfuric acid (two hydrogens, one sulfur, and four oxygen atoms)  
 (d) acetylene (two carbons and two hydrogens)

**2-43.** Write the formulas of the following molecular compounds.

- (a) phosphorus trichloride (one phosphorus and three chlorines)  
 (b) naphthalene (ten carbons and eight hydrogens)  
 (c) dibromine trioxide (two bromines and three oxygens)

### Ions and Ionic Compounds (SECTION 2-6)

**2-44.** How do the following concepts relate and differ?

- (a) an atom and an ion  
 (b) a molecule and a polyatomic ion  
 (c) a cation and an anion  
 (d) a molecular and an ionic compound  
 (e) a molecular unit and an ionic formula unit

**2-45.** The gaseous compound HF contains covalent bonds, and the compound KF contains ionic bonds. Sketch how the basic particles of these two compounds appear.

**2-46.** Write the formulas of the following ionic compounds.

- (a) calcium perchlorate (one  $Ca^{2+}$  and two  $ClO_4^-$  ions)  
 (b) ammonium phosphate (three  $NH_4^+$  ions and one  $PO_4^{3-}$  ion)  
 (c) iron(II) sulfate (one  $Fe^{2+}$  and one  $SO_4^{2-}$  ion)

**2-47.** What is the number of atoms of each element present in the compounds in problem 2-46?

**2-48.** Write the formulas of the following ionic compounds.

- (a) calcium hypochlorite (one  $Ca^{2+}$  ion and two  $ClO^-$  ions)  
 (b) magnesium phosphate (three  $Mg^{2+}$  ions and two  $PO_4^{3-}$  ions)  
 (c) chromium(III) oxalate (two  $Cr^{3+}$  ions and three  $C_2O_4^{2-}$  ions)

**2-49.** What is the number of atoms of each element present in the compounds in problem 2-48?

**2-50.** The formula of an ionic compound indicates one  $Fe^{2+}$  ion combined with one anion. Which of the following could be the other ion?

- (a)  $F^-$       (b)  $Ca^{2+}$       (c)  $S^{2-}$       (d)  $N^{3-}$

**2-51.** An ionic compound is composed of two  $ClO_4^-$  ions and one cation. Which of the following could be the other ion?

- (a)  $SO_4^{2-}$       (b)  $Ni^{2+}$       (c)  $Al^{3+}$       (d)  $Na^+$

**2-52.** An ionic compound is composed of one  $SO_3^{2-}$  and two cations. Which of the following could be the cations?

- (a)  $I^-$       (b)  $Ba^{2+}$       (c)  $Fe^{3+}$       (d)  $Li^+$

**2-53.** An ionic compound is composed of two  $Al^{3+}$  ions and three anions. Which of the following could be the anions?

- (a)  $S^{2-}$       (b)  $Cl^-$       (c)  $Sr^{2+}$       (d)  $N^{3-}$

**2-54.** Write the formulas of the compounds in problems 2-50 and 2-52.

**2-55.** Write the formulas of the compounds in problems 2-51 and 2-53.

**2-56.** Explain the difference between  $SO_3$  and  $SO_3^{2-}$ . Which one would be a gas?

**2-57.** What are the total number of protons and the total number of electrons in each of the following ions?

- (a)  $K^+$       (c)  $S^{2-}$       (d)  $NO_2^-$   
 (b)  $Br^-$       (d)  $NO_2^-$       (f)  $NH_4^+$

**2-58.** What are the total number of protons and the total number of electrons in each of the following ions?

- (a)  $Sr^{2+}$       (c)  $V^{3+}$       (e)  $SO_3^{2-}$   
 (b)  $P^{3-}$       (d)  $NO^+$

**2-59.** Write the element symbol or symbols and the charge for the following ions.

- (a) 20 protons and 18 electrons  
 (b) 52 protons and 54 electrons  
 (c) one phosphorus and three oxygens with a total of 42 electrons  
 (d) one nitrogen and two oxygens with a total of 22 electrons

**2-60.** Write the element symbol or symbols and the charge for the following ions.

- (a) 50 protons and 48 electrons  
 (b) 53 protons and 54 electrons  
 (c) one aluminum and two oxygens with a total of 30 electrons  
 (d) one chlorine and three fluorines with a total of 43 electrons

**2-61.** A monatomic bromine species has 36 electrons. Does it exist independently?

**2-62.** A species is composed of one chlorine atom chemically bonded to two oxygen atoms. It has a total of 33 electrons. Is this species most likely a gaseous molecular compound or part of an ionic compound?

## General Problems

**2-63.** Describe the difference between a molecular and an ionic compound. Of the two types of compounds discussed, is a stone more likely to be a molecular or an ionic compound? Is a liquid more likely to be a molecular or an ionic compound?

**2-64.** Write the symbol, mass number, atomic number, and electrical charge of the element given the following information. Refer to the table of the elements.

- An ion of Sr contains 36 electrons and 52 neutrons.
- An ion contains 24 protons, 28 neutrons, and 21 electrons.
- An ion contains 36 electrons and 45 neutrons and has a  $-2$  charge.
- An ion of nitrogen contains 7 neutrons and 10 electrons.
- An ion contains 54 electrons and 139 nucleons and has a  $+3$  charge.

**2-65.** Write the symbol, mass number, atomic number, and electrical charge of the element given the following information. Refer to the table of the elements.

- An ion of Sn contains 68 neutrons and 48 electrons.
- An ion contains 204 nucleons and 78 electrons and has a  $+3$  charge.
- An ion contains 45 neutrons and 36 electrons and has a  $-1$  charge.
- An ion of aluminum has 14 neutrons and a  $+3$  charge.

**2-66.** Give the number of protons, electrons, and neutrons represented by the following species. These elements are composed almost entirely of one isotope, which is implied by the atomic mass.

- Na and  $\text{Na}^+$
- Ca and  $\text{Ca}^{2+}$
- F and  $\text{F}^-$
- Sc and  $\text{Sc}^{3+}$

**2-67.** Give the number of protons, electrons, and neutrons represented by the following species. These elements are composed almost entirely of one isotope, which is implied by the atomic mass.

- Cr and  $\text{Cr}^{2+}$
- Au and  $\text{Au}^{3+}$
- I and  $\text{I}^-$
- P and  $\text{P}^{3-}$

**\*2-68.** An isotope of iodine has a mass number that is 10 amu less than two-thirds the mass number of an isotope of thallium. The total mass number of the two isotopes is 340 amu. What is the mass number of each isotope? (*Hint:* There are two equations and two unknowns.)

**\*2-69.** An isotope of gallium has a mass number that is 22 amu more than one-fourth the mass number of an isotope of osmium. The osmium isotope is 122 amu heavier than the gallium isotope. What is the mass number of each isotope? (*Hint:* There are two equations and two unknowns.)

**\*2-70.** A given element is composed of 57.5% of an isotope with an isotopic mass of 120.90 amu. The remaining percentage of isotope has an isotopic mass of 122.90 amu. What is the atomic mass of the element? What is the element? How many electrons are in a cation of this element if it has a charge of 3? How many neutrons are in each of the two isotopes of this element? What percent of the isotopic mass of each isotope is due to neutrons?

**2-71.** A given isotope has a mass number of 196, and 60.2% of the nucleons are neutrons. How many electrons are in a cation of this element if it has a charge of 2?

**2-72.** A given isotope has a mass number of 206. The isotope has 51.2% more neutrons than protons. What is the element?

**2-73.** A given molecular compound is composed of one atom of nitrogen and one atom of another element. The mass of nitrogen accounts for 46.7% of the mass of one molecule. What is the other element? What is the formula of the compound? This molecule can lose one electron to form a polyatomic ion. How many electrons are in this ion?

**2-74.** A given molecular compound is composed of one atom of carbon and two atoms of another element. The mass of carbon accounts for 15.8% of the mass of one molecule. What is the other element? What is the formula of the compound?

**2-75.** If the isotopic mass of  $^{12}\text{C}$  were defined as exactly 8 instead of 12, what would be the atomic mass of the following elements to three significant figures? Assume that the elements have the same masses relative to each other as before: that is, hydrogen still has a mass of one-twelfth that of carbon.

- H
- N
- Na
- Ca

**2-76.** Assume that the isotopic mass of  $^{12}\text{C}$  is defined as exactly 10 and that the atomic mass of an element is 43.3 amu on this basis. What is the element?

**2-77.** Assume that the isotopic mass of  $^{12}\text{C}$  is defined as exactly 20 instead of 12 and that the atomic mass of an element is 212.7 amu on this basis. What is the element?

## STUDENT WORKSHOP

## Chemical Formulas

**Purpose:** To evaluate chemical compounds for their composition, and to create new compounds from their constituent parts. (Work in groups of three or four. Estimated time: 25 min.)

Divide up the compounds listed in Making It Real, "Ionic Compounds and Essential Elements," so that each person has three or four. Using a periodic table, do the following:

- Name the elements found in each compound.
- Determine how many atoms of each element are contained within each compound.
- Calculate the total number of protons in each compound.

- Do the same for the number of neutrons. (You should assume that the isotope present is the one with the closest integer value to the mass number found on the periodic table.)
- Determine whether the compound contains a polyatomic ion.

Now, using the following ions (all found in the compounds above), construct three or four new compounds each, with the necessary numbers to make their formulas neutral.

Cations:  $\text{H}^+$     $\text{Cr}^{2+}$     $\text{Cu}^{2+}$     $\text{Na}^+$     $\text{Fe}^{2+}$     $\text{Mg}^{2+}$     $\text{Ca}^{2+}$   
 Anions:  $\text{BO}_3^{3-}$     $\text{CO}_3^{2-}$     $\text{I}^-$     $\text{SO}_4^{2-}$     $\text{O}^{2-}$     $\text{PO}_4^{3-}$



CHAPTER  
3

# The Properties of Matter and Energy



**T**he gold in these bars has well-known properties. The bars have a beautiful, shiny appearance that does not tarnish. They are also surprisingly heavy because of gold's very high density.



## PART A THE PROPERTIES OF MATTER

### 3-1 The Physical and Chemical Properties of Matter

### 3-2 Density—A Physical Property



#### MAKING IT REAL

*Identifying a Glass Shard from a Crime Scene by  
Density*

### 3-3 The Properties of Mixtures

## PART B THE PROPERTIES OF ENERGY

### 3-4 The Forms and Types of Energy

### 3-5 Energy Measurement and Specific Heat



#### MAKING IT REAL

*Body Solutions—Lose Weight (actually money)  
While You Sleep*



#### MAKING IT REAL

*Dark Matter and Energy*

**SETTING THE STAGE** In 2007, a spacecraft orbiting the planet Saturn made a close pass by its mysterious moon, Titan. Titan's surface is perpetually hidden from view by thick clouds. However, measurements and scans of the surface from the orbiter, named *Cassini*, indicated that there were huge lakes of liquid on the surface as well as valleys that seemed to be formed from flowing liquids. Because of the low temperature on Titan, however, the liquid could not be water. More likely, the bodies of liquid and the rain that formed the valleys would be composed of methane ( $\text{CH}_4$ ). How did the scientists determine all this? The answer lies in the known characteristics or properties of the compounds involved, like ice and methane. Under such cold conditions methane, which is a gas (i.e., natural gas) on Earth, would be a liquid on Titan. In fact, the liquid methane could evaporate and condense into clouds and rain just like water does on our planet. Our knowledge of the characteristics or properties of the matter involved, such as water and methane, allows us to determine what we are probably seeing.

Now we turn our focus to our home planet, with its abundant life. Life is dependent not only on the presence of liquid water but also on the constant supply of energy from the sun. *Energy is a second massless component of the universe in addition to matter.* When a log burns in the fireplace, it is obvious that a change in matter has occurred. The log is transformed into a small pile of ashes and hot gases. But there is more involved than simply a change in matter. The burning of the log warms us—it has given off heat. The heat and light liberated by the burning process are forms of energy. Energy is a more abstract concept than matter. It can't be weighed, and it doesn't have shape, form, or dimensions. But energy can be measured, and it does interact with matter (e.g., it warms us, starts our car, and makes trees grow). Since energy is involved in the changes that matter undergoes, it is also important in the study of the properties of matter.

How we describe the properties of matter is the topic of Part A of this chapter. In Part B, we will discuss the properties and measurement of energy.

## PART A THE PROPERTIES OF MATTER

### SETTING A GOAL

- You will learn how a sample of matter can be described by its properties and how they can be quantitatively expressed.

### OBJECTIVES

- 3-1** List and define several properties of matter and distinguish them as physical or chemical.
- 3-2** Perform calculations involving the density of liquids and solids.
- 3-3 (a)** Describe the differences in properties between a pure substance and a mixture. **(b)** Perform calculations involving percent as applied to mixtures.

### ▶ OBJECTIVE FOR SECTION 3-1

List and define several properties of matter and distinguish them as physical or chemical.

## 3-1 THE PHYSICAL AND CHEMICAL PROPERTIES OF MATTER



**LOOKING AHEAD!** People have a physical description, such as that found on a driver's license, and a personality description. Your physical description tells how you are observed, and your personality description tells how you interact with others. Similarly, there are two ways to describe an element or compound, depending on whether it is an observable description (a physical property) or on how it interacts with other substances (a chemical property). We will first consider physical properties and then proceed to chemical properties. ■

“The suspect in the robbery was a 6 ft 2 in. male with a heavy build, short hair, and a thin mustache.” These are a few of the physical properties of a person that we may hear in a news bulletin. These properties can be observed without interacting with this individual or getting too close. Like an individual, the **physical properties** of a substance *are those that can be observed or measured without changing the substance into another substance*. Some physical properties can simply be observed. Color, physical state, and sometimes odor are such properties that a substance may display. First we will consider physical state.

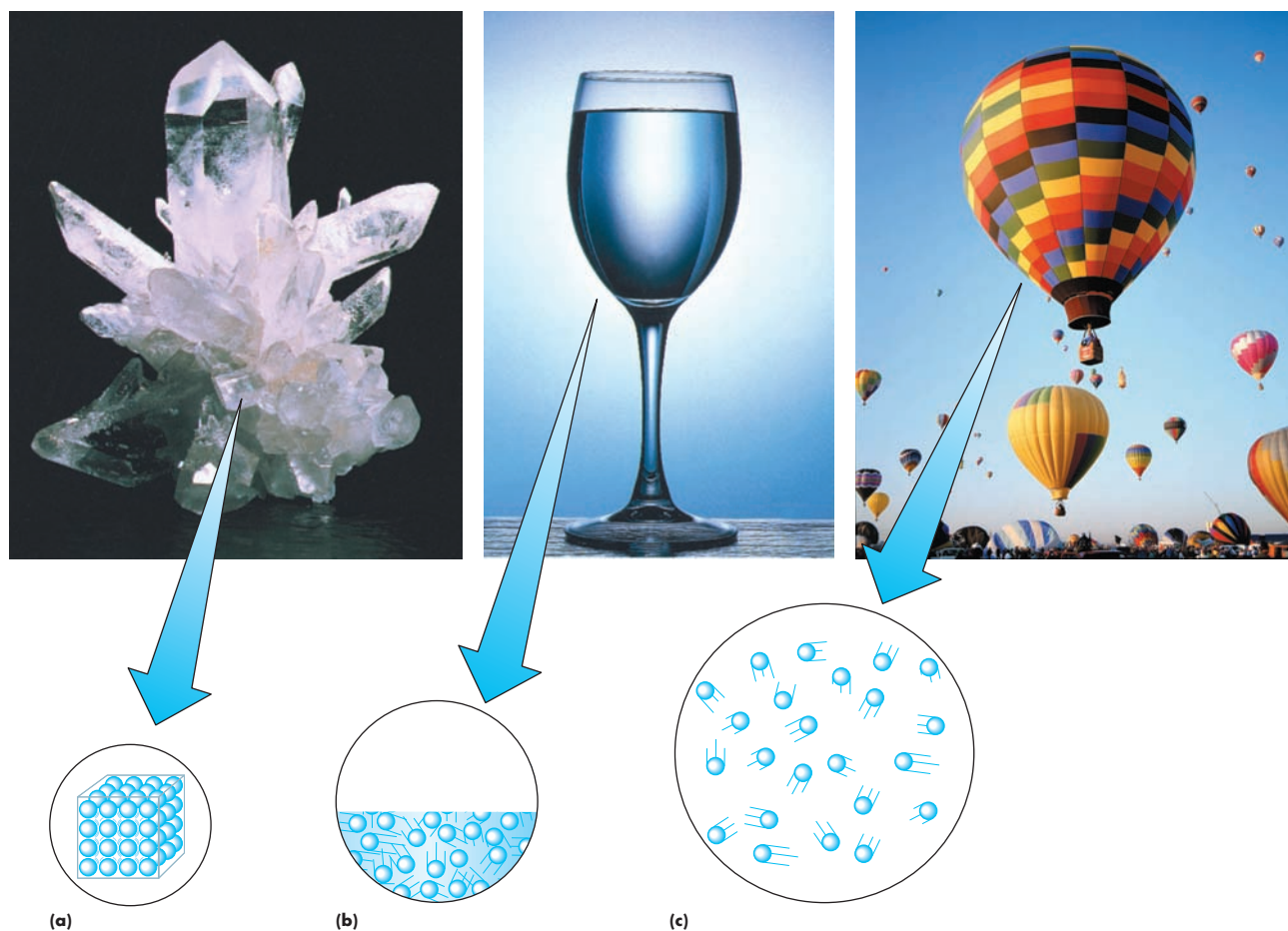
### 3-1.1 The Physical States of Matter

In the previous chapter, you learned that all matter is categorized as either elements or compounds. Recall that elements and compounds are composed of extremely tiny particles (atoms, molecules, or ions). Sometimes a sample of matter, such as in a container of argon, is composed of single atoms, but most matter is made of molecules or ions. The distance between these particles and their relative motion is what determines the **physical state** of a sample of matter: solid, liquid, or gas.

A **solid** is composed of matter where the particles are close together and remain in relatively fixed positions. Movement of the particles is very restricted and confined mostly to vibrations about these positions. Because of the fixed positions of the particles, *solids have a definite shape and a definite volume*.

A **liquid** is composed of matter where the particles are close together but are able to move past one another. Because of the movement of the particles, liquids flow and take the shape of the lower part of a container. *Liquids have a definite volume but not a definite shape*.

A **gas** is made up of atoms or molecules that are not all close to one another and move independently in all directions with random motion. The particles in gases



**FIGURE 3-1** The Three States of Matter (a) Solids have a definite shape and volume. (b) Liquids have a definite volume but an indefinite shape. (c) Gases have an indefinite shape and volume.

fill a container uniformly. *Gases have neither a definite volume nor a definite shape.* (See Figure 3-1.)

We are already familiar with many examples of all three physical states. Ice, rock, salt, and steel are substances that exist as solids; water, gasoline, and alcohol are liquids; ammonia, natural gas, and the components of air are present as gases. However, whether a particular element or compound is a solid, liquid, or gas depends not only on the nature of the substance but also on the temperature. For example, at low temperatures (i.e., below  $0^{\circ}\text{C}$ ), liquid water freezes to form a solid (ice), and at high temperatures (i.e., above  $100^{\circ}\text{C}$ ), liquid water boils to form a gas (vapor or steam). At very low temperatures (below  $-196^{\circ}\text{C}$ ), even the gases that form our atmosphere condense to liquid.

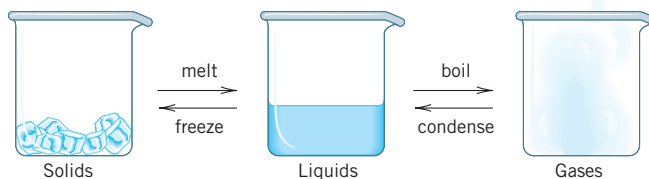
### 3-1.2 Changes in Physical State

The temperature at which a pure substance changes from one physical state to another is a fundamental and constant physical property. A substance *melts* when it changes from the solid to the liquid state and *freezes* when it changes from the liquid to the solid state. The **melting point** is *the temperature at which a particular element or compound changes from the solid state to the liquid state.* For example, ice begins to melt when the temperature is  $0^{\circ}\text{C}$ . In the reverse process, liquid water begins to change to the solid state when it is cooled to  $0^{\circ}\text{C}$ . This is known as the **freezing point**.



**FIGURE 3-2 A Physical Change** The ice is undergoing a physical change to liquid water at its melting point (32°F, or 0°C).

At a higher temperature, the liquid begins to boil. Boiling occurs when bubbles of vapor form in the liquid and rise to the surface. The **boiling point** is *the temperature at which boiling begins*. In the reverse process, the change from the gaseous state to the liquid state is known as **condensation**. The formation of dew on the grass on a summer morning is a result of condensation. The boiling point of a liquid is also a constant, but only at specific atmospheric pressure. For example, water boils at 100°C at average sea-level pressure but boils at 69°C on the top of Mt. Everest, the world's highest mountain. Boiling-point temperatures are usually listed as the boiling point of the liquid at average sea-level atmospheric pressure. These phase changes are summarized as follows:



When a liquid freezes or boils, it undergoes a change to another physical state. However, it is still the same substance. A **physical change** *in a substance does not involve a change in the composition of the substance but is simply a change in physical state or dimensions*. Liquid water, ice, and steam are all physical states of the same compound. (See Figure 3-2.)

### 3-1.3 Types of Physical Properties

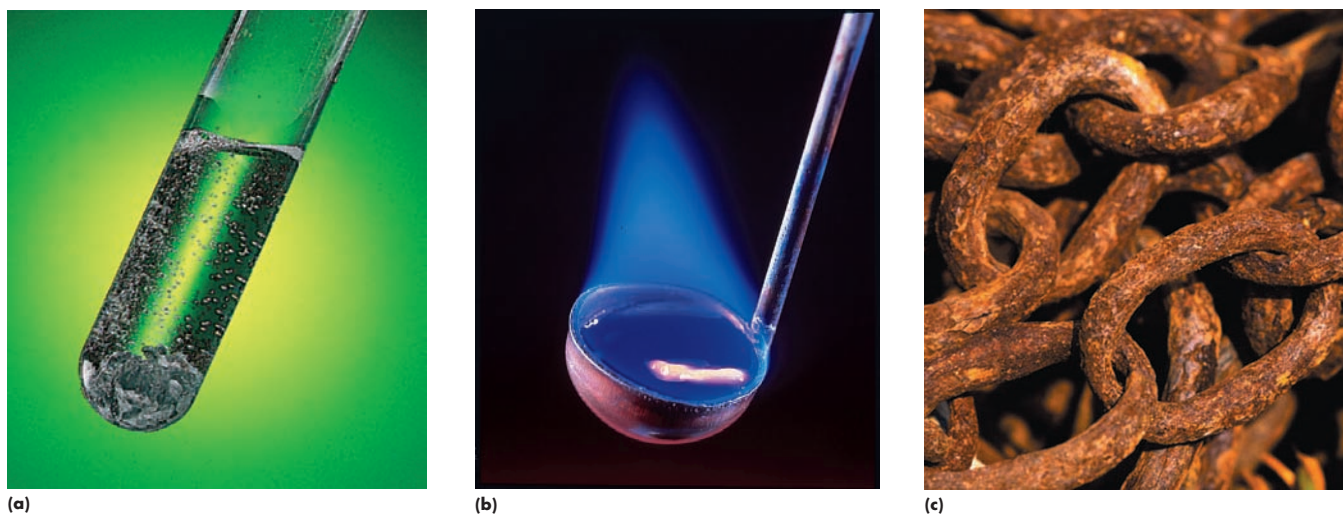
**Intensive properties**, such as clarity, color, and density, *are those whose value does not depend on the amount of material present*. **Extensive properties**, such as mass and volume, *are those whose value does depend on the amount of material present*. Both types of properties are used to identify a particular unknown substance, but intensive properties are more definitive. For example, an unidentified clear, colorless liquid (an extensive property) that freezes at 0°C and boils at 100°C and that has a density of 1.0 g/ml (three intensive properties) is most likely water.

### 3-1.4 Chemical Changes and Chemical Properties

When water is cooled, it solidifies into ice. When it is allowed to warm, the ice melts back to liquid water. Ice and liquid water are two different physical states of the same compound. On the other hand, when we heat a raw egg, it solidifies. When we cool the egg, however, it stays solid. Obviously, the contents of the egg are not the same—they have undergone profound changes into other compounds. When iron rusts, vegetation decays, and wood burns, the original substances have been transformed into one or more other substances. These processes all describe chemical changes.

**Chemical properties** *of a pure substance refer to its tendency to undergo chemical changes*. **Chemical changes** *transform one substance into one or more other substances*. A chemical property of the element iron is its tendency to react with oxygen from the air in the presence of water to form rust (a compound composed of iron and oxygen). The conversion of rust back into iron and oxygen is an involved and difficult chemical process. In some cases, chemical properties relate to the absence of specific changes. For example, a chemical property of the element gold is that it maintains its lustrous appearance because it resists rusting or tarnishing. Chemical properties of three substances are shown in Figure 3-3.





**FIGURE 3-3 Chemical Properties and Changes** Zinc reacts with acid (a), sulfur burns in air (b), and iron rusts (c).

### 3-1.5 Chemical Change and Conservation of Mass

What happens when a chemical change occurs? In fact, the total mass of the elements and compounds involved does not change—only the identity of the substances involved. The **law of conservation of mass** states that *matter is neither created nor destroyed in a chemical reaction*. Only three centuries ago, scientists were still puzzled over the apparent disappearance of mass when wood burned, since only a small portion of the original mass remained in the form of ashes. At that time, however, the involvement of gases in chemical reactions was not understood. We now know that most of the solid compounds of the wood have been simply transformed in the combustion process into gaseous compounds and smoke that drift away in the atmosphere. The mass of the wood plus the mass of the oxygen from the air equals the mass of the ashes plus the mass of the gaseous combustion products, as stated by the law of conservation of mass.

#### ASSESSING THE OBJECTIVE FOR SECTION 3-1

**EXERCISE 3-1(a) KNOWLEDGE:** Calcium, an element, is a dull, gray solid that melts at  $839^{\circ}\text{C}$ . When it is placed in water, bubbles form, as the solid calcium slowly disappears in the water. When the water is evaporated, a white powder remains, but elemental calcium is not recovered. Which are the physical properties of calcium? Which is a chemical property?

**EXERCISE 3-1(b) ANALYSIS:** A beaker of an unknown clear and colorless liquid has a volume of 100.0 mL and a mass of 78.9 g. Initially, its temperature is  $25^{\circ}\text{C}$ . When heated, it boils at  $78.5^{\circ}\text{C}$ . If ignited, it burns completely with a blue flame, leaving no residue behind. Which of these pieces of information will be helpful in identifying the liquid?

**EXERCISE 3-1(c) SYNTHESIS:** In lab you are handed a metallic object and charged with determining its identity. What types of things can you do to figure out what the object is made from?

*For additional practice, work chapter problems 3-4, 3-6, and 3-10.*



▶ **OBJECTIVE FOR SECTION 3-2**

Perform calculations involving the density of liquids and solids.

## 3-2 DENSITY—A PHYSICAL PROPERTY



**LOOKING AHEAD!** Some physical properties such as odor, color, and physical state can be determined by observation. Others, such as melting or boiling point, must be determined by measurements. Another important intensive physical property that is obtained from measurements is density. ■

A Styrofoam coffee cup is “light,” but a lead car battery is “heavy.” Actually, by themselves these terms, *light* and *heavy*, are not very useful because a truckload of Styrofoam would be quite heavy. The volume and mass of a substance are extensive properties that depend on the size of the sample. The physical property of density is an intensive property that allows us to compare the mass of substances for a specific volume. **Density** is the ratio of the mass (usually in grams) to the volume (usually in milliliters for a solid or liquid or liters for a gas). The density of a substance does not depend on the amount present. The density of lead will always be greater than the density of Styrofoam, no matter how much is present.

### 3-2.1 Density as a Physical Property

The density of a pure substance is a property that can be used to identify a particular element or compound. The densities of several liquids and solids are listed in Table 3-1. (Because the volume of liquids and solids expand slightly as the temperature rises, densities are usually given at a specific temperature. In this case, 20°C is the reference temperature.) Because 1 mL is the same as 1 cm<sup>3</sup>, density is also expressed as g/cm<sup>3</sup>. The densities of gases are discussed in Chapter 10.

You can prove that the density of a substance does not depend on sample size with a simple demonstration. If you had a beaker of water, you could measure its volume and mass and from those two measurements calculate its density. If your lab partners were evaluating some water in a smaller beaker, they would measure an appropriately smaller mass and smaller volume. If you compared the results, you would find that the density of water is the same regardless of the original amount present.

The calculation of density from the two measurements is discussed in the following two examples. As we will see, the volume of an unknown sample is often measured by the displacement of water. When a substance is added to water it will either sink or float depending on its density. (Assuming that it doesn’t dissolve in or react with water.) If the unknown is less dense than water, it will float and it is said to be *buoyant* in water. If it is more dense, it sinks. In the example that follows, the unknown sinks, so we can conclude that it is more dense than water and we can measure its volume by the volume of water that is displaced.

**TABLE 3-1** Density (at 20°C)

| SUBSTANCE (LIQUID)   | DENSITY (g/mL)   | SUBSTANCE (SOLID) | DENSITY (g/mL) |
|----------------------|------------------|-------------------|----------------|
| Ethyl alcohol        | 0.790            | Aluminum          | 2.70           |
| Gasoline (a mixture) | ~0.67 (variable) | Gold              | 19.3           |
| Carbon tetrachloride | 1.60             | Ice               | 0.92 (0°C)     |
| Kerosene (a mixture) | 0.82             | Lead              | 11.3           |
| Water                | 1.00             | Lithium           | 0.53           |
| Mercury              | 13.6             | Magnesium         | 1.74           |
| Table salt           | 2.16             |                   |                |

**EXAMPLE 3-1****Determining Density**

A sample of a pure substance is found to have a mass of 52.11 g. As shown below, a measured quantity of water has a volume of 12.5 mL. When the substance is placed in the water, it sinks and the volume of the water and substance now read 31.8 mL. What is the density?

**PROCEDURE**

The density equals the mass measured in grams divided by the volume measured in milliliters. The volume of the sample is the volume of water displaced when the substance is placed in the water. Therefore, the volume is calculated as the difference in the volume of the water before and after the sample is added.

**SOLUTION**

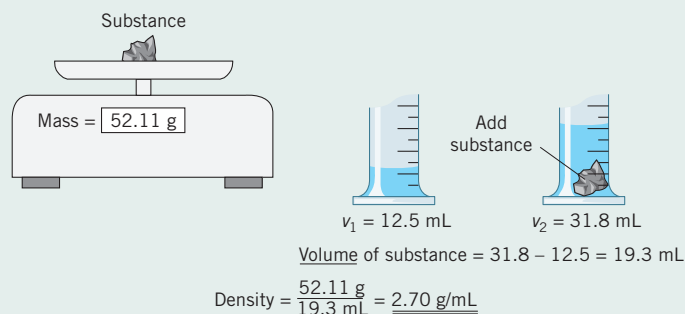
Determine volume:

$$\begin{aligned}\text{sample volume} &= \text{total volume} - \text{original volume} \\ \text{sample volume} &= 31.8 \text{ mL} - 12.5 \text{ mL} = 19.3 \text{ mL}\end{aligned}$$

Determine density:

$$\begin{aligned}\text{density} &= \text{mass} \div \text{volume} \\ \text{density} &= 52.11 \text{ g} \div 19.3 \text{ mL} = \underline{2.70 \text{ g/mL}}\end{aligned}$$

As shown below, the mass is obtained by placing the substance on an electronic balance, while the volume is measured from the volume differences of the water.

**ANALYSIS**

The problem stated that the sample was a pure substance. With the information given to you in Table 3-1, can you determine the substance? (Yes. Table 3-1 indicates that aluminum has a density of 2.70 g/mL. Therefore, the sample is most likely aluminum.)

**SYNTHESIS**

The volume of a symmetrical, uniform solid, like a cube, is easy to measure if you know its dimensions. You just witnessed an example of how to measure the volume of an asymmetrical, or nonuniform, solid using water displacement. Can you measure the volume of all asymmetrical solids using this method? (No. Not if they float above the surface, like Styrofoam, or dissolve, like salt.)

**EXAMPLE 3-2****Identifying a Substance from Density**

A person was interested in purchasing a ring of pure gold having a mass of 89.9 g. Being wise, she wished to confirm that it was actually gold before she paid for it. With a quick test using a graduated cylinder like that shown in the previous example, she found that the ring had a volume of 7.96 mL. Was it made of gold?

**PROCEDURE**

By calculating the density of the ring, we can provide evidence as to its identity. Density is a constant and unchanging property of a pure element or compound (at a specific temperature). From the volume and the mass, the density can be calculated by dividing the mass by the volume. Compare this value to that of gold in Table 3-1.

**SOLUTION**

$$\text{density of the ring} = 89.9 \text{ g} \div 7.96 \text{ mL} = 11.3 \text{ g/mL}$$

**ANALYSIS**

Is the ring pure gold? Should she buy it? Comparing the result to the values in Table 3-1, we see that it's not pure gold. Pure gold would have a density of 19.3 g/mL.

**SYNTHESIS**

What do you think the ring is made of? What might be going on here? On reexamining Table 3-1, you will discover that the ring has the same density as lead. It's probably a lead ring plated with a thin layer of gold to fool the unsuspecting. Lead is cheaper than gold, and so it would seem that the seller is trying to pull a fast one.

Density also has medical applications. The density of a person can be a measure of his or her amount of body fat. The density of fat is 0.900 g/mL, fat-free muscle is 1.066 g/mL, and normal bone is 3.317 g/mL. The more fat on a person, the lower the person's density and the less he or she will weigh when submerged in water. By consulting a chart, a specialist can give an accurate estimate of body fat from the person's density. For example, if a person has a density of 1.07 g/mL, the individual has about 12% body fat. If the density is down to 1.03 g/mL, the person has about 28% body fat.

**3-2.2 Density as a Conversion Factor**

Density is not only an important physical property but can also be used to convert the mass of a substance with a known density to an equivalent volume, or vice versa. These two conversions are illustrated in the following examples. Notice that since density originates from two measurements, it is not an exact factor such as the factor between meters and kilometers.

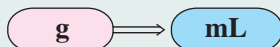
**EXAMPLE 3-3****Determining the Mass from the Volume Using Density**

What is the volume in milliliters occupied by 485 g of table salt?

**PROCEDURE**

Use the density of table salt as a conversion factor from mass to volume.

1. The unit map for the conversion is



2. The density of table salt is given in Table 3-1 as 2.16 g/mL. We need to invert this relationship so that g is in the denominator and mL is in the numerator. This factor then converts mass to the equivalent volume. The factor for this conversion is

$$\frac{1 \text{ mL}}{2.16 \text{ g}}$$

**SOLUTION**

$$485 \text{ g} \times \frac{1 \text{ mL}}{2.16 \text{ g}} = \underline{\underline{225 \text{ mL}}}$$

**ANALYSIS**

To check your answer, you can plug it back into the density formula.

$$\text{density} = \text{mass} \div \text{volume}$$

$$\text{density} = 485 \text{ g} \div 225 \text{ mL} = 2.16 \text{ g/mL}$$

This is the original reported density. The answer checks out.

**SYNTHESIS**

Does this answer make sense? If 1 mL has a mass of about 2 g, there would be about 240 mL (i.e.,  $485 \text{ g} \div 2 \text{ g/mL} = 242 \text{ mL}$ ) in the given sample. 225 mL is very close to the estimated value. The answer makes sense. Could you measure the volume by adding the salt to water as in the previous examples? No. Salt dissolves in water, so the use of density as a conversion factor is appropriate.

**EXAMPLE 3-4****Determining the Volume from the Mass Using Density**

What is the mass in grams of 1.52 L of kerosene?

**PROCEDURE**

Using the density of kerosene from Table 3-1 as a conversion factor, convert volume to mass. Notice that the volume is not given in milliliters, however. A two-step conversion is necessary.

- In the first step (a), L is converted into mL, and in the second step (b), mL is converted into g. The unit map for the conversion is



- The proper relationships are  $1 \text{ mL} = 10^{-3} \text{ L}$  (from Table 1-4) and  $0.82 \text{ g/mL}$  (from Table 3-1). Expressed as proper conversion factors, the relationships are

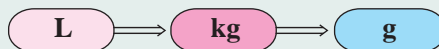
$$(a) \frac{1 \text{ mL}}{10^{-3} \text{ L}} \quad \text{and} \quad (b) \frac{0.82 \text{ g}}{\text{mL}}$$

**SOLUTION**

$$1.52 \text{ L} \times \frac{1 \text{ mL}}{10^{-3} \text{ L}} \times \frac{0.82 \text{ g}}{\text{mL}} = \underline{\underline{1.2 \times 10^3 \text{ g}}}$$

**ANALYSIS**

The same value for the density can also be expressed as kg/L as well as g/mL (i.e.,  $0.82 \text{ kg/L}$  and  $0.82 \text{ g/mL}$ ). If the density is a little less than 1 kg per liter, we would expect the mass of 1 L to be around 1 kg, which it is. What does the unit map for the conversion using kg/L look like?



The necessary conversions are  $0.82 \text{ kg/L}$  and  $1000 \text{ g/kg}$ .

**SYNTHESIS**

When solving a problem involving conversion of units, is there a single correct way to work it out? Clearly, there isn't. We've supplied two different pathways for this single problem. Interestingly, though the pathways differ, the exact same numbers end up being manipulated. We multiply by 0.82 and then either multiply by  $10^3$  or divide by  $10^{-3}$ , which works out the same.

**3-2.3 Specific Gravity**

In place of density, certain applications, especially in the medical field, use the term *specific gravity*. **Specific gravity** is the ratio of the mass of a substance to the mass of an equal volume of water under the same conditions. Since the mass of water is  $1.00 \text{ g/mL}$ , specific gravity has the same value as density, only expressed without units. For example, the density of aluminum is  $2.70 \text{ g/mL}$ , so its specific gravity is simply 2.70.

MAKING

IT

REAL

### Identifying a Glass Shard from a Crime Scene by Density

A woman is struck down by a hit-and-run driver, but there are glass fragments from the car in the street. A burglar breaks through a glass display window but doesn't realize that some small glass shards stick to his clothes. Identification of the origin of a tiny piece of glass by matching it to a specific automobile or to a certain plate-glass window provides strong forensic evidence that can help connect the car or a suspect to a crime scene.

Glass may all look the same, but it is not. Even glass from different glass windows in the same building may have very small variations in properties depending on the type, the manufacturer, or even the time when it was made. However, these small differences can be used effectively by the crime scene investigator. Glass fragments can be matched with other glass by the use of density and refractive index. When two pieces of glass have the same or very close values for these two measurements, it can be assumed that they have the same origin. We will see how density is used at the crime scene in this discussion. Refractive index relates to the nature of light, so it will be discussed at the appropriate time in Chapter 5.

The density of a piece of glass can be determined by its buoyancy. Two liquids are used for the determination of glass density, bromoform ( $\text{CHBr}_3$ , density 2.8899 g/mL) and bromobenzene ( $\text{C}_6\text{H}_5\text{Br}$ , density 1.4950 g/mL). Window glass has a density range of 2.47 to 2.54 g/mL. Thus, all glass sinks in pure bromobenzene but floats in

pure bromoform. By mixing the two liquids, however, we can produce a mixture that has a precise range of densities intermediate between the two pure liquids. By adding the less dense liquid to the more dense, the mixture of the two liquids gradually becomes less dense. Eventually, a mixture is produced whereby the glass shard is no longer buoyant and becomes suspended in the liquid. At that point, the density of the glass is the same as that of the liquid. The density is then determined from a table that relates the density of the mixture to the measured proportion of the two liquids. Under ideal conditions, this procedure has a precision of around  $\pm 0.0001$  g/mL. It is a very simple laboratory procedure but can provide valuable information. If two fragments of glass have the same density, they most likely originated from the same source. Refractive index, which is described later, should confirm this evidence.



Refer to Student Workshop at the end of the chapter.

#### ASSESSING THE OBJECTIVE FOR SECTION 3-2

**EXERCISE 3-2(a) KNOWLEDGE:** What is the volume in milliliters occupied by 285 g of mercury? (See Table 3-1.)

**EXERCISE 3-2(b) KNOWLEDGE:** The volume of water in a graduated cylinder measures 21.95 mL. After addition of a 53.5-g sample of cadmium metal, the volume of the water and metal reads 32.72 mL. What is the density of the metal?

**EXERCISE 3-2(c) ANALYSIS:** A sample of a given pure liquid has a mass of 254 g and a volume of 159 mL. What might the liquid be? Refer to Table 3-1. Does this liquid float or sink when mixed in a beaker with water?

**EXERCISE 3-2(d) SYNTHESIS:** Antifreeze is made up of equal portions of ethylene glycol and water. Ethylene glycol is more dense than water, but the two liquids mix together. How can density be used to determine the quality of the antifreeze in a radiator?

*For additional practice, work chapter problems 3-12, 3-17, and 3-21.*



## 3-3 THE PROPERTIES OF MIXTURES



**LOOKING AHEAD!** It is not often in the world around us that we encounter an element or compound in such a highly concentrated state that we may judge it as “pure.” Even the water we drink contains other compounds (e.g., salt) and elements (e.g., oxygen). How we describe mixtures is the subject of this discussion. ■

### 3-3.1 Heterogeneous Mixtures

You probably know that you can’t mix oil and water. Oil and water form a heterogeneous mixture. A **heterogeneous mixture** is a nonuniform mixture containing two or more phases with definite boundaries or interfaces between the phases. A **phase** is one physical state (solid, liquid, or gas) with distinct boundaries and uniform properties.

Besides oil and water (two liquid phases), an obvious heterogeneous mixture is a handful of soil from the backyard. If we look closely, we see bits of sand, some black matter, and perhaps pieces of vegetation. One can easily detect several solid phases with the naked eye. Other examples of heterogeneous mixtures are carbonated beverages (liquid and gas) and muddy water (liquid and solid). Heterogeneous mixtures can often be separated into their components by simple laboratory procedures. For example, suspended solid matter can be removed from water by *filtration*. (See Figure 3-4.) When the turbid water is passed through the filter, the suspended matter remains on the filter paper and the clear liquid phase passes through. In the purification of water for drinking purposes, the first step is the removal of suspended particulate matter.

Sometimes heterogeneous mixtures cannot be detected with the naked eye. For example, creamy salad dressing and smoke both appear uniform at first glance. However, if we were to magnify each, it becomes apparent that these are actually heterogeneous mixtures. The salad dressing has little droplets of oil suspended in the vinegar (two liquid phases), and the smoke has tiny solid and liquid particles suspended in the air (solid, liquid, and gas phases).

### 3-3.2 Homogeneous Mixtures and Solutions

Oil and water don’t mix, but when you pour alcohol into water, both liquids disperse into each other and no boundary between the two liquids is apparent. A **homogeneous mixture** is the same throughout and contains only one phase. In Figure 3-5, a heterogeneous mixture, on the left, is compared to a homogeneous mixture, on the right. Notice on the left that the oil floats on top of the water because the density of oil ( $\approx 0.90$  g/mL) is less than that of water (1.00 g/mL).



(a)



(b)



(c)



(d)

**FIGURE 3-5 Mixtures** Water and oil (a, b) form a heterogeneous mixture with two liquid phases. Water and an alcohol (c) form a homogeneous mixture with one liquid phase (d).

### OBJECTIVES FOR SECTION 3-3

(a) Describe the differences in properties between a pure substance and a mixture. (b) Perform calculations involving percent as applied to mixtures.



**FIGURE 3-4 Filtration** A heterogeneous mixture of a solid and liquid can be separated by filtration.



**FIGURE 3-6 Distillation**

A homogeneous mixture of a solid in a liquid or two liquids can be separated by distillation.

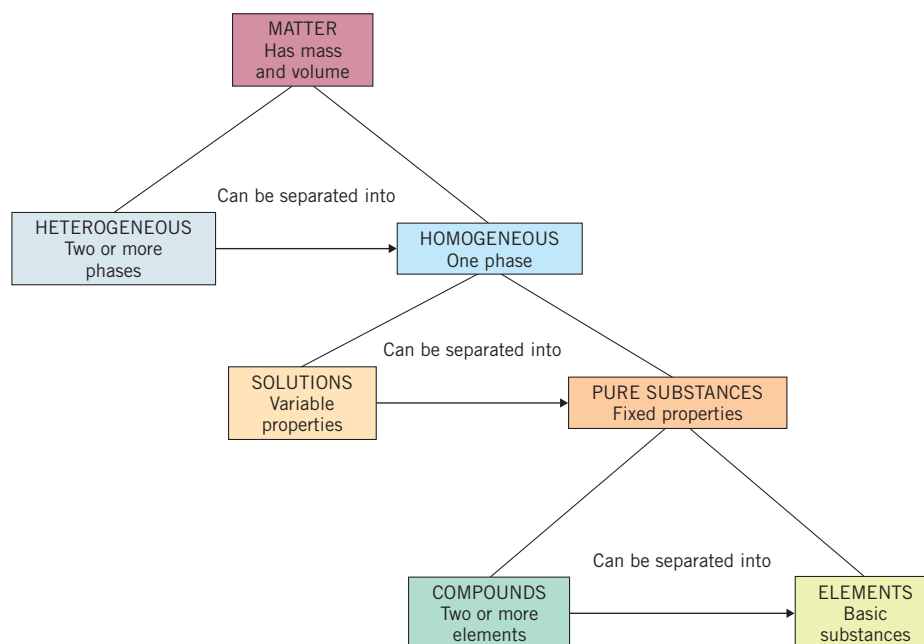
In heterogeneous mixtures, portions of each component are large enough to be detected, although some magnification may be necessary. In homogeneous mixtures, the components disperse uniformly into each other. As mentioned earlier, matter is composed of fundamental particles. In a typical homogeneous mixture, the mixing extends all the way to the molecular level. Thus, there is no detectable boundary between components. No amount of magnification would reveal pieces of solid salt when it is dissolved in the water. When table salt is added to water, it forms a solution. A **solution** usually refers to homogeneous mixtures with one liquid phase. Thus components of a solution cannot be separated by filtration. However, the two components can be separated by a laboratory procedure called *distillation*. (See Figure 3-6.) In

the distillation of a salt solution, the water is boiled away from the solution and then retrieved by condensation through a water-cooled tube. When all the water has boiled away, the solid table salt remains behind in the distilling flask.

A glass of salt water and a glass of pure water look exactly the same. They do taste different, however. In fact, *since both solutions and pure substances (elements and compounds) are homogeneous matter, one must examine the physical properties to distinguish between the two.* Mixtures have properties that vary with the proportion of the components. Elements and compounds have definite and unchanging properties. A simple example of a variable property is the taste and color of a cup of coffee. The more coffee that is dissolved in the water, the stronger the taste and the darker the solution.

Now consider the properties of two compounds alone: table salt and water. Solid table salt (sodium chloride) melts at  $801^{\circ}\text{C}$  and water ice melts at  $0^{\circ}\text{C}$ . A solution of salt in water begins to freeze anywhere from  $-18^{\circ}\text{C}$  to just under  $0^{\circ}\text{C}$ , depending on the amount of salt dissolved. Also, a particular saltwater solution does not have a sharp, unchanging boiling point or freezing point, as does pure water.

Density is another physical property that is different for a solution compared to the pure liquid component. For example, battery acid is a solution of a



**FIGURE 3-7 The Classification of Matter**

Heterogeneous mixtures can eventually be separated into elements.

compound, sulfuric acid, in water. Its density is greater than that of pure water. The more sulfuric acid present, the denser the solution. In a fully charged battery, the density is about 1.30 g/mL; if it is mostly discharged, the density is about 1.15 g/mL.

The classification of matter from the most complex, a sample of heterogeneous matter (at the upper left), to the most basic form of homogeneous matter, a pure element (at the lower left), is illustrated in Figure 3-7.

### 3-3.3 Alloys—Homogeneous Mixtures of Metals

Many of the metals that we use in our daily lives are actually alloys. An **alloy** is a homogeneous mixture of metallic elements existing in one solid phase. Although an alloy is considered a *solid solution*, it is made by mixing the metals in the molten state and then allowing the liquid solution to cool and resolidify. Pure gold (24 K) is a comparatively soft element and is easily bent. It is made harder by mixing with other elements. For example, 18-K gold is 75% (by mass) gold, with the rest silver and/or copper. Stainless steel is a mixture of three elements: 80% iron, 12% chromium, and 8% nickel.

Since the composition of alloys and other chemical mixtures is often expressed as a percent by mass, it would serve us well to review the use of percent in calculations. We will do this using alloys as examples.

Percent can be used as a conversion factor that relates the component part of a sample to the total mass of that sample. These calculations are illustrated in the following two examples. Further examples in the use of percent are found in Appendixes A and B.



An artificial hip joint is made of a titanium–iron alloy.

#### EXAMPLE 3-5

#### Determining the Mass of a Component Using Percent

Manganese steel is very strong and is used as railroad rails. It is composed of 86.0% iron, 13.0% manganese, and 1.0% carbon. What is the mass of each of the three elements in a 254-kg sample of manganese steel?

#### PROCEDURE

The most common use of percent is to calculate the mass of a component part, such as the mass of each element in a given sample of a mixture. *Percent* means “parts per 100.” In this case, a conversion factor can be constructed from each percent, relating kilograms of a component to kilograms of the steel as follows.

$$86.0\% \text{ iron} = \frac{86.0 \text{ kg iron}}{100 \text{ kg steel}} \quad 13.0\% \text{ manganese} = \frac{13.0 \text{ kg manganese}}{100 \text{ kg steel}}$$

If there are three components, the third can be determined by subtraction of the first two from the total. These conversion factors can now be used as written to convert kilograms of steel to kilograms of a component.

#### SOLUTION

$$\begin{aligned} 254 \text{ kg steel} \times \frac{86.0 \text{ kg iron}}{100 \text{ kg steel}} &= \underline{218 \text{ kg iron}} \\ 254 \text{ kg steel} \times \frac{13.0 \text{ kg manganese}}{100 \text{ kg steel}} &= \underline{33.0 \text{ kg manganese}} \\ 254 \text{ kg} - 218 \text{ kg iron} - 33.0 \text{ kg manganese} &= \underline{3 \text{ kg carbon}} \end{aligned}$$

#### ANALYSIS

Notice that any units of mass can be used. The problem would have been solved the same way if pounds were given rather than kilograms. What would the conversion factor be for the amount of manganese in pounds?

$$\frac{13.0 \text{ lb manganese}}{100 \text{ lb steel}}$$

Notice also that the total masses of the components all add to the original mass of the steel, which is 254 kg. If a problem with three components gave you only two of the percentages, could you determine the third? It is clearly the difference between the sum of the first two and 100.

**SYNTHESIS**

Besides finding the mass of a component given the percent, what other types of problems could you solve using component masses and percentages? You can solve for any component mass or percent as long as only one variable is missing. You could also solve for total mass if you can determine all the component masses and their corresponding percentages. The following example demonstrates this calculation.

**EXAMPLE 3-6****Determining a Component Mass from the Total Mass Using Percent**

A sample of brass is composed of 72% copper with the remainder being zinc. What mass of brass can be made from 25 kg of zinc?

**PROCEDURE**

Percent can also be used as a factor to convert the mass of a component part to the mass of the total, which in this case is brass. The percent composition of zinc is  $100\% - 72\% = 28\%$  zinc. The conversion factor and its reciprocal are

$$\frac{28 \text{ kg zinc}}{100 \text{ kg brass}} \quad \text{and} \quad \frac{100 \text{ kg brass}}{28 \text{ kg zinc}}$$

The latter factor can now be used to convert kg zinc to kg brass.

**SOLUTION**

$$25 \text{ kg zinc} \times \frac{100 \text{ kg brass}}{28 \text{ kg zinc}} = \underline{\underline{89 \text{ kg brass}}}$$

**ANALYSIS**

We could also set up a conversion factor that would allow us to figure out the amount of copper that would mix with the 25 kg of zinc. What would that conversion factor look like?

$$\frac{72 \text{ kg copper}}{28 \text{ kg zinc}}$$

**SYNTHESIS**

Let's consider what would happen if we used the wrong factors in the conversions. 25 kg zinc times the inverted conversion factor  $28/100$  gives 7 kg of brass as an answer. 25 kg zinc times the inverted conversion factor  $28/72$  gives 9.7 kg of copper needed to form the alloy. How would we know automatically that these aren't correct? In the first case, the mass of the component is greater than the mass of the total product. In the second case, the mass of the smaller-percentage component is greater than the mass of the larger-percentage component. Applying a little common sense alerts us to when a mistake is made. Based on the numbers, we'd expect the amount of copper to be roughly three times greater, and the amount of brass four times greater, than the amount of zinc.

Actually, everything is a mixture, at least to some extent, since complete 100% purity may be impossible. What we call fresh drinking water is hardly pure. It contains dissolved gases and solids. Even rainwater contains some dissolved gases from the air. What we consider pure may depend on the application. For example, if a sample of matter is composed of 99% of one element or compound, it may be considered pure for most purposes. On the other hand, the element silicon must be ultrapure to be used in computer chips. In this case, it is composed of more than 99.9999% silicon.

**ASSESSING THE OBJECTIVES FOR SECTION 3-3**

**EXERCISE 3-3(a) KNOWLEDGE:** Is the listed property a description of a heterogeneous or homogenous mixture?

- (a) has distinct boundaries
- (b) visibly shows several components
- (c) contains only one phase
- (d) has a single concentration throughout

**EXERCISE 3-3(b) ANALYSIS:** Carbon tetrachloride and water are two liquids that do not mix homogeneously with one another. What type of mixture will they form? Describe the appearance of the mixture.

**EXERCISE 3-3(c) ANALYSIS:** In a fishbowl, there appears to be only water. A fish placed in there, however, can retrieve oxygen from the water with its gills. What type of mixture do the water and oxygen form?

**EXERCISE 3-3(d) SYNTHESIS:** The separation technique you use is dependent on the type of mixture you have. Could you use distillation to separate the heterogeneous mixture of water and sand? Could you use filtration to separate the homogeneous mixture of water and salt?

**EXERCISE 3-3(e) ANALYSIS:** 14-K gold is 58.0% gold. What is the weight of pure gold in 4.00 oz of 14-K gold?

**EXERCISE 3-3(f) ANALYSIS:** What mass of 14-K gold can be made from 128 g of pure gold?

**EXERCISE 3-3(g) ANALYSIS:** Solder is an alloy made from 60.0% tin and 40.0% lead. What mass of each metal is found in a 72-g roll of solder?

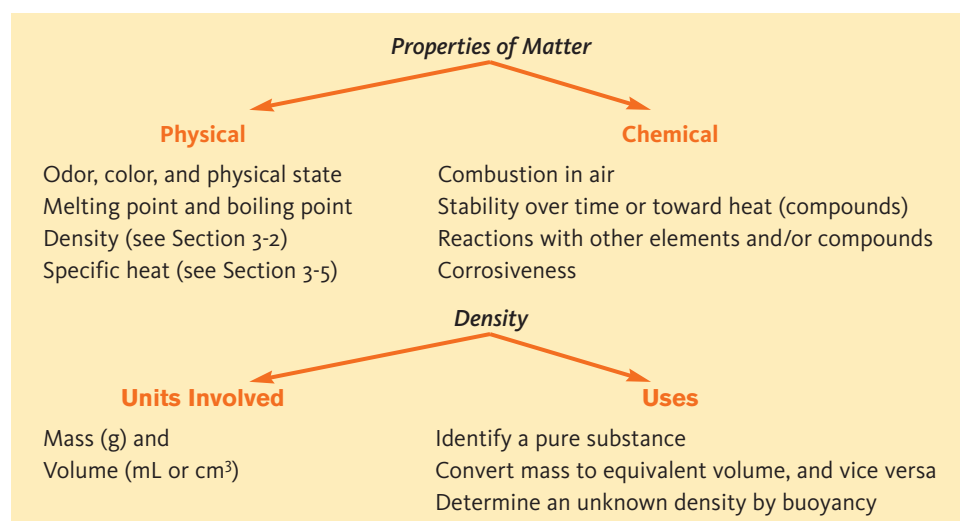
For additional practice, work chapter problems 3-41, 3-48, 3-50, and 3-54.

## PART A SUMMARY

### KEY TERMS

- 3-1** A **physical property** can be observed or measured without changing the substance. p. 80
- 3-1.1** **Physical state** describes whether the substance is a **solid, liquid, or gas** at a specific temperature. p. 80
- 3-1.2** **Melting** and **freezing point** is the temperature at which a substance changes between the liquid and solid states. p. 81
- 3-1.2** **Boiling** and **condensation** refer to the changes between the gaseous and liquid states. The **boiling point** of a pure liquid is a constant at a specific pressure. p. 82
- 3-1.2** A **physical change** involves a change in phase or dimensions. p. 82
- 3-1.3** An **extensive property** depends on the amount present, while an **intensive property** is independent of the amount. p. 82
- 3-1.4** A **chemical property** refers to the tendency to undergo a chemical change from one substance into another substance. p. 82
- 3-1.5** Chemical reactions illustrate the **law of conservation of mass**. p. 83
- 3-2.1** **Density** is the mass per unit volume. It is an intensive physical property that can be used to help identify a substance and convert between mass and volume. p. 84
- 3-2.3** **Specific gravity** is used in certain medical applications and has the same numerical value as density. p. 87
- 3-3.1** **Heterogeneous mixtures** exhibit more than one identifiable **phase**. p. 89
- 3-3.2** **Homogeneous mixtures** and **solutions** involve an intimate mixture with one phase. pp. 89, 90
- 3-3.3** **Alloys** are homogeneous mixtures of metals in one solid phase. Their composition is often described in terms of percent by mass. p. 91

### SUMMARY CHARTS





## PART B THE PROPERTIES OF ENERGY

### SETTING A GOAL

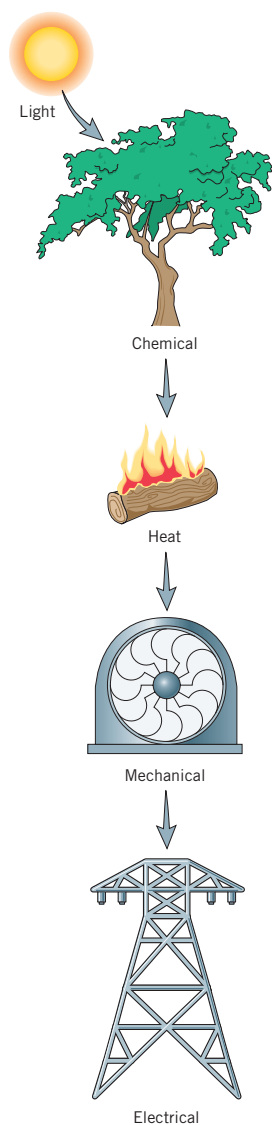
- You will be able to qualitatively and quantitatively describe processes in terms of the forms and types of energy associated with them.

### OBJECTIVES

- 3-4 (a)** Distinguish among the forms and types of energy.
- (b)** Define the terms *endothermic* and *exothermic*, providing several examples of each type of process.
- 3-5** Perform calculations involving the specific heat of a substance, and use them to identify a substance.

### OBJECTIVES FOR SECTION 3-4

**(a)** Distinguish among the forms and types of energy. **(b)** Define the terms *endothermic* and *exothermic*, providing several examples of each type of process.



**FIGURE 3-8** Energy is neither created nor destroyed but can be transformed.

## 3-4 THE FORMS AND TYPES OF ENERGY



**LOOKING AHEAD!** We bask in the heat from the sun, but energy can take other forms as well. How we describe and measure heat energy is the focus of this section. ■

When we don't feel like we have much energy, we sure don't feel like working. Actually, that is the definition of energy. **Energy** is the *capacity or the ability to do work*. Work involves the transfer of energy when an object is moved a certain distance.

### 3-4.1 Forms of Energy

Just as matter has more than one physical state, energy has more than one form. Most of the energy on Earth originates from the sun. Deep in the interior of our ordinary star, transformations of elements occur that liberate a form of energy called *nuclear energy*. Some of this energy, however, changes in the sun into *light* or *radiant energy* that then travels through space to illuminate Earth. Light energy from the sun bathes our planet and shines on the surface vegetation, where some of it is converted into *chemical energy* by a process called photosynthesis. Chemical energy is stored in the energy-rich compounds that make up the bulk of the vegetation. When logs from a tree are burned, the chemical energy is released in the form of *heat energy*. In a similar process, the metabolism of food in our bodies releases energy to keep us alive. In the burning, or metabolism, process, energy-poor compounds are produced and recycle to the environment.

In the production of electrical power, the heat energy is used to produce steam that turns a turbine. The movement of the turbine is *mechanical energy*. The mechanical energy powers a generator that converts the mechanical energy into *electrical energy*. (See Figure 3-8.) Other conversions between energy forms are possible. For example, in the chemical change that occurs in a car battery, chemical energy is converted directly into electrical energy. Energy changes are subject to the same law as matter changes in chemical reactions.

The **law of conservation of energy** states that energy cannot be created or destroyed but only transformed from one form to another. In the production of electrical energy in Figure 3-8, only about 35% of the chemical energy is eventually transformed into electrical energy. The rest of the energy is lost as heat energy in the various transformations. However, the total energy remains constant.

### 3-4.2 Exothermic and Endothermic Changes

Chemical or physical changes may be accompanied by either the release or the absorption of heat energy. *When a change releases heat, it is said to be exothermic. When a change absorbs heat, it is said to be endothermic.* Combustion (burning) is a common example

of an exothermic chemical reaction. An “instant cold pack” is an example of an endothermic process. When the compounds ammonium nitrate (a solid) and water are brought together in a plastic bag, a solution is formed. The endothermic solution process causes enough cooling to make an ice pack useful for treating sprains and minor aches. (See Figure 3-9.) Melting ice is a physical change but is also an endothermic process. That is, to melt ice cubes, we supply heat by taking a tray of cubes out of the freezer and letting it sit in the warmer room. Boiling water is another example of an endothermic process: when water absorbs enough heat from the stove, it boils.

### 3-4.3 Kinetic and Potential Energy

In addition to the *forms* of energy, there are two *types* of energy. These depend on whether the energy is available but not being used or is actually in use. **Kinetic energy** is the energy produced from motion. A moving baseball, a speeding train, and water flowing down a spillway from a dam (see Figure 3-10) all have kinetic energy. **Potential energy** is energy that is available because of position or composition. For example, a weight suspended above the ground has energy available because of its position and the attraction of gravity for the weight. Water stored behind a dam (Figure 3-10), a compressed spring, and a stretched rubber band all have potential energy. The chemical energy stored in the compounds of a tree log is also classified as potential energy.



**FIGURE 3-9** Instant Cold Pack When capsules of ammonium nitrate are broken and mixed with water, a cooling effect results.



**FIGURE 3-10** Potential and Kinetic Energy Water stored behind a dam has potential energy. The water flowing over the spillway has kinetic energy.

#### ASSESSING THE OBJECTIVES FOR SECTION 3-4

**EXERCISE 3-4(a) KNOWLEDGE:** Identify the following as endothermic or exothermic.

- (a) sweat evaporating
- (b) natural gas combusting
- (c) wax melting
- (d) leaves decaying

**EXERCISE 3-4(b) KNOWLEDGE:** Identify the principal type of energy, kinetic or potential, exhibited by each of the following.

- (a) a car parked on a hill
- (b) a train traveling at 60 mph
- (c) chemical energy of a nutrition bar
- (d) an uncoiling spring in an alarm clock
- (e) a falling brick

**EXERCISE 3-4(c) SYNTHESIS:** Sunlight causes corn to grow. A substance in corn can be converted to ethanol. The ethanol is used as automobile fuel. What forms of energy are involved in each of these changes? Is a particular form of energy potential or kinetic energy?

For additional practice, work chapter problems 3-56, 3-59, and 3-62.

**OBJECTIVE FOR SECTION 3-5**

Perform calculations involving the specific heat of a substance, and use them to identify a substance.

**3-5 ENERGY MEASUREMENT AND SPECIFIC HEAT**

**LOOKING AHEAD!** Heating a substance may cause it to melt or boil. If adding heat does not cause a physical or chemical change, it just raises the temperature. However, each compound or element is affected to a different extent by the same amount of heat. We will now consider how heat affects the temperature of a given substance. ■

The most obvious thing that happens when heat is applied to a pan of water is that the temperature of the pan and water increases. The amount of temperature change for a specific mass of substance is an intensive physical property known as specific heat capacity, or simply specific heat. **Specific heat** is defined as the amount of heat required to raise the temperature of 1 gram of a substance 1 degree Celsius (or kelvin).

**3-5.1 Units of Heat Energy**

Units of heat energy are based on the specific heat of water. A **calorie** is the amount of heat energy required to raise the temperature of 1 gram of water from 14.5°C to 15.5°C. The unit of heat energy most often used in chemistry is the SI unit called the **joule**. The calorie is now defined in terms of the joule.

$$1 \text{ cal} = 4.184 \text{ joule(J)} \text{ (exactly)}$$

The definition of the calorie provides us with the specific heat of water in joules:

$$1.000 \frac{\text{cal}}{\text{g} \cdot ^\circ\text{C}} = 4.184 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$$

Notice that there are approximately 4 joules per calorie. The units read: calories (or joules) per gram per degree Celsius. The degree Celsius unit represents a *temperature change*, not a specific temperature reading. (Change is represented by the Greek letter  $\Delta$ , pronounced delta.) Thus, a change in temperature is represented as  $\Delta T$ . The Kelvin scale can also be used in

place of the Celsius scale since the Kelvin and Celsius degrees are the same. The formula used to calculate the specific heat is

$$\text{specific heat} = \frac{\text{amount of heat energy (J or cal)}}{\text{mass (g)} \times \Delta T (^\circ\text{C})}$$

The specific heats of several pure substances are listed in Table 3-2.

The following two examples illustrate the calculation of specific heat and the use of specific heat to calculate temperature change.

**TABLE 3-2** Specific Heats

| SUBSTANCE     | SPECIFIC HEAT [cal/(g · °C)] | SPECIFIC HEAT [J/(g · °C)] |
|---------------|------------------------------|----------------------------|
| Water         | 1.000                        | 4.184                      |
| Ice           | 0.492                        | 2.06                       |
| Aluminum (Al) | 0.214                        | 0.895                      |
| Gold (Au)     | 0.031                        | 0.129                      |
| Copper (Cu)   | 0.092                        | 0.385                      |
| Zinc (Zn)     | 0.093                        | 0.388                      |
| Iron (Fe)     | 0.106                        | 0.444                      |

**EXAMPLE 3-7****Determining Specific Heat**

It takes 628 J to raise the temperature of a 125-g quantity of silver from 25.00°C to 32.14°C. What is the specific heat of silver in joules?

**PROCEDURE**

Determine a specific heat from the heat required to change a given mass and a given temperature change.

(a) Calculate the actual temperature change [ $\Delta T = T(\text{final}) - T(\text{initial})$ ]

(b) The specific heat is calculated by substituting the appropriate quantities in the formula.

**SOLUTION**

$$\Delta T = 32.14^{\circ}\text{C} - 25.00^{\circ}\text{C} = 7.14^{\circ}\text{C}$$

$$\text{specific heat} = \frac{628 \text{ J}}{125 \text{ g} \times 7.14^{\circ}\text{C}} = 0.704 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}}$$

**ANALYSIS**

What would this value be in units of cal/g $^{\circ}$ C? Use the relationship that 1 cal = 4.184 J. Then

$$0.704 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = \frac{0.168 \text{ cal}}{\text{g} \cdot ^{\circ}\text{C}}$$

**SYNTHESIS**

From an evaluation of Table 3-2, what seems to be the relationship between the atomic mass of a metal and its specific heat? The higher the atomic mass, the lower the specific heat of an element. That is referred to as an inverse relationship. It results from there being fewer atoms in a gram of a heavier metal compared to a lighter metal. Therefore, there are fewer particles to absorb energy.

**EXAMPLE 3-8****Determining Temperature Change Using Specific Heat**

If 1.22 kJ of heat is added to 50.0 g of water at 25.0 $^{\circ}$ C, what is the final temperature of the water? [The specific heat of water is 4.184 J/(g  $\cdot$   $^{\circ}$ C).]

**PROCEDURE**

Calculate how much the temperature increases (from 25 $^{\circ}$ C) by addition of a specific amount of heat to a specific mass of water.

- (a) Convert kJ to J using the relationship 1 kJ = 10<sup>3</sup> J.  
 (b) Solve the specific heat formula for  $\Delta T$  and substitute in the known values.

$$\text{specific heat} = \frac{\text{heat energy (J)}}{\text{mass (g)} \times \Delta T (^{\circ}\text{C})}$$

$$\Delta T = \frac{\text{heat energy (J)}}{\text{mass (g)} \times \text{specific heat}}$$

- (c) Find the final temperature of the water by adding the temperature change to the original temperature.

**SOLUTION**

$$\text{(a)} \quad 1.22 \text{ kJ} \times \frac{10^3 \text{ J}}{\text{kJ}} = 1.22 \times 10^3 \text{ J} \quad \text{(b)} \quad \Delta T = \frac{1.22 \times 10^3 \text{ J}}{50.0 \text{ g} \times 4.184 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}}} = 5.83^{\circ}\text{C}$$

The temperature change of the water is 5.83 $^{\circ}$ C. Make sure you read on.

**ANALYSIS**

Is 5.83 $^{\circ}$ C the answer to the question “what is the final temperature”? It can't be. Heat was added, and yet the answer is less than the original temperature of 25.0 $^{\circ}$ C. The 5.83 is the *change* in temperature, and since heat was added, it makes sense that the new temperature is 5.83 degrees *higher* than the initial temperature.

$$\text{(c)} \quad T_{\text{final}} (^{\circ}\text{C}) = 25.0 + 5.83 = \underline{\underline{30.8^{\circ}\text{C}}}$$

**SYNTHESIS**

Is our answer reasonable now? Adding heat to the water will cause the temperature to go up. Notice from the specific heat that about 4 joules raises 1 gram of water 1 degree, so it would take about 200 J (50  $\times$  4) to raise 50 g of water 1 degree. 1220 J divided by 200 J indicates a temperature rise of about 6 degrees. The answer is reasonable.

You may have noticed how fast an iron skillet heats up compared to an equivalent amount of water. It takes longer to heat water because it has a comparatively high specific heat. Notice in Table 3-2 that the specific heat of water is almost 10 times higher than that of the iron in the skillet. Thus, in a calculation similar to the one in Example 3-8b, the same amount of heat will raise the temperature of the iron

| Nutrition Facts                 |                  |
|---------------------------------|------------------|
| Serving Size 1 Tablespoon (14g) |                  |
| Servings Per Container 96       |                  |
| Amount Per Serving              |                  |
| <b>Calories</b> 120             | Fat Calories 120 |
| % Daily Value*                  |                  |
| <b>Total Fat</b> 14g            | <b>22%</b>       |
| Saturated Fat 1g                | 6%               |
| Polyunsaturated Fat 5g          |                  |
| Monounsaturated Fat 7g          |                  |
| <b>Sodium</b> 0mg               | <b>0%</b>        |
| <b>Total Carbohydrate</b> 0g    | <b>0%</b>        |
| <b>Protein</b> 0g               | <b>0%</b>        |

Many people are very conscious of the energy content (Calories) of the food they eat.

almost 10°C for every 1°C for the same weight of water. (Iron also conducts heat rapidly from the fire to the handle.)

### 3-5.2 The Nutritional Calorie and Heat Exchange

The amount of energy that we obtain from food can also be measured and expressed in calories. The nutritional calorie is actually one *kilocalorie* ( $10^3$  cal) as defined above. To distinguish between the two calories, the *c* in calorie is capitalized in the nutritional Calorie (1 Cal).

The Calorie content of a portion of food is measured by burning the dried food. The heat released by the combustion process is then used to heat a known amount of water at a known original temperature. The principle of heat exchange states that *heat lost equals heat gained*, assuming no heat is lost to the surroundings. Heat exchange is a practical example of the conservation of energy. In this case, the water gains the heat lost by the portion of food. This is illustrated in Example 3-9.

The application of the principle of heat exchange can also be used to measure the specific heat of a substance. When two substances at different temperatures are mixed, the hotter item will lose heat energy and the cooler one will gain heat energy. Thus, the temperature of the hotter item comes down as the temperature of the other increases. Eventually, the two substances come to the same temperature, which is somewhere in between the two original temperatures. In the following example, we have a known mass of water and a metal with an unknown specific heat. The metal starts at a high temperature and the water at a lower temperature. When the two are mixed, the temperature settles between the two original temperatures.

#### EXAMPLE 3-9

##### Counting Calories

A piece of cake is dried and burned so that all the heat energy released heats some water. If 3.15 L of water is heated a total of 75.0°C, how many Calories does the cake contain?

##### PROCEDURE

Use the equation for specific heat to solve for the amount of heat in calories. The heat required to heat the specific amount of water is the heat content of the piece of cake.

- Determine the mass. First, convert the volume of water in liters to milliliters using  $1 \text{ L} = 10^3 \text{ mL}$ . Next, convert the volume of water in milliliters to the mass of water using the density, which is 1.00 g/mL.
- Use the formula for specific heat (in cal) to solve for the amount of heat energy.

$$\text{amount of heat energy} = \text{mass} \times \Delta T \times \text{specific heat}$$

- Convert calories to Calories using the relationship  $1 \text{ Cal} = 10^3 \text{ cal}$ .

##### SOLUTION

$$(a) \quad 3.15 \text{ L} \times \frac{10^3 \text{ mL}}{\text{L}} \times \frac{1.00 \text{ g}}{\text{mL}} = 3.15 \times 10^3 \text{ g}$$

$$(b) \quad 3.15 \times 10^3 \text{ g} \times 75.0^\circ\text{C} \times \frac{1.00 \text{ cal}}{\text{g} \cdot ^\circ\text{C}} = 236 \times 10^3 \text{ cal}$$

$$(c) \quad 236 \times 10^3 \text{ cal} \times \frac{1 \text{ Cal}}{10^3 \text{ cal}} = \underline{\underline{236 \text{ Cal}}}$$

##### ANALYSIS

We could have saved a step if we had noted that specific heat could be expressed as 1.00 kcal (Cal)/kg (water)  $\times \Delta T$ . If we use those units, what does the second calculation look like?  $315 \text{ kg} \times 75^\circ\text{C} \cdot 1.00 \text{ Cal/kg} \cdot ^\circ\text{C} = 236 \text{ Cal}$ .

##### SYNTHESIS

Does this answer make sense? If we were interested in weight control, we'd have to exercise off that amount of energy. Typical exercise machines like stairs, rowing machines, and bikes that allow you to count calories can burn about 500 Calories each hour, depending on the activity. Is eating the cake worth it? 236 Calories for a piece of cake is a very reasonable answer. At 500 Calories each hour, it would take half that time to burn 236 Calories, or about a half an hour of constant exercise. Only you can decide whether the enjoyment of a slice of cake is worth that amount of exertion.



MAKING

IT

REAL

### Body Solutions—Lose Weight (actually money) While You Sleep



Evening Weight Loss Formula. Its claim was that by using its product, you could lose weight while you slept. By taking a teaspoon of the product with a glass of water before you went to bed and by refraining from eating for three hours before going to bed, you would begin to lose weight. The marketing strategy was to have well-known and respected DJs in major markets use and promote the product. The airwaves were busy with testimonials touting the product's benefits. Many people who tried the product initially experienced weight loss, which they were happy to talk

There are two ways to lose weight. Either reduce the total amount of Calories that you consume to a level lower than you burn, or increase your activity so that the amount of Calories you burn rises above the amount you consume. Ideally, someone interested in weight loss would do both at the same time. Back in 1999, however, there appeared to be a third option that was receiving a lot of attention.

A company called Mark Nutritionals Inc. began marketing a product called Body Solutions

about, adding to the excitement about the product. By May 2002, Body Solutions was becoming available in reputable drugstores throughout the country.

By October, though, the Federal Trade Commission (FTC) was actively pursuing Mark Nutritionals Inc. for advertising fraud. The company had paid the radio personalities to make claims without merit and given them a percentage of the profits that their market generated. Scientific studies found no evidence supporting Body Solutions as a weight-loss supplement, and there were even reports of adverse health effects from some of Mark Nutritionals' supplementary products. In the settlement of the case, Body Solutions was put out of business. Why, then, did so many people experience an initial weight loss?

If it is part of your normal lifestyle to eat throughout the evening, but instead you stopped eating for three hours before you went to bed, it is possible that you would eat 400 or 500 fewer Calories each day than you otherwise would. A pound of fat in the body stores 3500 Calories, so by refraining from eating for three hours before going to bed, and not consuming more during the other hours, you could expect to lose 1 pound per week by doing nothing else. It really comes down to just reducing Calories; it had nothing to do with the diet supplement, for which consumers had paid a total of \$155 million over three years.

#### EXAMPLE 3-10

### Determining a Specific Heat by Heat Exchange

A 440-g quantity of a certain metal is heated to 100.0°C. It is immediately thrust into 258 g of water that is initially at 25.0°C. The temperature of the metal–water mixture eventually settles at 36.5°C. What is the metal? (Refer to Table 3-2.)

#### PROCEDURE

To establish its specific heat, we need the metal's mass, temperature change, and the heat released by cooling to cause the change. The heat released by the metal is the same as the heat gained by the water.

(a) The heat gained by the water is given by the equation

$$\text{heat gained} = \Delta^{\circ}\text{C}(\text{water}) \times \text{mass}(\text{g water}) \times \text{specific heat}(\text{water})$$

$$\Delta^{\circ}\text{C} = T_{\text{final}} - T_{\text{initial}}$$

(b) The heat gained by the water is equal to the heat lost by the metal. Heat lost is assigned a negative sign by convention. The heat lost by the metal is

$$\text{heat lost} = -\Delta^{\circ}\text{C}(\text{metal}) \times \text{mass}(\text{g metal}) \times \text{specific heat}(\text{metal})$$

(c) Set the heat gained by the water equal to the heat lost by the metal. Solve for the specific heat of the metal.

$$-\text{heat lost} = \text{heat gained}$$

$$-\Delta^{\circ}\text{C}(\text{water}) \times \text{mass}(\text{water}) \times \text{specific heat}(\text{water}) = \Delta^{\circ}\text{C}(\text{metal})$$

$$\times \text{mass}(\text{metal}) \times \text{specific heat}(\text{metal})$$

**SOLUTION**

Substituting all of the given values we have

$$-(25.0 - 36.5)^{\circ}\text{C} \times 258 \text{ g} \times 4.184 \text{ J}/^{\circ}\text{C} \cdot \text{g} = (100 - 36.5)^{\circ}\text{C} \\ \times 440 \text{ g} \times \text{specific heat (metal)}$$

Solving for specific heat (metal),

$$\text{specific heat (metal)} = \frac{-(25.0 - 36.5)^{\circ}\text{C} \times 258 \text{ g} \times 4.184 \text{ J/g} \cdot ^{\circ}\text{C}}{(100 - 36.5)^{\circ}\text{C} \times 440 \text{ g}} \\ \text{specific heat (metal)} = \underline{0.444 \text{ J/g}^{\circ}\text{C}}$$

**ANALYSIS**

What is the metal? Matching the calculated value with those in Table 3.2, we find that the metal is *iron*.

**SYNTHESIS**

Notice that the temperature of the water increases by only  $11.5^{\circ}\text{C}$ , while the temperature of the metal decreases by  $63.5^{\circ}\text{C}$ . This is mostly due to the comparatively low specific heat of a metal. The same amount of heat causes more temperature change in the metal compared to water. If the metal in question were gold, instead of iron, how would that have affected the overall temperature change of the water and the metal? Since gold has an even lower specific heat than iron, there is less heat to transfer into the water. The overall temperature change of the water would be even less than before, while the temperature change of the gold would be greater.

**Dark Matter and Energy**

In this chapter we have discussed the matter and energy components of the universe that we can see or measure. However, there is apparently much more out there, and it borders on the bizarre. In recent years, scientists have come to understand that there may be other forms of matter and energy that reveal their presence only indirectly.

First consider the possibility of invisible matter. A Swiss astronomer, Fred Zwicky, first proposed its existence in 1933 by observation of the stars. Galaxies are huge groupings of stars rotating around a central core. (Our home galaxy is known as the Milky Way.) Zwicky noted that the visible matter in the galaxy could not control the motion of the stars around the core. It was as if some unseen, exotic part of nature was at work controlling the motions of stars. Most scientists now accept the existence of this invisible stuff, known as *dark matter*. In fact, as much as 95% of the matter in the universe may actually be dark matter. But it is hard to prove its existence if it is invisible. We have only indirect evidence (gravity) of its existence.

Quite recently, in 1998, more science fiction became reality. While dark matter accounts for most of the motion of the stars within a galaxy, it now appears that the galaxies of the universe are moving more and more rapidly away from one another. This is a reversal of thinking of just a few years ago, when we thought the expansion of the universe was slowing because of gravity. It has been proposed that an exotic form of energy also exists that causes matter to move apart. This “antigravity” energy has been called *dark energy*. The effect of dark energy would be opposite that of normal gravity.

Science fiction has long suggested an invisible world and devices that defy gravity. Maybe they are not as far out as we think. There seems to be an invisible mass around us that leaves only gravity as the marker of its existence. And now we also have antigravity—a force that would make us “fall up” rather than “fall down.”

The study of dark matter and dark energy are rapidly developing and exciting areas of astronomy. We will know more in the next few years as we look for ways to prove their existence.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 3-5

**EXERCISE 3-5(a) KNOWLEDGE:** Compare the specific heats of water and copper. If a hot piece of copper was placed in a similar mass of cool water, would the final temperature of the two be closer to the original temperature of the water or the copper?

**EXERCISE 3-5(b) ANALYSIS:** A 44.0-g sample of an element absorbs 1870 J of energy and increases in temperature from 25.0°C to 72.5°C. What is the specific heat of the element? What is the element?

**EXERCISE 3-5(c) ANALYSIS:** How much energy (in joules) is released when 18.5 g of copper cools from 285°C down to 45°C?

**EXERCISE 3-5(d) ANALYSIS:** A 20.0-g piece of hot iron at 225°C is placed in 51.0 g of water. No heat escapes to the surroundings. The water and iron equilibrate at 45.0°C. How much did the temperature of the water increase?

**EXERCISE 3-5(e) ANALYSIS:** A 0.0625-lb sample of fat (1 oz) is burned. The heat from the combustion raises the temperature of 10.0 L of water from 25.0°C to 45.5°C. How many Calories are in the sample of fat?

**EXERCISE 3-5(f) SYNTHESIS:** If you've ever been camping, and used aluminum foil to cook with, you know you can reach right into the fire and pull out the aluminum foil without burning yourself. Why doesn't the aluminum foil feel hot?

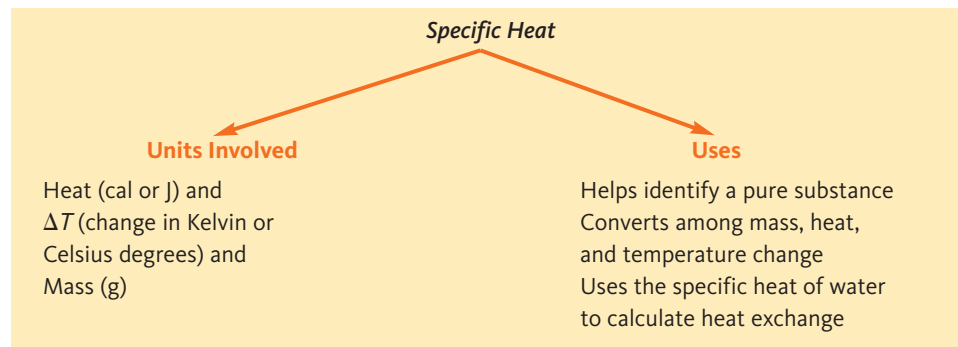
*For additional practice, work chapter problems 3-63, 3-66, and 3-74.*

PART B  
SUMMARY

## KEY TERMS

- 3-4** **Energy** has several different forms, including heat, electrical, mechanical, chemical, and nuclear energy. p. 94
- 3-4.1** The **law of conservation of energy** states that energy cannot be created or destroyed. p. 94
- 3-4.2** An **exothermic** process refers to the production of heat, while **endothermic** refers to the absorption of heat. p. 94
- 3-4.3** Energy may either be used as **kinetic energy** or stored as **potential energy**. p. 95
- 3-5** **Specific heat** is a physical property that interrelates heat, mass, and temperature change. p. 96
- 3-5.1** Heat is measured in **joules** or **calories**. p. 96
- 3-5.2** The specific heat of water can be used to calculate **calories** or unknown specific heats. p. 96

## SUMMARY CHART



## CHAPTER SUMMARY

Elements and compounds are distinguished by their properties. They display **physical properties** and undergo **physical changes**. An important physical property of a substance is its **physical state: solid, liquid, or gas**. A physical change takes place when the substance changes to a different physical state. The temperatures at which an element or compound changes to a different **phase** are known as the **melting point** of a solid (or **freezing point** of a liquid) and **boiling point** of a liquid (or **condensation point** of a gas). A pure substance also has **chemical properties** that relate to the **chemical changes** it undergoes. In chemical changes the **law of conservation of mass** is observed.

An important physical property of a substance is its **density**. Density relates the mass of a substance to its volume; thus, it is independent of the size of the sample. Mass and volume are **extensive properties**, which may vary. Density is independent of the amount present, so it is an **intensive property**. Density can be used as an identifying property as well as a conversion factor between the mass and volume of a sample. When density is expressed in units of g/mL or g/cm<sup>3</sup>, **specific gravity** has the same numerical quantity but is expressed without units.

Elements and compounds may form either **homogeneous** or **heterogeneous mixtures**. Heterogeneous mixtures of solids and liquids can be separated by

filtration. Two types of homogeneous mixtures are **solutions**, which are composed of one liquid phase, and **alloys**, which are found in one solid phase. The components of a solution can be separated by distillation. Aqueous (water) solutions and pure water often look identical. Pure water, however, has definite and unchanging properties. The properties of a solution vary according to the proportions of the mixture. Among those properties that vary for a solution is density.

The other component of the universe, **energy**, is also intimately involved in physical and chemical processes. Besides heat, there are other *forms* of energy such as chemical, mechanical, and electrical energy. There are also two *types* of energy: **potential energy** and **kinetic energy**. Forms and types of energy can be converted into each other, but in all cases the **law of conservation of energy** is observed. When a chemical or physical process liberates heat energy, the chemical change is said to be **exothermic**. When heat energy is absorbed, the reaction is said to be **endothermic**.

How much the temperature of 1 gram of a substance is affected by a certain amount of heat is a physical property known as **specific heat**. Specific heat is a measure of the amount of heat in **calories** or **joules** (or kcal or kJ) that will raise the temperature of 1 gram of the substance 1 degree Celsius.

## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES            | EXERCISES              | CHAPTER PROBLEMS               |
|---------|---|---------------------|------------------------|--------------------------------|
| 3-1     | List and define several properties of matter and distinguish them as physical or chemical.                      |                     | 1a, 1b, 1c             | 4, 5, 6, 9, 11                 |
| 3-2     | Perform calculations involving the density of liquids and solids.   | 3-1, 3-2, 3-3, 3-4  | 2a, 2b, 2c             | 12, 14, 16, 20, 22, 24, 28, 29 |
| 3-3     | Describe the differences in properties between a pure substance and a mixture.                                  |                     | 3a, 3b, 3c, 3d         | 41, 42, 48, 49                 |
|         | Perform calculations involving percent as applies to mixtures.  | 3-5, 3-6            | 3e, 3f, 3g             | 50, 52, 53, 55                 |
| 3-4     | Distinguish among the forms and types of energy.  |                     | 4b, 4c                 | 57, 59, 60                     |
|         | Define the terms <i>endothermic</i> and <i>exothermic</i> , providing several examples of each type of process. |                     | 4a                     | 56                             |
| 3-5     | Perform calculations involving the specific heat of a substance, and use them to identify a substance.          | 3-7, 3-8, 3-9, 3-10 | 5a, 5b, 5c, 5d, 5e, 5f | 63, 64, 67, 68, 69, 71, 79, 81 |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**3-1(a)** The physical properties of calcium are its gray color, its solid state, its dull sheen, and its reported melting point. The chemical property is its reactivity with water to form a gas and a chemical soluble in water.

**3-1(b)** The fact that it's a liquid at room temperature tells us its melting point is lower than 25°C. Clear and colorless are also important properties. The fact that it's flammable gives us a good idea of the type of chemical it is. The most important piece of information is its exact boiling point.

**3-1(c)** Make note of the intensive properties of the substance. Is it silver or gold? Heavy or light? Hard or soft? At what temperature does it melt? Consult a handbook or Internet site to find a list of physical properties of metals, and see if you can find a match.

**3-2(a)** Mercury's reported density is 13.6 g/mL. The volume the sample occupies is 21.0 mL.

**3-2(b)** The volume of the cadmium is 10.77 mL. Its density is 4.97 g/mL (three significant figures).

**3-2(c)** Density = 1.60 g/mL. We can now scan the list of densities in Table 3-1 and note that carbon tetrachloride also has a density of 1.60 g/mL. It is very likely that the pure liquid is carbon tetrachloride. Since the liquid does not dissolve in water and its density is greater than 1.0 g/mL, carbon tetrachloride sinks to the bottom of a beaker of water.

**3-2(d)** The density of antifreeze should be halfway between the densities of water and ethylene glycol. If you measured the density of a small sample of antifreeze, and it was closer to the density of water, then clearly some of the glycol has broken down and more needs to be added.

**3-3(a)** (a) heterogeneous (b) heterogeneous (c) homogeneous (d) homogeneous

**3-3(b)** Since they do not mix, one will not dissolve in the other. Therefore, they will form two individual phases separated by a visible interface (or boundary). This is a heterogeneous mixture. A quick check of densities reveals the water layer to be the less dense, which means that it will be found on top.

**3-3(c)** The oxygen is completely dissolved (no bubbles). Furthermore, the concentration of the oxygen is the same throughout the bowl. This is a *solution* of a gas dissolved in a liquid.

**3-3(d)** Distillation will separate water and sand, but filtration would be easier. The water boils away, leaving the sand behind. Filtration will not separate water and salt. Since the

salt is dissolved, it will pass through the filter along with the water. Distillation is necessary to separate salt and water.

**3-3(e)** 2.32 oz

**3-3(f)** 221 g of 14-K gold

**3-3(g)** 43 g of tin and 29 g of lead

## PART B

## EXERCISES

**3-4(a)** Does the process require energy, in the form of heat? Or does the process release heat energy when it occurs? (a) endothermic (b) exothermic (c) endothermic (d) exothermic

**3-4(b)** Is the energy stored? Or does it result from motion? (a) potential (b) kinetic (c) potential (d) kinetic (e) kinetic

**3-4(c)** The sunlight is solar energy that becomes stored potential chemical energy in the corn. The energy in the corn is converted into a useful source by its fermentation to ethanol. As the ethanol combusts in the car's engine, both the form and type of energy change. Potential energy stored in the ethanol is converted to kinetic energy as the car moves. This is also a conversion of chemical into mechanical energy.

**3-5(a)** The water. With the higher specific heat, it takes more energy to change water's temperature.

**3-5(b)** The temperature change is 47.5°C. The specific heat is 0.895 J/(g·°C). The element is most likely aluminum.

**3-5(c)**  $1.71 \times 10^3$  J

**3-5(d)** The hot piece of iron lost  $1.60 \times 10^3$  J of energy. The water absorbed the same. The water's temperature would have increased 7.5°C. (Its original temperature before heating was therefore 37.5°C.)

**3-5(e)** 205 Cal ( $8.58 \times 10^5$  J)

**3-5(f)** There are two reasons. The aluminum foil is very thin, so its mass is not great. Further, metal (in this case, aluminum) has a much lower specific heat than water (a major component of your fingers). Both these factors combine to produce very little heat transfer to your fingertips, which then do not heat up very much at all.



## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Physical and Chemical Properties and Changes (SECTION 3-1)

**3-1.** Which of the following describes the liquid phase?

- (a) It has a definite shape and a definite volume.
- (b) It has a definite shape but not a definite volume.
- (c) It has a definite volume but not a definite shape.
- (d) It has neither a definite shape nor a definite volume.

**3-2.** Which state of matter is compressible? Why?

**3-3.** A fluid is a substance that flows and can be poured. Which state or states can be classified as fluids?

**3-4.** Identify the following as either a physical or a chemical property.

- (a) Diamond is one of the hardest known substances.
- (b) Carbon monoxide is a poisonous gas.
- (c) Soap is slippery.
- (d) Silver tarnishes.
- (e) Gold does not rust.
- (f) Carbon dioxide freezes at  $-78^{\circ}\text{C}$ .
- (g) Tin is a shiny, gray metal.
- (h) Sulfur burns in air.
- (i) Aluminum has a low density.

**3-5.** Identify the following as either a physical or a chemical property.

- (a) Sodium burns in the presence of chlorine gas.
- (b) Mercury is a liquid at room temperature.
- (c) Water boils at  $100^{\circ}\text{C}$  at average sea-level pressure.
- (d) Limestone gives off carbon dioxide when heated.
- (e) Hydrogen sulfide has a pungent odor.

**3-6.** Identify the following as a physical or a chemical change.

- (a) the frying of an egg
- (b) the vaporization of dry ice
- (c) the boiling of water
- (d) the burning of gasoline
- (e) the breaking of glass

**3-7.** Identify the following as a physical or a chemical change.

- (a) the souring of milk
- (b) the fermentation of apple cider
- (c) the compression of a spring
- (d) the grinding of a stone

**3-8.** When table sugar is heated to its melting point, it bubbles and turns black. When it cools, it remains a black solid. Describe the change as chemical or physical.

**3-9.** Aluminum metal melts at  $660^{\circ}\text{C}$  and burns in oxygen to form aluminum oxide. Identify a physical property and change and a chemical property and change.

**3-10.** A pure substance is a green solid. When heated, it gives off a colorless gas and leaves a brown, shiny solid that melts at  $1083^{\circ}\text{C}$ . The shiny solid cannot be decomposed to simpler substances, but the gas can. List all the properties given and tell whether they are chemical or physical. Tell whether each substance is a compound or an element.

**3-11.** A pure substance is a greenish-yellow, pungent gas that condenses to a liquid at  $-35^{\circ}\text{C}$ . It undergoes a chemical reaction with a given substance to form a white solid that melts at  $801^{\circ}\text{C}$  and a brown, corrosive liquid with a density of  $3.12\text{ g/mL}$ . The white solid can be decomposed to simpler substances, but the gas and the liquid cannot. List all the properties given and tell whether they are chemical or physical. Tell whether each substance is a compound or an element.

### Density (SECTION 3-2)

**3-12.** A handful of sand has a mass of  $208\text{ g}$  and displaces a volume of  $80.0\text{ mL}$ . What is its density?

**3-13.** A  $125\text{-g}$  quantity of iron has a volume of  $15.8\text{ mL}$ . What is its density?

**3-14.** A given liquid has a volume of  $0.657\text{ L}$  and a mass of  $1064\text{ g}$ . What might the liquid be? (Refer to Table 3-1.)

**3-15.** A  $25.0\text{-g}$  quantity of magnesium has a volume of  $14.4\text{ mL}$ . What is its density? What is the volume of  $1.00\text{ kg}$  of magnesium?

**3-16.** What is the volume in milliliters occupied by  $285\text{ g}$  of mercury? (See Table 3-1.)

**3-17.** What is the mass of  $671\text{ mL}$  of table salt? (See Table 3-1.)

**3-18.** What is the mass of  $1.00\text{ L}$  of gasoline? (See Table 3-1.)

**3-19.** What is the mass in pounds of  $1.00\text{ gal}$  of gasoline? (See Tables 3-1 and 1-5.)

**3-20.** What is the mass of  $1.50\text{ L}$  of gold? (See Table 3-1.)

**3-21.** What is the volume in milliliters occupied by  $1.00\text{ kg}$  of carbon tetrachloride?

**3-22.** The volume of liquid in a graduated cylinder is  $14.00\text{ mL}$ . When a certain solid is added, the volume reads  $92.5\text{ mL}$ . The mass of the solid is  $136.5\text{ g}$ . What might the solid be? (Refer to Table 3-1.)

**3-23.** A  $1.05\text{-lb}$  quantity of a solid has a volume of  $1.00\text{ L}$ . What is its density? Does this material float on water?

**3-24.** Pumice is a volcanic rock that contains many trapped air bubbles. A  $155\text{-g}$  sample is found to have a volume of  $163\text{ mL}$ . What is the density of pumice? What is the volume of a  $4.56\text{-kg}$  sample? Will pumice float or sink in water? In ethyl alcohol? (Refer to Table 3-1.)

**3-25.** A bottle weighs  $44.75\text{ g}$ . When  $13.0\text{ mL}$  of a liquid is added to the bottle, it weighs  $59.20\text{ g}$ . What might the liquid be? (Refer to Table 3-1.) Does it form a layer below water or above water?

**3-26.** The density of diamond is  $3.51\text{ g/mL}$ . What is the volume of the Hope diamond if it has a mass of  $44.0\text{ carats}$ ? ( $1\text{ carat} = 0.200\text{ g}$ )

**3-27.** A small box is filled with liquid mercury. The dimensions of the box are 3.00 cm wide, 8.50 cm long, and 6.00 cm high. What is the mass of the mercury in the box? ( $1.00 \text{ mL} = 1.00 \text{ cm}^3$ )

**3-28.** A 125-mL flask has a mass of 32.5 g when empty. When the flask is completely filled with a certain liquid, it weighs 143.5 g. What is the density of the liquid?

**3-29.** Which has a greater volume, 1 kg of lead or 1 kg of gold?

**3-30.** Which has the greater mass, 1 L of gasoline or 1 L of water?

**3-31.** A large nugget of a shiny metal is found in a mountain stream. It weighs 5.65 oz (16 oz/lb). 25.0 mL of water is placed in a graduated cylinder. When the nugget is placed in the cylinder, the water level reads 33.3 mL. Did we find a nugget of gold? (Refer to Tables 3-1 and 1-5.)

**3-32.** What is the difference between density and specific gravity?

**\*3-33.** What is the mass of 1 gal of carbon tetrachloride in grams? In pounds?

**\*3-34.** Calculate the density of water in pounds per cubic foot ( $\text{lb}/\text{ft}^3$ ).

**\*3-35.** In certain stars, matter is tremendously compressed. In some cases the density is as high as  $2.0 \times 10^7 \text{ g/mL}$ . A tablespoon full of this matter is about 4.5 mL. What is the mass of this tablespoon of star matter in pounds?

### Mixtures and Pure Substances (SECTION 3-3)

**3-36.** Carbon dioxide is not a mixture of carbon and oxygen. Explain.

**3-37.** Which of the following is a mixture: water, sulfur dioxide, pewter, or ammonia?

**3-38.** List the following waters in order of increasing purity: ocean water, rainwater, and drinking water. Explain.

**3-39.** Iron is attracted to a magnet, but iron compounds are not. How could you use this information to tell whether a mixture of iron and sulfur forms a compound when heated?

**3-40.** When a teaspoon of solid sugar is dissolved in a glass of liquid water, what phase or phases are present after mixing?

- (a) liquid only                      (c) solid only  
(b) still solid and liquid

**3-41** Identify the following as homogeneous or heterogeneous matter.

- (a) gasoline                      (e) a new nail  
(b) dirt                              (f) vinegar  
(c) smog                            (g) aerosol spray  
(d) alcohol                        (h) air

**3-42.** Identify the following as homogeneous or heterogeneous matter.

- (a) a cloud                        (d) bourbon  
(b) dry ice                        (e) natural gas  
(c) whipped cream              (f) a grapefruit

**3-43.** In which physical state or states does each of the substances listed in problem 3-41 exist?

**3-44.** In which physical state or states does each of the substances listed in problem 3-42 exist?

**3-45.** Carbon tetrachloride and kerosene mix with each other, but neither mixes with water. How can water be used to keep the carbon tetrachloride and kerosene apart? Which liquid is on the top? (Refer to Table 3-1.)

**3-46.** How could liquid mercury be used to tell whether a certain sample of metal is lead or gold? (Refer to Table 3-1.)

**3-47.** Why does ice float on water? (Refer to Table 3-1.) Is ice water homogeneous or heterogeneous matter? Pure or a mixture?

**3-48.** Tell whether each of the following properties describes a heterogeneous mixture, a solution (homogeneous mixture), a compound, or an element.

- (a) a homogeneous liquid that, when boiled away, leaves a solid residue  
(b) a cloudy liquid that, after a time, seems more cloudy toward the bottom  
(c) a uniform red solid that has a definite, sharp melting point and cannot be decomposed into simpler substances  
(d) a colorless liquid that boils at one unchanging temperature and can be decomposed into simpler substances  
(e) a liquid that first boils at one temperature but, as the heating continues, boils at slowly increasing temperatures (there is only one liquid phase)

**3-49.** Tell whether each of the following properties describes a heterogeneous mixture, a solution (homogeneous mixture), a compound, or an element.

- (a) a nonuniform powder that, when heated, first turns mushy and then continues to melt as the temperature rises  
(b) a colored gas that can be decomposed into a solid and another gas (the entire sample of the new gas seems to have the same chemical properties)  
(c) a sample of colorless gas, only part of which reacts with hot copper

**3-50.** A sample of bronze is made by mixing 85 kg of molten tin with 942 kg of molten copper. What is the mass percent tin in this bronze?

**3-51.** A sample of brass weighs 22.8 lb. It contains 14.8 lb of copper, and the rest is zinc. What is the mass percent zinc in this brass?

**3-52.** A U.S. "nickel" is actually only 25% nickel. What mass of the element nickel is in 255 kg of "nickels"?

**3-53.** 10-K gold is only 42% gold. What mass of gold is in 186 g of 10-K gold?

**3-54.** Duriron is used to make pipes and kettles. It contains 14% silicon, with the remainder being iron. What mass of duriron can be made from 122 lb of iron?

**3-55.** A sample of a gold alloy is 7% copper and 10% silver in addition to the gold. What mass of the gold alloy can be made from 175 kg of pure gold?

**Energy (SECTION 3-4)**

**3-56.** From your own experiences, tell whether the following processes are exothermic or endothermic.

- (a) decay of grass clippings
- (b) melting of ice
- (c) change in an egg when it is fried
- (d) condensation of steam
- (e) curing of freshly poured cement

**3-57.** A car battery can be recharged after the engine starts. Trace the different energy conversions from the burning of gasoline to energy stored in the battery.

**3-58.** Windmills are used to generate electricity. What are all of the different forms of energy involved in the generation of electricity by this method?

**3-59.** Identify the principal type of energy (kinetic or potential) exhibited by each of the following.

- (a) a book on top of a table
- (b) a mud slide
- (c) methane gas ( $\text{CH}_4$ )
- (d) the wind
- (e) waves on a beach

**3-60.** Identify the following as having either potential or kinetic energy or both.

- (a) an arrow in a fully extended bow
- (b) a baseball traveling high in the air
- (c) two magnets that are separated from each other
- (d) a chair on the fourth floor of a building

**3-61.** When you apply your brakes to a moving car, the car loses kinetic energy. What happens to the lost energy?

**3-62.** When a person rides on a swing, at what point in the movement is kinetic energy the greatest? At what point is potential energy the greatest? Assume that once started, the person will swing to the same height each time without an additional push. At what point is the total of the kinetic energy and the potential energy greatest?

**Specific Heat (SECTION 3-5)**

**3-63.** It took 73.2 J of heat to raise the temperature of 10.0 g of a substance  $8.58^\circ\text{C}$ . What is the specific heat of the substance?

**3-64.** When 365 g of a certain pure metal cooled from  $100^\circ\text{C}$  to  $95^\circ\text{C}$ , it liberated 56.6 cal. Identify the metal from among those listed in Table 3-2.

**3-65.** A 10.0-g sample of a metal requires 22.4 J of heat to raise the temperature from  $37.0^\circ\text{C}$  to  $39.5^\circ\text{C}$ . Identify the metal from those listed in Table 3-2.

**3-66.** If 150 cal of heat energy is added to 50.0 g of copper at  $25^\circ\text{C}$ , what is the final temperature of the copper? Compare this temperature rise with that of 50.0 g of water initially at  $25^\circ\text{C}$ . (Refer to Table 3-2.)

**3-67.** A large cube of ice weighing 558 g is cooled in a freezer to  $-15.0^\circ\text{C}$ . It is removed and allowed to warm to  $0.0^\circ\text{C}$  but does not melt. What is the specific heat of ice if 17.2 kJ of heat is required in the process?

**3-68.** How many joules are evolved if 43.5 g of aluminum is cooled by  $13^\circ\text{C}$ ? (Refer to Table 3-2.)

**3-69.** What mass of iron is needed to absorb 16.0 cal if the temperature of the sample rises from  $25^\circ\text{C}$  to  $58^\circ\text{C}$ ?

**3-70.** If one has a copper and an iron skillet of the same weight, which would fry an egg faster? Explain.

**3-71.** When 486 g of zinc absorbs 265 J of heat energy, what is the rise in temperature of the metal?

**3-72.** Given 12.0-g samples of iron, gold, and water, calculate the temperature rise that would occur when 50.0 J of heat is added to each.

**3-73.** A 10.0-g sample of water cools  $2.00^\circ\text{C}$ . What mass of aluminum is required to undergo the same temperature change?

**3-74.** A can of diet soda contains 1.00 Cal (1.00 kcal) of heat energy. If this energy was transferred to 50.0 g of water at  $25^\circ\text{C}$ , what would be the final temperature?

**3-75.** The specific heat of platinum is one of the lowest among the metals. What is its specific heat if a 5.44-g quantity evolves 7.36 cal when it cools from  $55.0^\circ\text{C}$  to  $12.3^\circ\text{C}$ ?

**3-76.** If 50.0 g of aluminum at  $100.0^\circ\text{C}$  is allowed to cool to  $35.0^\circ\text{C}$ , how many joules are evolved?

**3-77.** A 22.5-J quantity of heat raises the temperature of a piece of zinc  $2.0^\circ\text{C}$ . How many degrees Celsius would the same amount of heat raise the temperature of the same amount of aluminum?

**3-78.** In the preceding problem, assume that the hot aluminum was added to water originally at  $30.0^\circ\text{C}$ . What mass of water was present if the final temperature of the water was  $35.0^\circ\text{C}$ ?

**3-79.** If 50.0 g of water at  $75.0^\circ\text{C}$  is added to 75.0 g of water at  $42.0^\circ\text{C}$ , what is the final temperature?

**\*3-80.** A 100.0-mL volume of water is originally at  $25.0^\circ\text{C}$ . When a chunk of lead that is originally at  $42.8^\circ\text{C}$  is added to the water, the temperature of the water increases to  $28.7^\circ\text{C}$ . If the specific heat of lead is  $0.128 \text{ J/g} \cdot ^\circ\text{C}$ , what was the weight of the lead?

**\*3-81.** If 100.0 g of a metal at  $100.0^\circ\text{C}$  is added to 100.0 g of water at  $25.0^\circ\text{C}$ , the final temperature is  $31.3^\circ\text{C}$ . What is the specific heat of the metal? Identify the metal from Table 3-2.

**General Problems**

**3-82.** A 22-mL quantity of liquid A has a mass of 19 g. A 35-mL quantity of liquid B has a mass of 31 g. If they form a heterogeneous mixture, explain what happens.

**3-83.** The volume of water in a graduated cylinder reads 25.5 mL. What does the volume read when a 25.0-g quantity of pure nickel is added to the cylinder? (The density of nickel is  $8.91 \text{ g/mL}$ .)

**3-84.** A solution of table sugar in water is 14% by mass sugar. The density of the solution is  $1.06 \text{ g/mL}$ . What is the mass of sugar in 100 mL of the solution?

**3-85.** A solid metal weighing 62.485 g was introduced into a small flask having a total volume of 24.96 mL. To completely fill the flask, 18.22 mL of water was required. What is the density of the metal expressed to the proper number of significant figures?

**3-86.** What is the volume occupied by 22.175 g of the metal in problem 3-85?

**3-87.** A 10.0-g quantity of table salt was added to 305 mL of water. What is the percent table salt in the solution?

**3-88.** Battery acid is 35% sulfuric acid in water and has a density of 1.29 g/mL. What is the mass of sulfuric acid in 1.00 L of battery acid?

**3-89.** An alloy is prepared by mixing 50.0 mL of gold with 50.0 mL of aluminum. What is the mass percent gold in the alloy?

**3-90.** How many kilocalories are required to raise 1.25 L of ice from  $-45^{\circ}\text{C}$  to its melting point? (Refer to Tables 3-1 and 3-2.)

**3-91.** When 215 J of heat is added to a 25.0-g sample of a given substance, the temperature increases from  $25^{\circ}\text{C}$  to  $91^{\circ}\text{C}$ . What is the volume of the sample? (Refer to Tables 3-1 and 3-2.)

**3-92.** A 21.8-mL quantity of magnesium is at an initial temperature of  $25.0^{\circ}\text{C}$ . When 18.4 cal of heat energy is added to the sample, the temperature increases to  $27.0^{\circ}\text{C}$ . What is the specific heat of magnesium? (Refer to Tables 3-1 and 3-2.)

**3-93.** 25.0 mL of a given pure substance has a mass of 67.5 g. How much heat in kilojoules (kJ) is required to heat this sample from  $15^{\circ}\text{C}$  to  $88^{\circ}\text{C}$ ? (Refer to Tables 3-1 and 3-2.)

**3-94.** When a log burns, the ashes have less mass than the log. When zinc reacts with sulfur, the zinc sulfide has the same mass as the combined mass of zinc and sulfur. When iron burns in air, the compound formed has more mass than the original iron. Explain each reaction in terms of the law of conservation of mass.

## STUDENT WORKSHOP

### Graphing Physical Properties

**Purpose:** To depict a physical property using graphical analysis, and evaluate an unknown by comparison to a standard. (Work in groups of three or four. Estimated time: 20 min.)

This exercise is based on Making It Real, "Identifying a Glass Shard from a Crime Scene by Density." Assuming that the volumes of solutions of bromoform and bromobenzene are additive, we can construct a graph that shows what the density of each exact mixture of the two chemicals would be.

1. Obtain a piece of graph paper. Draw your  $x$ -axis 20 spaces across. This axis will be your solution percentage, and each space will represent a 5% increase in the amount of bromoform (0% on the left, 100% on the right). Label every other line.
2. Draw your  $y$ -axis 28 spaces high. This axis is your density and will start at 1.50 g/mL, the approximate density of bromobenzene. It will continue to 2.90 g/mL, the density of bromoform. Each line, then, is 0.05 g/mL. Label every fourth line.
3. The density of the different percent solutions should be a straight-line relationship. Plot a point at 0% and 1.50 g/mL for pure bromobenzene, and at 100% and 2.90 g/mL for bromoform. Connect the two points with a straight line.

You now have a graph on which you can read the density for any percentage of bromoform and bromobenzene or can find a percentage for any given density. Now proceed to analyze some data. Several glass samples were obtained, and they were experimentally analyzed in the bromobenzene/bromoform mixtures. The percentage of bromoform indicates the mixture that suspended the particles.

| GLASS SAMPLES | PERCENTAGE OF BROMOFORM | ESTIMATED DENSITY |
|---------------|-------------------------|-------------------|
| A             | 71%                     | ???               |
| B             | 75%                     | ???               |
| C             | 63%                     | ???               |
| D             | 78%                     | ???               |
| E             | 67%                     | ???               |

Note that the glass samples were all suspended over a very small range of mixtures. That's because the densities of glass do not vary much, one from another. In reality, the range is even smaller.

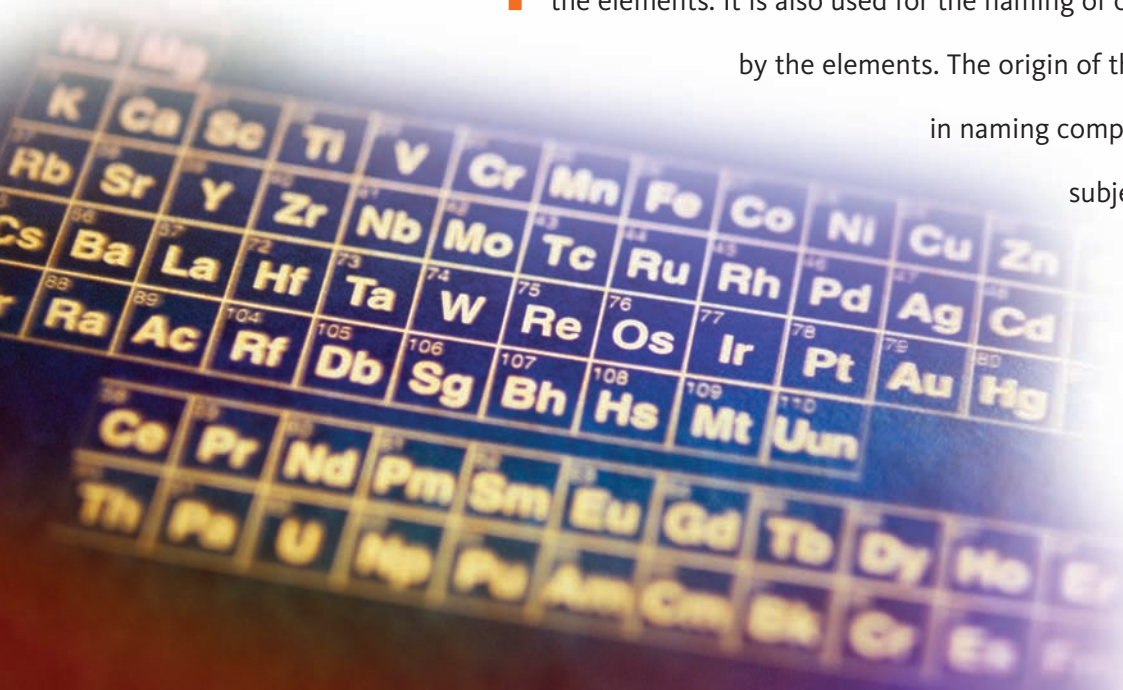
Using your graph, determine the approximate densities for the five samples. A sixth sample of glass found on a suspect had a density of 2.60 g/mL. Which of the five evidence samples matches up with the suspect's? If that was the sample taken from the crime scene, our suspect will have some explaining to do.





# The Periodic Table and Chemical Nomenclature

The periodic table helps the chemist systematize the properties of the elements. It is also used for the naming of compounds formed by the elements. The origin of this table and its use in naming compounds are the subjects of this chapter.





## PART A

### RELATIONSHIPS AMONG THE ELEMENTS AND THE PERIODIC TABLE

#### 4-1 The Origin of the Periodic Table

#### 4-2 Using the Periodic Table



#### MAKING IT REAL

*The Discovery of a Group VIIA Element, Iodine*

## PART B

### THE FORMULAS AND NAMES OF COMPOUNDS

#### 4-3 Naming and Writing Formulas of Metal–Nonmetal Binary Compounds

#### 4-4 Naming and Writing Formulas of Compounds with Polyatomic Ions



#### MAKING IT REAL

*Ionic Compounds in the Treatment of Disease*

#### 4-5 Naming Nonmetal–Nonmetal Binary Compounds

#### 4-6 Naming Acids

**SETTING THE STAGE** Two things may strike the casual and uninformed observer about chemists and students of chemistry: (1) they seem to glance frequently at an ever-present wall poster containing the symbols of the elements, and (2) they seem to have their own language. The observer is correct on both counts. The wall poster is obviously important, since it hangs in almost every chemical laboratory and classroom. Known as the *periodic table*, it is as important to a chemist as a map is to a world traveler. The location of a city on a map tells us a wealth of information about climate and culture. Likewise, the location of a specific element on the periodic table gives us important information about physical and chemical properties of the element.

Now consider the language of chemistry. Chemists have their own vocabulary for the 10 million or so known compounds. Why is it necessary for us to learn the language of chemistry? The answer is the same as why you learn any language other than your native tongue—so you can communicate directly with others who speak the same language. The vocabulary of chemistry is known as *chemical nomenclature*. Like learning any other tongue, learning chemical nomenclature requires some memorization.

These two topics, the periodic table and chemical nomenclature, may at first seem unrelated. However, the periodic table groups the elements into two broad categories, and the naming of compounds relates to these classifications. The periodic table displays this information in an easy-to-read manner that simplifies the rules of chemical nomenclature.

In Part A of this chapter, we will present the periodic table and much of the information found in it. We will put the periodic table to use in Part B, by writing formulas and naming compounds.

**PART A**  
**RELATIONSHIPS AMONG THE**  
**ELEMENTS AND THE**  
**PERIODIC TABLE**

**SETTING A GOAL**

- You will be able to explain the significance of the periodic table, its origins, and how different properties of an element can be predicted by its location on the table.

**OBJECTIVES**

- 4-1** Describe the origins of the periodic table.
- 4-2** Using the periodic table, identify a specific element as a metal or nonmetal and give its period, group number, the name of the group if appropriate, and its physical state.

**OBJECTIVE FOR SECTION 4-1**

Describe the origins of the periodic table.

**4-1 THE ORIGIN OF THE PERIODIC TABLE**



**LOOKING AHEAD!** It had been known for centuries that there were chemical similarities among certain elements. How these similarities led to a chart called the periodic table is the subject of this section. ■

**4-1.1 Metals and Nonmetals**

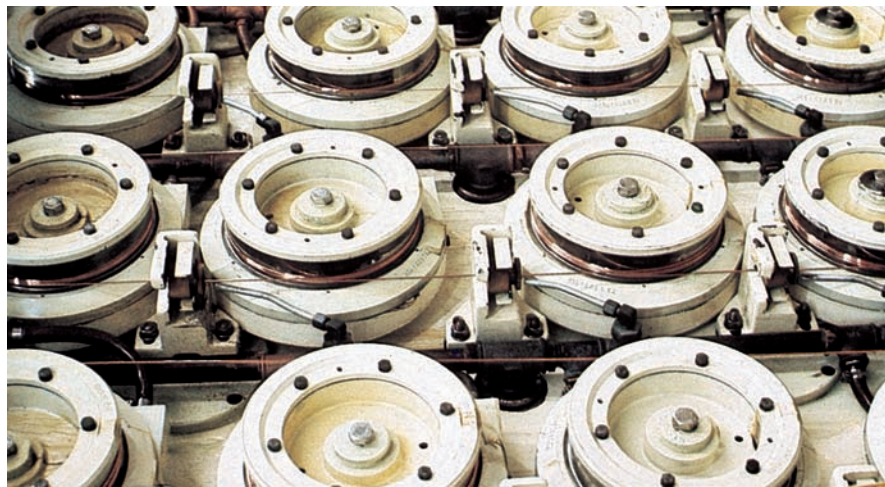
It seems like many sciences divide their subject into two categories. Biology studies flora (plants) and fauna (animals). Geology studies the continents and the oceans. Chemistry also divides the elements into two categories, *metals* and *nonmetals*.

**Metals** are generally hard, lustrous elements that are *malleable* (can be pounded into thin sheets) and *ductile* (can be drawn into wires). (See Figure 4-1.). We also know they readily conduct electricity and heat. Many metals such as iron, copper, and aluminum form the strong framework on which our modern society is built. Recall from the Prologue that the discovery and use of metals over 5000 years ago moved civilization beyond the Stone Age.

The second type of element is noted by its *lack* of metallic properties. These are the nonmetals. **Nonmetals** are generally gases or soft solids that do not conduct electricity. (See Figure 4-2.)



(a)



(b)

**FIGURE 4-1 Two Properties of Metals** (a) Metals can be pressed into thin sheets (malleable) or (b) drawn into wires (ductile).

There are notable exceptions to the general properties of metals and nonmetals. Still, almost everyone has a general idea of what a metal is like. In addition to these physical properties, there are some very important chemical differences between metals and nonmetals, which we will explore in Chapter 9. The division between metallic and nonmetallic properties is not distinct. Some elements have intermediate properties and are sometimes classified as a separate group called **metalloids**.

### 4-1.2 Two Kinds of Metals

Classifying the elements doesn't stop with the division of elements into metals and nonmetals. Further classification is possible because some elements have remarkable chemical similarities to each other. For example, several important metals are found in the free state in nature because of their low chemical reactivity. Copper, silver, and gold are metals that are very resistant to the chemical reactions of corrosion and rust. Because of this as well as their luster and beauty, they are the prized metals of coins and jewelry. Gold and silver coins on the ocean bottom, deposited from ships that foundered hundreds of years ago, can be easily polished to their original luster. (See Figure 4-3.)

Other metals are very much different. They are found in nature only as parts of compounds because of their high chemical reactivity. In fact, their free metals react spontaneously with air and water. Lithium, sodium, and potassium must be stored under oil because they react violently (to the point of explosion) when placed in water.

Historically, elements with similar or related properties were grouped into what was referred to as *families* of elements. Thus, copper, silver, and gold were classified as one family, sometimes referred to as the *noble metals*, while lithium, sodium, and potassium were classified into another family, sometimes referred to as the *active metals*. There are many other elements that early chemists grouped into families with similar chemical properties.

The fact that many elements could be grouped into families seemed to suggest some sort of systematic relationships among the elements. Indeed there is. In fact, about 140 years ago, the big picture of the relationships among the elements was presented in a chart known as the **periodic table**. (See Figure 4-4.)

### 4-1.3 The Origin of the Periodic Table

The earliest version of this table was introduced in 1869 by Dmitri Mendeleev of Russia. Lothar Meyer of Germany independently presented a similar table in 1870. When these two scientists arranged the elements in order of increasing atomic masses (atomic numbers were still unknown), they observed that elements in families appeared at regular (periodic) intervals. The periodic table was constructed so that elements in the same families (e.g., Li, Na, and K) fell into vertical columns.

At first this did not always happen. Sometimes the next-heaviest element did not seem to chemically fit in a certain family. For example, the next-heaviest known element after zinc (Zn) was arsenic (As). Arsenic seemed to belong under phosphorus (P), not aluminum (Al). Mendeleev solved this problem by leaving two blank spaces. For example, a space was left under silicon (Si) and above tin (Sn) for what Mendeleev suggested was a yet-undiscovered element. Mendeleev called the missing element "ekasilicon" (meaning one place away from silicon). Later, an element was discovered that had properties intermediate between silicon and tin, as predicted by the location of the blank space. The element was later named germanium (Ge). Gallium (Ga) was eventually discovered and fit comfortably under aluminum.

A second problem involved some misfits when the elements were ordered according to atomic mass. For example, notice that tellurium (number 52, Te) is heavier



**FIGURE 4-2 Nonmetals** The bottle on the left contains liquid bromine and its vapor. The flask in the back contains pale-green chlorine gas. Solid iodine is in the flask on the right. Powdered red phosphorus is in the dish in the middle, and black powdered graphite (carbon) is in the watch glass in front. Lumps of yellow sulfur are shown in the front.



**FIGURE 4-3 Silver and Gold** With a little polish, these gold and silver coins regained their original luster after three centuries at the bottom of the ocean.

|   |        | Atomic number      |                    |                    |                   |                   |                   |                   |                    |                    |                    |                    |                    |                    |                   |                    |                   | Noble gases       |                   |                 |                |                 |                  |
|---|--------|--------------------|--------------------|--------------------|-------------------|-------------------|-------------------|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|-------------------|--------------------|-------------------|-------------------|-------------------|-----------------|----------------|-----------------|------------------|
|   |        | metal              |                    |                    |                   |                   |                   |                   |                    |                    |                    |                    |                    |                    |                   |                    |                   | metalloid         |                   | nonmetal        |                | VIIIA (18)      |                  |
| 1 | IA (1) | 1 H<br>1.00794     |                    |                    |                   |                   |                   |                   |                    |                    |                    |                    |                    |                    |                   |                    | 2 He<br>4.00260   |                   |                   |                 |                |                 |                  |
| 2 |        | 3 Li<br>6.941      | 4 Be<br>9.01218    |                    |                   |                   |                   |                   |                    |                    |                    |                    |                    |                    |                   |                    |                   | 5 B<br>10.811     | 6 C<br>12.011     | 7 N<br>14.00674 | 8 O<br>15.9994 | 9 F<br>18.99840 | 10 Ne<br>20.1797 |
| 3 |        | 11 Na<br>22.98977  | 12 Mg<br>24.3050   | 13 Al<br>26.98154  | 14 Si<br>28.0855  | 15 P<br>30.97376  | 16 S<br>32.066    | 17 Cl<br>35.4527  | 18 Ar<br>39.948    |                    |                    |                    |                    |                    |                   |                    |                   |                   |                   |                 |                |                 |                  |
| 4 |        | 19 K<br>39.0983    | 20 Ca<br>40.078    | 21 Sc<br>44.95591  | 22 Ti<br>47.88    | 23 V<br>50.9415   | 24 Cr<br>51.9961  | 25 Mn<br>54.9380  | 26 Fe<br>55.847    | 27 Co<br>58.93320  | 28 Ni<br>58.69     | 29 Cu<br>63.546    | 30 Zn<br>65.39     | 31 Ga<br>69.723    | 32 Ge<br>72.61    | 33 As<br>74.92159  | 34 Se<br>78.96    | 35 Br<br>79.904   | 36 Kr<br>83.80    |                 |                |                 |                  |
| 5 |        | 37 Rb<br>85.4678   | 38 Sr<br>87.62     | 39 Y<br>88.90585   | 40 Zr<br>91.224   | 41 Nb<br>92.90638 | 42 Mo<br>95.94    | 43 Tc<br>98.9072  | 44 Ru<br>101.07    | 45 Rh<br>102.90550 | 46 Pd<br>106.42    | 47 Ag<br>107.8682  | 48 Cd<br>112.411   | 49 In<br>114.82    | 50 Sn<br>118.710  | 51 Sb<br>121.75    | 52 Te<br>127.60   | 53 I<br>126.90447 | 54 Xe<br>131.29   |                 |                |                 |                  |
| 6 |        | 55 Cs<br>132.90543 | 56 Ba<br>137.327   | 57 *La<br>138.9055 | 72 Hf<br>178.49   | 73 Ta<br>180.9479 | 74 W<br>183.85    | 75 Re<br>186.207  | 76 Os<br>190.2     | 77 Ir<br>192.22    | 78 Pt<br>195.08    | 79 Au<br>196.96654 | 80 Hg<br>200.59    | 81 Tl<br>204.3833  | 82 Pb<br>207.2    | 83 Bi<br>208.98037 | 84 Po<br>208.9824 | 85 At<br>209.9871 | 86 Rn<br>222.0176 |                 |                |                 |                  |
| 7 |        | 87 Fr<br>223.0197  | 88 Ra<br>226.0254  | 89 †Ac<br>227.0278 | 104 Rf<br>261.11  | 105 Db<br>262.114 | 106 Sg<br>263.118 | 107 Bh<br>262.12  | 108 Hs<br>(265)    | 109 Mt<br>(266)    | 110 Uun<br>(269)   | 111 Uuu<br>(272)   | 112 Uub<br>(277)   |                    |                   | 114<br>(285)       |                   |                   | 116<br>(289)      |                 |                |                 |                  |
|   |        | * †                |                    |                    |                   |                   |                   |                   |                    |                    |                    |                    |                    |                    |                   |                    |                   |                   |                   |                 |                |                 |                  |
|   |        | 58 Ce<br>140.115   | 59 Pr<br>140.90765 | 60 Nd<br>144.24    | 61 Pm<br>144.9127 | 62 Sm<br>150.36   | 63 Eu<br>151.965  | 64 Gd<br>157.25   | 65 Tb<br>158.92534 | 66 Dy<br>162.50    | 67 Ho<br>164.93032 | 68 Er<br>167.26    | 69 Tm<br>168.93421 | 70 Yb<br>173.04    | 71 Lu<br>174.967  |                    |                   |                   |                   |                 |                |                 |                  |
|   |        | 90 Th<br>232.0381  | 91 Pa<br>231.0359  | 92 U<br>238.0289   | 93 Np<br>237.0482 | 94 Pu<br>244.0642 | 95 Am<br>243.0614 | 96 Cm<br>247.0703 | 97 Bk<br>247.0703  | 98 Cf<br>242.0587  | 99 Es<br>252.083   | 100 Fm<br>257.0951 | 101 Md<br>258.10   | 102 No<br>259.1009 | 103 Lr<br>260.105 |                    |                   |                   |                   |                 |                |                 |                  |

FIGURE 4-4 The Periodic Table

than iodine (number 53, I). But Mendeleev realized that iodine clearly belonged under bromine and tellurium under selenium, not vice versa. Mendeleev simply reversed the order, suggesting that perhaps the atomic masses reported were in error. (That was known to happen sometimes.) We now know that this problem does not occur when the elements are listed in order of increasing atomic number instead of atomic mass. This method of ordering conveniently displays the **periodic law**, which states that *the properties of elements are periodic functions of their atomic numbers*.

### ASSESSING THE OBJECTIVE FOR SECTION 4-1

#### EXERCISE 4-1(a) KNOWLEDGE: Fill in the blanks.

The periodic table was first displayed by \_\_\_\_\_ in the year \_\_\_\_\_. Elements are grouped vertically into \_\_\_\_\_ that share the same \_\_\_\_\_. \_\_\_\_\_ are lustrous and malleable. \_\_\_\_\_ are dull and brittle.

**EXERCISE 4-1(b) SYNTHESIS:** Many individuals attempted to create arrangements of atoms that illustrated their repetitive properties. Why did Mendeleev succeed where others failed?

*For additional practice, work chapter problems 4-1 and 4-2.*

### OBJECTIVE FOR SECTION 4-2

Using the periodic table, identify a specific element as a metal or nonmetal and give its period, group number, the name of the group if appropriate, and its physical state.

## 4-2 USING THE PERIODIC TABLE



**LOOKING AHEAD!** There is a good deal of information that can be determined about a specific element from its position in the periodic table. We will discuss some of the categories and properties of elements that are predictable from their positions in the table. ■



### 4-2.1 Locating the Metals and Nonmetals

A quick glance at the periodic table shown in Figure 4-4 reveals the two broad classifications of the elements that we discussed. The heavy stair-step line separates the metals and nonmetals. Metals (about 80% of the elements) are on the left of the line and are shown in blue; nonmetals are on the right and are shown in pink. Hydrogen appears to the left of the line but is definitely a nonmetal. The metalloids, on either side of borderline, are shown in orange. For example, silicon is a brittle solid typical of nonmetals, but it is shiny like a metal and conducts a limited amount of electricity (a semiconductor). Conduction of electricity is also a metallic property. In any case, we will use only the two broad classifications (metal and nonmetal) in the nomenclature discussed later in the chapter.

### 4-2.2 Periods

The periodic table allows us to locate families of elements in vertical columns. In fact, there are common characteristics in the horizontal rows as well. *Horizontal rows of elements in the table are called periods.* Each period ends with a member of the family of elements called the **noble gases**. The first period contains only 2 elements, hydrogen and helium. The second and third contain 8 each (Figure 4-4); the fourth and fifth contain 18 each; the sixth, 32; and the seventh, 31, as of this writing. (The seventh would also contain 32 if there were enough elements.)

### 4-2.3 Groups

*Families of elements fall into vertical columns called groups.* Each group is designated by a number at the top of the group. The most commonly used label employs Roman numerals followed by an A or a B. Another method, which eventually may be accepted, numbers the groups 1 through 18. It is not clear at this time which method will win out, or if some alternative will yet be proposed and universally accepted. The periodic tables used in the text display both numbering systems. In the discussion, however, we will use the traditional method involving Roman numerals along with the letters A and B.

The groups of elements can be classified even further into four main categories of elements.

#### 1. The Main Group or Representative Elements (Groups IA–VIIA)

Most of the familiar elements we will discuss and use as examples in this text are **main group** or **representative elements**. These are the elements labeled A in the periodic table. For example, the four main elements of life—carbon, oxygen, nitrogen, and hydrogen—are in this category. One group of the representative elements includes the highly reactive metals that we discussed earlier. Notice that lithium, sodium, and potassium are found in Group IA. This family of elements (not including hydrogen) is known as the **alkali metals**. Another set of metals that are also chemically reactive is found in Group IIA and are known as the **alkaline earth metals**. Group VIIA elements are all nonmetals and are known as the **halogens**. Group VIA elements are known as the **chalcogens**, although this title is rarely used anymore. The other representative element groups (IIIA, IVA, and VA) are not generally referred to by a family name but are instead identified by the element at the top of the column. Hence, any element in column VA is part of the nitrogen family. In Chapter 9, we will discuss in more detail some of the physical and chemical properties of the representative elements.

#### 2. The Noble or Inert Gases (Group VIIIA)

These elements form few chemical compounds. In fact, helium, neon, and argon do not form any compounds. They all exist as individual atoms in nature.



**3. The Transition Metals (Group B Elements)**

**Transition metals** include many of the familiar structural metals, such as iron and chromium, as well as the noble metals—copper, silver, and gold (Group IB)—which we discussed earlier.

**4. The Inner Transition Metals**

The 14 **inner transition metals** between lanthanum (number 57) and hafnium (number 72) are known as the **lanthanides** or *rare earths*, and the 14 metals between actinium (number 89) and rutherfordium (number 104) are known as the **actinides**.

**4-2.4 Physical States and the Periodic Table**

Next we will consider what the periodic table can tell us about the physical state of an element. We must be cautious, however, as to the temperature conditions we define. If the temperature is low enough, all elements exist as solids (except helium); if it is high enough, all elements are in the gaseous state. On Triton, a moon of the planet Neptune, the temperature is  $-236^{\circ}\text{C}$  (37 K). The atmosphere is very thin because most substances that are gases under Earth conditions are solids or liquids under Triton conditions. At the outer part of the sun, however, the temperature is  $50,000^{\circ}\text{C}$ , so only gases exist. Thus, we must come to some agreement as to a reference temperature to define the physical state of an element. **Room temperature**, which is defined as exactly  $25^{\circ}\text{C}$ , is the *standard reference temperature* used to describe physical

**The Discovery of a Group VIIA Element, Iodine**

It was a cold day in a small seaside town on the Atlantic coast of France in 1811. A few dozen seamen were extracting potassium salts with acid from the sludge of seaweed. Bernard Courtois, the employer of these seamen, was a chemist by training and a graduate of the Polytechnical Institute in Paris. His factory prepared saltpeter

(potassium nitrate) to be used in ammunition for Napoleon's armies. Today, however, the workers' efforts turned fruitless. One of the workers decided to use a more concentrated form of acid. At that point, a huge volume of violet fumes rose from the tanks and dark crystals started depositing on every cold surface that was nearby. Their observations would lead to the discovery of a very important element.

Courtois collected those unique crystals for examination and found out they would combine with hydrogen and phosphorus, but not with oxygen. He also discovered they would form an explosive compound with ammonia. He later gave samples to two of his Paris Polytechnical Institute friends, C. Desormes and N. Clement, who published the discoveries two years later. Soon thereafter, Frenchman

Joseph Louis Gay-Lussac and Englishman Sir Humphry Davy announced the discovery of a new element, which was first named *iode* (from the Greek word for "violet") by Gay-Lussac and finally *iodine*, to give it the same ending as *chlorine*, an element with similar properties. (Because of its chemical properties, iodine would later be classified as a *halogen* along with chlorine and bromine in Group VIIA.)

What happened on that day in 1811? Seaweed concentrates several ionic compounds other than sodium chloride (table salt), but no one had attached very much importance to them. That day, however, the iodine compounds must have become considerably concentrated after the extraction of the sodium chloride. The concentrated acid converted the iodine compounds to elemental iodine. The iodine vaporized (sublimed) but quickly condensed on the cool surfaces.

The practical applications of the new element had an immediate impact on patients with goiter, the enlargement of the thyroid gland. In 1820, Jean Francois Coinder associated the lack of goiter among seamen with the presence of iodine compounds in their working environment. The thyroid gland, he concluded, needs iodine to function properly and this could be achieved by adding small amounts of sodium iodide to table salt (i.e., iodized salt).

state. At this temperature, all three physical states are found among the elements on the periodic table. Fortunately, except for hydrogen, the gaseous elements are all found at the extreme right top of the table (nitrogen, oxygen, fluorine, and chlorine) and in the right-hand vertical column (the noble gases). There are only two liquids: a metal, mercury, and a nonmetal, bromine. All other elements are solids. (See Figure 4-5.) (Two solid metals, gallium and cesium, melt to become liquids at approximately 29°C, slightly above the reference temperature. Since body temperature is 37°C, both of these elements would melt in your hand.)

Many of the nonmetals exist as diatomic molecules rather than individual atoms. The periodic table can help us locate these elements. All the gaseous elements except for the noble gases, which exist as individual atoms, are composed of diatomic molecules (e.g., N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>). Or one may notice that all the naturally occurring halogens (Group VIIA) are diatomic. Not all molecular nonmetals are diatomic, however. The formula for the most common form of phosphorus is P<sub>4</sub>, which indicates the presence of molecules composed of four atoms. The most common form of sulfur is S<sub>8</sub>, indicating eight-atom molecules. The forms of carbon will be discussed in Chapter 11.

|                       |          |          |                      |                      |                       |                       |
|-----------------------|----------|----------|----------------------|----------------------|-----------------------|-----------------------|
| 1<br>H <sub>2</sub> * |          |          |                      |                      |                       | 2<br>He               |
|                       | 5<br>B   | 6<br>C   | 7<br>N <sub>2</sub>  | 8<br>O <sub>2</sub>  | 9<br>F <sub>2</sub>   | 10<br>Ne              |
|                       | 13<br>Al | 14<br>Si | 15<br>P <sub>4</sub> | 16<br>S <sub>8</sub> | 17<br>Cl <sub>2</sub> | 18<br>Ar              |
|                       | 30<br>Zn | 31<br>Ga | 32<br>Ge             | 33<br>As             | 34<br>Se              | 35<br>Br <sub>2</sub> |
|                       | 48<br>Cd | 49<br>In | 50<br>Sn             | 51<br>Sb             | 52<br>Te              | 53<br>I <sub>2</sub>  |
|                       | 80<br>Hg | 81<br>Tl | 82<br>?Pb            | 83<br>Bi             | 84<br>Po              | 85<br>At              |
|                       |          |          |                      |                      |                       | 86<br>Rn              |

Solids  
 Gas  
 Liquids

\*The subscript 2 indicates diatomic molecules at 25°C

**FIGURE 4-5 The Physical States of the Elements** The elements are found in all three physical states at room temperature.

### ASSESSING THE OBJECTIVE FOR SECTION 4-2

(Answer these questions using a periodic table.)

**EXERCISE 4-2(a) KNOWLEDGE:** Fill in the blanks.

Of the two general classifications of elements, nickel is a \_\_\_\_\_ and sulfur is a \_\_\_\_\_. Some borderline elements such as germanium are sometimes referred to as \_\_\_\_\_. In the periodic table, elements are ordered according to increasing \_\_\_\_\_ so that \_\_\_\_\_ of elements fall into vertical columns. Of the four general categories of elements, calcium is a \_\_\_\_\_ element, nickel is a \_\_\_\_\_, and xenon is a \_\_\_\_\_. An element in Group IIA, such as calcium, is also known as an \_\_\_\_\_ metal. A solid nonmetal that is composed of diatomic molecules is in the group known as the \_\_\_\_\_. Metals are all solids except for \_\_\_\_\_.

**EXERCISE 4-2(b) ANALYSIS:** Assign each of the following elements to one of the four major categories, give its symbol and physical state, tell whether it's a metal or nonmetal, and give its period and group number.

(a) copper    (b) argon    (c) barium    (d) bromine    (e) uranium

**EXERCISE 4-2(c) ANALYSIS:** Identify the element that fits each description.

- the fourth-period alkaline earth metal
- the liquid halogen
- the IIIA nonmetal
- the last transition metal of the fifth period
- the gaseous chalcogen

**EXERCISE 4-2(d) SYNTHESIS:** A few elements that have been created in recent years have never existed outside of a laboratory. Yet we can still use the periodic table to predict what these elements would be like if we could somehow isolate a measurable quantity. Evaluate element 118 and the hypothetical 119 for category, physical state, period, group number, and whether they are metals or nonmetals.

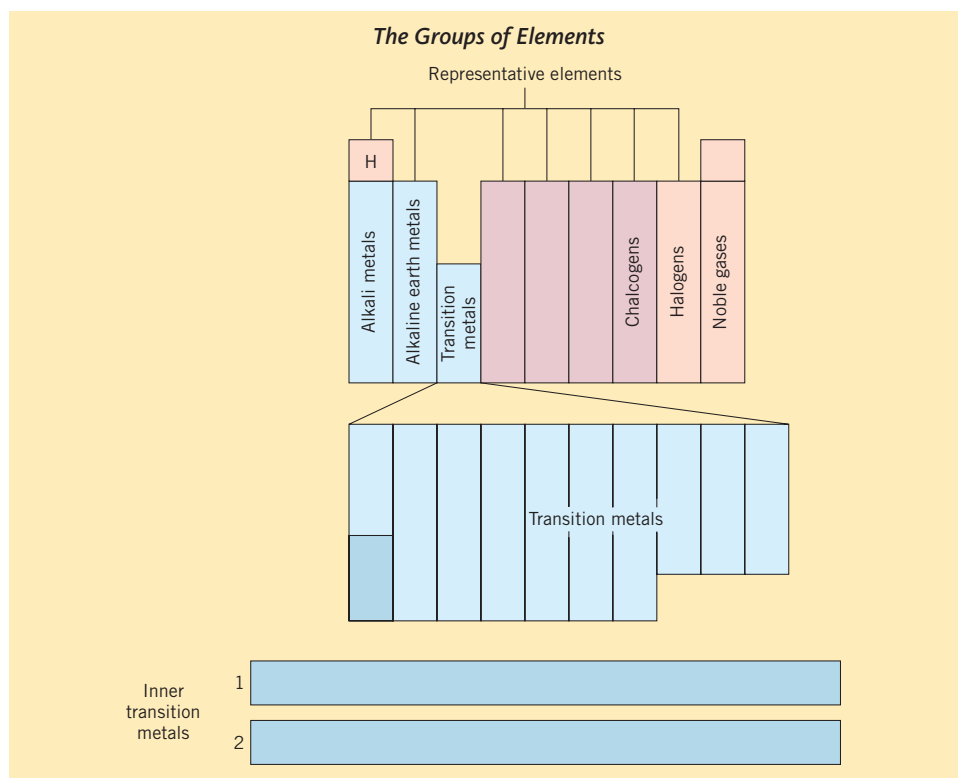
For additional practice, work chapter problems 4-4, 4-10, 4-12, and 4-14.

PART A  
SUMMARY

## KEY TERMS

- 4-1.1** The elements can be classified as either **metals** or **nonmetals**. p. 110
- 4-1.1** The **metalloids** are elements with intermediate properties between metals and nonmetals. p. 111
- 4-1.2** The **periodic table** is a chart that displays the relationships among the elements. p. 111
- 4-1.3** The **periodic law** describes the ordering of the elements based on atomic numbers. p. 112
- 4-2.2** All elements can be assigned to a specific **period**. p. 113
- 4-2.3** The main classifications of **groups** of elements are the **main groups or representative elements**, the **noble gases**, the **transition metals**, and the **inner transition metals**. pp. 113–114
- 4-2.3** The named groups of representative elements are the **alkali metals**, the **alkaline earth metals**, and the **halogens**. p. 113
- 4-2.3** The inner transition elements are known as either the **lanthanides** or **actinides**. p. 114
- 4-2.4** The physical state of an element at **room temperature** can be determined from the periodic table. p. 114

## SUMMARY CHART

PART B  
THE FORMULAS AND NAMES  
OF COMPOUNDS

## SETTING A GOAL

- You will learn how to systematically name various types of molecular and ionic compounds and determine the formulas of compounds from the names.

## OBJECTIVES

- 4-3** Write and name ionic compounds involving a metal and nonmetal using IUPAC conventions.
- 4-4** Write and name compounds containing polyatomic ions using IUPAC conventions.
- 4-5** Name binary molecular (nonmetal–nonmetal) compounds using proper Greek prefixes.
- 4-6** Name and write the formulas of acids.

## 4-3 NAMING AND WRITING FORMULAS OF METAL–NONMETAL BINARY COMPOUNDS

### ▶ OBJECTIVE FOR SECTION 4-3

Write and name ionic compounds involving a metal and nonmetal using IUPAC conventions.



**LOOKING AHEAD!** There are now over 10 million recorded compounds.

With such a number, systematic methods of naming the compounds must be employed. We will need a periodic table, since we need to know whether an element is a metal or nonmetal. Our first task is to look at binary (i.e., two-element) compounds made from a metal and a nonmetal. For the most part, these are ionic compounds, which is one of the two major classes of compounds described in Chapter 2. ■

Chemical compounds can be roughly divided into two groups: organic and inorganic. Organic compounds are composed principally of carbon, hydrogen, and oxygen. These are the compounds of life and will not be discussed at this time. All other compounds are called inorganic compounds, and we will focus on these. As mentioned, many inorganic compounds were given common names, and some of these names have survived the years. For example,  $\text{H}_2\text{O}$  is certainly known as *water* rather than the more exact systematic name of *hydrogen oxide*. Ammonia ( $\text{NH}_3$ ) and methane ( $\text{CH}_4$ ) are two other compounds that are known exclusively by their common names. Other compounds have ancient common names but are best described by their more modern systematic names, which we will use here.

One of the most important chemical properties of a metal is its tendency to form positive ions (cations). Most nonmetals, on the other hand, can form negative ions (anions). (The noble gases form neither cations nor anions.) Inorganic compounds composed of just two elements—metal cations and nonmetal anions—will be referred to as *metal–nonmetal binary compounds*. Metals fall into two categories. Some metals form cations with only one charge (e.g.,  $\text{Ca}^{2+}$ ). Others form cations with two or more charges (e.g.,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ). The rules for the latter compounds are somewhat different from those for the first. So we initially consider metals with ions of only one charge.

### 4-3.1 Metals with Ions of Only One Charge

As organized by Mendeleev, the periodic table places elements with similar chemical properties in the same column. It is not surprising, then, to find out that the charge of an atom's ion can in many cases be predicted based on what column it is in. Almost all metals that have only one charge on their ions are located in one of two groups. Representative element metals in Group IA (alkali metals) form +1 cations exclusively. Likewise, the metals in Group IIA (alkaline earth metals) form +2 ions exclusively. Aluminum, in Group IIIA, forms a +3 ion exclusively, but other metals in this group also form a +1 ion. (See Figure 4-6.) (There are also several transition metals that form only one cation charge, but they are not included in this discussion.)

When present in metal–nonmetal binary compounds, the nonmetals form one type of anion. Hydrogen and Group VIIA (halogens) form  $-1$  ions, Group VIA elements form  $-2$  ions, and N and P in Group VA form  $-3$  ions. (Figure 4-6.) *Note that positive and negative ions do not exist separately. They are always found together in ordinary matter.* In both naming and writing the formula for a binary ionic compound, the metal comes first and the nonmetal second. The unchanged English name of the metal is used. (If a metal cation is named alone, the word *ion* is also included to distinguish it from the free metal.) The name of the anion includes only the English root plus *-ide*. For example, *chlorine* as an anion is named *chloride* and *oxygen* as an anion is named *oxide*. So the names for  $\text{NaCl}$  and  $\text{CaO}$  are sodium chloride and calcium oxide.

Some other examples of writing names from formulas are shown in Example 4-1. Writing formulas from names can be a somewhat more challenging task, since we must determine the number of each element present in the formula. In Chapter 2, we practiced writing formulas given specific ions with specific charges. In this chapter, we are now able to determine the charge on the ion by reference to the periodic table. Recall

**FIGURE 4-6 Monatomic Ions of the Representative Elements** Metals form specific cations, and nonmetals form specific anions.

| IA                        | IIA                           | IIIA                         | IVA                        | VA                           | VIA                           | VIIA                      |
|---------------------------|-------------------------------|------------------------------|----------------------------|------------------------------|-------------------------------|---------------------------|
| Hydride<br>$\text{H}^-$   |                               |                              |                            |                              |                               |                           |
| Lithium<br>$\text{Li}^+$  | Beryllium<br>$\text{Be}^{2+}$ |                              | Carbide<br>$\text{C}^{4-}$ | Nitride<br>$\text{N}^{3-}$   | Oxide<br>$\text{O}^{2-}$      | Fluoride<br>$\text{F}^-$  |
| Sodium<br>$\text{Na}^+$   | Magnesium<br>$\text{Mg}^{2+}$ | Aluminum<br>$\text{Al}^{3+}$ |                            | Phosphide<br>$\text{P}^{3-}$ | Sulfide<br>$\text{S}^{2-}$    | Chloride<br>$\text{Cl}^-$ |
| Potassium<br>$\text{K}^+$ | Calcium<br>$\text{Ca}^{2+}$   |                              |                            |                              | Selenide<br>$\text{Se}^{2-}$  | Bromide<br>$\text{Br}^-$  |
| Rubidium<br>$\text{Rb}^+$ | Strontium<br>$\text{Sr}^{2+}$ |                              |                            |                              | Telluride<br>$\text{Te}^{2-}$ | Iodide<br>$\text{I}^-$    |
| Cesium<br>$\text{Cs}^+$   | Barium<br>$\text{Ba}^{2+}$    |                              |                            |                              |                               |                           |

also from Chapter 2 that the formulas represent neutral compounds where the positive and negative charges add to zero. In other words, the total positive charge is canceled by the total negative charge. Thus, NaCl is neutral because one  $\text{Na}^+$  is balanced by one  $\text{Cl}^-$  [i.e.,  $+1 + (-1) = 0$ ] and CaO is neutral because one  $\text{Ca}^{2+}$  is balanced by one  $\text{O}^{2-}$  [i.e.,  $+2 + (-2) = 0$ ]. The formula for magnesium chloride, however, requires two  $\text{Cl}^-$  ions to balance the one  $\text{Mg}^{2+}$  ion, so it is written as  $\text{MgCl}_2$  [i.e.,  $+2 + (2 \times -1) = 0$ ]. We will practice writing formulas from names in Example 4-2.

### EXAMPLE 4-1

#### Naming Binary Ionic Compounds

Name the following binary ionic compounds: KI,  $\text{Li}_2\text{S}$ , and  $\text{Mg}_3\text{N}_2$ .

#### PROCEDURE

A quick glance at the periodic table reveals that the first element in each compound is a representative metal and the second is a representative nonmetal. Use the metal name unchanged, and change the ending of the nonmetals to *-ide*.

#### SOLUTION

| FORMULA                 | METAL     | NONMETAL | COMPOUND NAME            |
|-------------------------|-----------|----------|--------------------------|
| KI                      | potassium | iodine   | <u>potassium iodide</u>  |
| $\text{Li}_2\text{S}$   | lithium   | sulfur   | <u>lithium sulfide</u>   |
| $\text{Mg}_3\text{N}_2$ | magnesium | nitrogen | <u>magnesium nitride</u> |

### EXAMPLE 4-2

#### Writing the Formulas of Binary Ionic Compounds

Write the formulas for the following binary metal–nonmetal compounds: (a) aluminum fluoride and (b) calcium selenide.

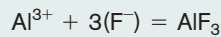
#### PROCEDURE

From the names, recognize that these compounds are representative elements. Identify their charges based on their column on the periodic table. Determine how many of each element are necessary to produce a neutral compound. Use these as subscripts in the formula.

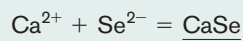


**SOLUTION**

(a) Aluminum is in Group IIIA, so it forms a cation with a +3 charge exclusively. Fluorine is in Group VIIA, so it forms an anion with a  $-1$  charge. Since the positive charge must be balanced by the negative charge, we need three  $F^{1-}$  anions to balance one  $Al^{3+}$  ion [e.g.,  $+3 + (3 \times -1) = 0$ ]. Therefore, the formula is written as



(b) Calcium is in Group IIA, so it forms a +2 cation. Selenium is in Group VIA, so it forms a  $-2$  anion. Together the charges add to zero, so one of each atom is sufficient in the formula:

**ANALYSIS**

Another convenient way to establish the formula is to write the ions with their appropriate charges side by side. The numerical value of the charge on the cation becomes the subscript on the anion, and vice versa. The number 1 is understood instead of written as a subscript. This is known as the *cross-charge* method. Notice that, in (b), by exchanging values of the charge, we first indicate a formula of  $Ca_2Se_2$ . This is not a correct representation, however. Ionic compounds should be expressed with the simplest whole numbers for subscripts. Therefore, the proper formula is written as  $CaSe$ .

**SYNTHESIS**

What is the formula of a compound made from a metal (M) with a +3 charge and a nonmetal (X) with a  $-2$  charge? Using the cross-charge method, we get a formula of  $M_2X_3$ . Charges are rarely higher than +3 or  $-3$ , so this is typically as complicated as balancing the charges in ionic compounds ever gets.

**4-3.2 Metals with Ions of More Than One Charge**

Except for Groups IA, IIA, and aluminum, other representative metals and most transition metals can form more than one cation. Therefore, a name such as iron chloride would be ambiguous since there are two iron chlorides,  $FeCl_2$  and  $FeCl_3$ . An even more dramatic case is that of the oxides of manganese—there are five different compounds ( $MnO$ ,  $Mn_3O_4$ ,  $Mn_2O_3$ ,  $MnO_2$ , and  $Mn_2O_7$ ). To distinguish among these compounds, the charge on the metal ion follows the name of the metal in Roman numerals and in parentheses. This is referred to as the **Stock method**. By this convention, the two chlorides of iron are named iron(II) chloride ( $FeCl_2$ ) and iron(III) chloride ( $FeCl_3$ ).

Another method of naming compounds is known as the **classical method**. Though no longer widely used in chemistry, it is still found in many pharmaceuticals and drug labels. In this system, *the name of the metal ion that has the lower charge ends in -ous and the higher ends in -ic*.

If the symbol of the element is derived from a Latin word, the Latin root is generally used rather than an English root. Thus the two chlorides of iron are named ferrous chloride ( $FeCl_2$ ) and ferric chloride ( $FeCl_3$ ). The disadvantage of this method is that you have to know in advance what the possible charges of a metal are. The Stock method, on the other hand, tells you explicitly. The classical method will not be included in examples or problems in this text. However, several common examples of names of ions of metals that form more than one cation are shown in Table 4-1.

In order to use the Stock method, it is necessary to determine the charge on the metal cation by working backward from the known charge on the anion. For example, in a compound with the formula  $FeS$ , we can establish from Figure 4-6 that the charge on the S is  $-2$ . Therefore, the charge on the one Fe must be  $+2$ . The compound is named *iron(II) sulfide*. In the following examples, we will use a simple algebra equation that will help us determine the charge on the metal and thus the proper Roman numeral to use for more complex compounds. The equation is

$$\begin{aligned} &(\text{number of metal cations}) \times (+ \text{ charge on metal}) + \\ &(\text{number of nonmetal anions}) \times (- \text{ charge on nonmetal}) = 0 \end{aligned}$$

**TABLE 4-1** Metals That Form More Than One Ion

| ION              | STOCK NAME    | CLASSICAL NAME | ION              | STOCK NAME     | CLASSICAL NAME |
|------------------|---------------|----------------|------------------|----------------|----------------|
| Cr <sup>2+</sup> | chromium(II)  | chromous       | Cu <sup>+</sup>  | copper(I)      | cuprous        |
| Cr <sup>3+</sup> | chromium(III) | chromic        | Cu <sup>2+</sup> | copper(II)     | cupric         |
| Fe <sup>2+</sup> | iron(II)      | ferrous        | Mn <sup>2+</sup> | manganese(II)  | manganous      |
| Fe <sup>3+</sup> | iron(III)     | ferric         | Mn <sup>3+</sup> | manganese(III) | manganic       |
| Pb <sup>2+</sup> | lead(II)      | plumbous       | Sn <sup>2+</sup> | tin(II)        | stannous       |
| Pb <sup>4+</sup> | lead(IV)      | plumbic        | Sn <sup>4+</sup> | tin(IV)        | stannic        |
| Au <sup>+</sup>  | gold(I)       | aurous         | Co <sup>2+</sup> | cobalt(II)     | cobaltous      |
| Au <sup>3+</sup> | gold(III)     | auric          | Co <sup>3+</sup> | cobalt(III)    | cobaltic       |

**EXAMPLE 4-3****Naming Binary Compounds with Metals with More Than One Charge**

Name the following compounds: SnO<sub>2</sub> and Co<sub>2</sub>S<sub>3</sub>.

**PROCEDURE**

To determine the charge on the metal cation, we can work backward from the known charge on the anion. Recall that Group VIA nonmetals form a  $-2$  charge in binary compounds. We can use the general algebra equation introduced in the preceding discussion to determine the proper Roman numeral to use for the metal.

**SOLUTION**

The equation applied to the given compound is

$$[1 \times (\text{Sn charge})] + [2 \times (\text{O charge})] = 0$$

Substitute the known charge on the oxygen and solve for the charge on the tin.

$$\begin{aligned} \text{Sn} + (2 \times -2) &= 0 \\ \text{Sn} - 4 &= 0 \\ \text{Sn} &= +4(\text{IV}) \end{aligned}$$

The name of the compound is, therefore, tin(IV)oxide.

For Co<sub>2</sub>S<sub>3</sub>, we can construct the following equation.

$$[2 \times (\text{Co charge})] + [3 \times (\text{S charge})] = 0$$

The charge on a Group VIA nonmetal such as S is  $-2$ .

$$\begin{aligned} 2\text{Co} + (3 \times -2) &= 0 \\ 2\text{Co} &= +6 \\ \text{Co} &= +3(\text{III}) \end{aligned}$$

The name of the compound is cobalt(III)sulfide.

**EXAMPLE 4-4****Writing the Formulas of Compounds with Metals That Form More Than One Charge**

Write the formulas for lead(IV) oxide, nickel(II) bromide, and chromium(III) sulfide.

**PROCEDURE**

These types of compounds are actually easier than those with normal representative elements. The charge on the metal is already stated explicitly for you. Determine the charge on the nonmetal, balance the charges, and write the formula.

**SOLUTION**

Lead(IV) oxide: If lead has a +4 charge, two  $\text{O}^{2-}$  ions are needed to form a neutral compound [i.e.,  $(1 \times +4) - (2 \times -2) = 0$ ].



Nickel(II) bromide: Two bromines are needed to balance the +2 nickel [i.e.,  $1 \times +2 - (2 \times -1) = 0$ ].



Chromium(III) sulfide: Two  $\text{Cr}^{3+}$  ions are needed to balance three  $\text{S}^{2-}$  ions [i.e.,  $2 \times +3 - (3 \times -2) = 0$ ].

**ANALYSIS**

The key to successful nomenclature is recognizing the type of compound you are dealing with, and then naming it according to the rules set down for that type of compound. A periodic table is indispensable in this regard. With it, you can determine whether the metal in question is in column I or II (or Al) and therefore does *not* require a charge in the name, or whether it is any of the other metals available to us and therefore does.

**SYNTHESIS**

Students often become confused over the meaning of the number in parenthesis. Remember that it is the *charge* on the metal, not the number of metal atoms in the compound. So what are the formulas of copper(I) sulfide and copper(II) sulfide?  $\text{Cu}_2\text{S}$  and  $\text{CuS}$ , respectively. Notice that copper(I) requires two atoms of copper and copper(II) requires one atom of copper. Can you see from the charges why this is so?

**ASSESSING THE OBJECTIVE FOR SECTION 4-3**

**EXERCISE 4-3(a) KNOWLEDGE:** For which of the following metals must a charge be placed in parenthesis when naming one of its compounds? Co, Li, Sn, Al, Ba

**EXERCISE 4-3(b) ANALYSIS:** Name the following compounds.

(a)  $\text{Li}_2\text{O}$     (b)  $\text{CrI}_3$     (c)  $\text{PbS}$     (d)  $\text{Mg}_3\text{N}_2$     (e)  $\text{Ni}_3\text{P}_2$

**EXERCISE 4-3(c) ANALYSIS:** Provide the formula for the following compounds.

(a) aluminum iodide    (c) tin(IV) bromide  
(b) iron(III) oxide    (d) calcium nitride

**EXERCISE 4-3(d) SYNTHESIS:** Using an M to represent the metal and an X to represent the nonmetal, write theoretical formulas for all possible combinations of M and X with charges of +1, +2, +3 and -1, -2, and -3.

*For additional practice, work chapter problems 4-18, 4-20, 4-22, and 4-24.*

**4-4 NAMING AND WRITING FORMULAS OF COMPOUNDS WITH POLYATOMIC IONS****OBJECTIVE FOR SECTION 4-4**

Write and name compounds containing polyatomic ions using IUPAC conventions.



**LOOKING AHEAD!** Two or more atoms that are chemically combined with covalent bonds may have an imbalance of electrons and protons just like monatomic cations and anions. This results in a charged species called a polyatomic ion. How compounds containing these ions are named is our next topic.

Again, you should recognize these as ionic compounds, so we find them as solids under normal conditions. ■

We use bicarbonates and carbonates for indigestion, as well as sulfites and nitrites to preserve foods. So we are probably familiar with some of these names, which are

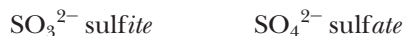
**TABLE 4-2** Polyatomic Ions

| ION                                | NAME                                 |
|------------------------------------|--------------------------------------|
| $\text{C}_2\text{H}_3\text{O}_2^-$ | acetate                              |
| $\text{NH}_4^+$                    | ammonium                             |
| $\text{CO}_3^{2-}$                 | carbonate                            |
| $\text{ClO}_3^-$                   | chlorate                             |
| $\text{ClO}_2^-$                   | chlorite                             |
| $\text{CrO}_4^{2-}$                | chromate                             |
| $\text{CN}^-$                      | cyanide                              |
| $\text{Cr}_2\text{O}_7^{2-}$       | dichromate                           |
| $\text{H}_2\text{PO}_4^-$          | dihydrogen phosphate                 |
| $\text{HCO}_3^-$                   | hydrogen carbonate<br>or bicarbonate |
| $\text{HPO}_4^{2-}$                | monohydrogen phosphate               |
| $\text{HSO}_4^-$                   | hydrogen sulfate or bisulfate        |
| $\text{HSO}_3^-$                   | hydrogen sulfite or bisulfite        |
| $\text{OH}^-$                      | hydroxide                            |
| $\text{ClO}^-$                     | hypochlorite                         |
| $\text{NO}_3^-$                    | nitrate                              |
| $\text{NO}_2^-$                    | nitrite                              |
| $\text{C}_2\text{O}_4^{2-}$        | oxalate                              |
| $\text{ClO}_4^-$                   | perchlorate                          |
| $\text{MnO}_4^-$                   | permanganate                         |
| $\text{PO}_4^{3-}$                 | phosphate                            |
| $\text{SO}_4^{2-}$                 | sulfate                              |
| $\text{SO}_3^{2-}$                 | sulfite                              |

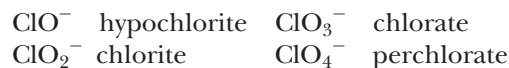
commonly used. A list of some common polyatomic ions is given in Table 4-2. Notice that all but one ( $\text{NH}_4^+$  ammonium) are anions.

### 4-4.1 Oxyanions

There is some systematization possible that will help in understanding Table 4-2. In most cases, *the anions are composed of oxygen and one other element*. Thus these anions are called **oxyanions**. When there are two oxyanions of the same element (e.g.,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ), they, of course, have different names. The anion with the smaller number of oxygens uses the root of the element plus *-ite*. The one with the higher number uses the root plus *-ate*.



There are four oxyanions containing Cl. The middle two are named as before (i.e., with *-ite* and *-ate*). The one with one less oxygen than the chlorite has a prefix of *hypo-*, which means “under.” (as in *hypoglycemic*, meaning “low blood sugar”). The one with one more oxygen than chlorate has a prefix of *per-*, which in this usage means “highest” (a shortening of *hyper*, as in *hyperactive*, meaning “overactive”).



Certain anions are composed of more than one atom but behave similarly to monatomic anions in many of their chemical reactions. Two such examples in Table 4-2 are the  $\text{CN}^-$  ion and the  $\text{OH}^-$  ion. Both of these have *-ide* endings similar to the monatomic anions. Thus, the  $\text{CN}^-$  anion is known as the cyanide ion and the  $\text{OH}^-$  as the hydroxide ion, just as the  $\text{Cl}^-$  ion is named the chloride ion.

Most of the ionic compounds that we have just named are also referred to as salts. A **salt** is an ionic compound formed by the combination of a cation with an anion. (Cations combined with hydroxide or oxide form a class of compounds that are not considered salts and are discussed in the next chapter.) For example, potassium nitrate is a salt composed of  $\text{K}^+$  and  $\text{NO}_3^-$  ions, and calcium sulfate is a salt composed of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions. Ordinary table salt is  $\text{NaCl}$ , composed of  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

### 4-4.2 Naming and Writing the Formulas of Salts with Polyatomic Ions

In naming and writing the formulas of compounds with polyatomic ions, as in Example 4-5, we follow the same procedures as with metal–nonmetal compounds. The metal is written first with its charge (if it is not Al or in Group IA or IIA) followed by the name of the polyatomic ion. To calculate the charge on the cation, if necessary, we can use the same simple algebra equation as before. For example, consider  $\text{Cr}_2(\text{SO}_4)_3$ . Since the sulfate ion has a  $-2$  charge, the charge on the chromium is

$$\begin{aligned} (2 \times \text{Cr}) + (3 \times -2) &= 0 \\ 2\text{Cr} &= +6 \\ \text{Cr} &= +3 \end{aligned}$$

The name of the compound is *chromium(III) sulfate*.

When writing formulas from names, as in Example 4-6, we recall from Chapter 2 that when more than one polyatomic ion is present in the compound, parentheses enclose the polyatomic ion. If only one polyatomic ion is present, parentheses are not used (e.g.,  $\text{CaCO}_3$ ).

**EXAMPLE 4-5****Naming Compounds Containing Polyatomic Ions**

Name the following compounds:  $K_2CO_3$  and  $Fe_2(SO_4)_3$ .

**PROCEDURE**

Evaluate the metal as in Section 4-3. Recognize that after the metal in each compound is a grouping of atoms that form polyatomic ions. Name the anion with the appropriate ending: *-ate*, *-ite*, or *-ide*.

**SOLUTION**

$K_2CO_3$ : The cation is  $K^+$  (Group IA). The charge is not included in the name because it forms a +1 ion only. The anion is  $CO_3^{2-}$  (the carbonate ion).

potassium carbonate

$Fe_2(SO_4)_3$ : The charge on the Fe cation can be determined from the charge on the  $SO_4^{2-}$  (sulfate) ion.

$$2Fe + 3SO_4^{2-} = 0$$

$$2Fe + 3(-2) = 0$$

$$2Fe = +6$$

$$Fe = +3$$

iron(III)sulfate

**EXAMPLE 4-6****Writing the Formulas for Ionic Compounds Containing Polyatomic Ions**

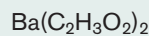
Give the formulas for barium acetate, ammonium sulfate, and manganese(II) phosphate.

**PROCEDURE**

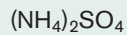
Write the formulas for the metal ion and the polyatomic ion, including their charges. Determine how many of each are needed to balance the charges. Write the formulas with those appropriate subscripts.

**SOLUTION**

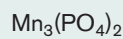
Barium acetate: Barium is in Group IIA, so it has a +2 charge. Acetate is the  $C_2H_3O_2^-$  ion. Two acetates are required to balance one  $Ba^{2+}$  ion. The formula is



Ammonium sulfate: From Table 4-2, ammonium =  $NH_4^+$ , sulfate =  $SO_4^{2-}$ . Two ammoniums are needed to balance one sulfate. The formula is



Manganese(II) phosphate: The stated charge on manganese is +2. Phosphate is the  $PO_4^{3-}$  ion. Using the cross-charge method [(Example 4-2(b))], we will need three manganese ions to balance two phosphate ions. Since there is more than one polyatomic ion, the whole ion is placed in parentheses.

**ANALYSIS**

While it is not a major mistake to use parentheses when there is only one polyatomic ion, as in  $Mg(SO_3)$ , parentheses do have an important purpose. Subscripts affect only what they immediately follow. In order to demonstrate two or three of the group of atoms that make up the polyatomic ion, parentheses are placed around the entire group so that the subscript refers to all. What is the formula of calcium hydroxide?  $Ca(OH)_2$ . Some students may write  $CaOH_2$ , assuming that because hydroxide has no subscript itself, no parentheses are necessary. However, notice the difference in the two formulas. The first shows one calcium, two oxygens, and two hydrogens. The second incorrectly shows one calcium, *one* oxygen, and two hydrogens. The parentheses are necessary to indicate the correct number of elements.

**SYNTHESIS**

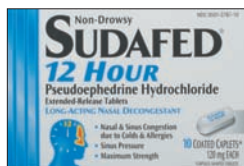
There are clear patterns in the names of the polyatomic ions that can be used to decipher the names of compounds with ions that are not in Table 4-2. What would we name  $NaBrO_4$  and  $Cu(IO)_2$ ? When Mendeleev organized the periodic table,



he placed elements with similar properties in the same column. Notice that Br and I are in the same column as Cl. It is not unreasonable, then, to assume that the ions  $\text{BrO}_4^-$  and  $\text{IO}^-$  might be named similarly to  $\text{ClO}_4^-$  and  $\text{ClO}^-$ . Perchlorate, then, becomes the model for perbromate and hypochlorite suggests hypoiodite. The charges, too, should remain constant.  $\text{NaBrO}_4$  then becomes sodium perbromate.  $\text{Cu}(\text{IO})_2$  requires two  $-1$ 's to balance the single Cu ion. Copper in this compound, then, must be  $+2$ , and the compound is named copper(II) hypoiodite.



## Ionic Compounds in the Treatment of Disease



Since antiquity, it has been believed that drinking mineral waters from certain spas can have a soothing effect on the mood as well as the body. Some of these magical minerals may have been compounds containing the lithium ion. Lithium (in the form of the  $\text{Li}^+$  ion) is found in certain rocks, in seawater, and in some freshwater springs. It is not known for sure that lithium was present in these

waters, but it may have been an ancient treatment for manic-depressive disorder, which is now known more commonly as *bipolar disorder*. This is a debilitating disease that affects about 2.5 million Americans alone. Its symptoms include exaggerated mood swings from exhilarating highs to extremely depressive lows. In the manic mood, a person has boundless energy but acts impulsively and makes poor judgments. In the depressive state, the same person goes in the other direction and the world feels hopelessly glum. If untreated, about one in five commit suicide when in the depressive stage. The disease is known to be hereditary, with a neurological basis in certain chromosomes. It is certainly not due to weakness or any character flaw.

In 1949 John Cade, an Australian physician, found that lithium compounds had a calming effect on small animals. He then tested the toxicity of the compound on himself. Since he

seemed OK and suffered no adverse effects, he began treating manic patients with lithium. Unfortunately, it was not known at the time that lithium can build up to toxic levels in the blood. In other uses, such as for cardiac patients, lithium caused several deaths so its use in treating bipolar disorder did not gain much ground at that time in the United States. In the 1960s, however, it was reintroduced along with careful monitoring of the levels of lithium in the patient's blood. Under controlled conditions, studies quickly found that lithium was extremely effective. It was approved by the Food and Drug Administration (FDA) in 1970 to treat mania. In 1974 it was approved for use as a preventive (i.e., prophylactic) treatment for bipolar disease.

Treatment for bipolar disorder is most effective when lithium is combined with "talk therapy" with a trained professional. It is taken in the form of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) or lithium citrate ( $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7$ ). In any case, those that suffer from this illness can now lead normal, productive lives.

There are many other ionic compounds that we ingest for their curative value. Magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] and calcium carbonate ( $\text{CaCO}_3$ ) treat indigestion or "heartburn." Many antihistamines and decongestants are also ionic compounds. If the drug name ends in "hydrochloride" or "HCl," it is an ionic compound. For example, pseudoephedrine hydrochloride ( $\text{C}_{10}\text{H}_{14}\text{NOH}_2^+\text{Cl}^-$ ) is an ionic compound used as a nasal decongestant in products such as Sudafed. Like other ionic compounds, it is a solid and can be taken in pill form.

### ASSESSING THE OBJECTIVE FOR SECTION 4-4

**EXERCISE 4-4(a) KNOWLEDGE:** What are the names of the following ions?

- (a)  $\text{NO}_2^-$     (b)  $\text{OH}^-$     (c)  $\text{C}_2\text{H}_3\text{O}_2^-$     (d)  $\text{PO}_4^{3-}$     (e)  $\text{HSO}_4^-$

**EXERCISE 4-4(b) ANALYSIS:** What are the formulas for the following compounds?

- (a) nickel(II) cyanide    (d) iron(III) perchlorate  
 (b) aluminum sulfite    (e) ammonium phosphate  
 (c) magnesium bicarbonate

**EXERCISE 4-4(c) ANALYSIS:** What are the names of the following compounds?

(a)  $\text{Ba}(\text{OH})_2$     (b)  $\text{LiH}_2\text{PO}_4$     (c)  $\text{AgClO}$     (d)  $\text{K}_2\text{CrO}_4$     (e)  $\text{Co}_2(\text{CO}_3)_3$

For additional practice, work chapter problems 4-29, 4-32, 4-34, and 4-35.

## 4-5 NAMING NONMETAL–NONMETAL BINARY COMPOUNDS



**LOOKING AHEAD!** The compounds that we have named so far are generally ionic compounds. They constitute much of the hard, solid part of nature. When nonmetals bond to other nonmetals, however, molecular compounds are formed. These are very likely to be gases or liquids. How we name molecular compounds is the topic of this section. ■

### 4-5.1 Writing the Formulas of Binary Molecular Compounds

When a metal is combined with a nonmetal, it is simple to decide which element to name and write first. But which do we write first if neither is a metal? In these cases, we generally write the one closer to being a metal first—that is, the nonmetal closer to the metal–nonmetal border in the periodic table (farther down or farther to the left). Thus, we write  $\text{CO}_2$  rather than  $\text{O}_2\text{C}$  but  $\text{OF}_2$  rather than  $\text{F}_2\text{O}$ . In cases where both elements are equidistant from the border, Cl is written before O (e.g.,  $\text{Cl}_2\text{O}$ ) and the others in the order S, N, then Br (e.g.,  $\text{S}_4\text{N}_4$  and  $\text{NBr}_3$ ). When hydrogen is one of the nonmetals and is combined with nonmetals in Groups VIA and VIIA (e.g.,  $\text{H}_2\text{O}$  and  $\text{HF}$ ), hydrogen is written first. When combined with other nonmetals (Groups IIIA, IVA, and VA) and metals, however, it is written second (e.g.,  $\text{NH}_3$  and  $\text{CH}_4$ ).\*

### 4-5.2 Naming Binary Molecular Compounds

The nonmetal closer to the metal borderline is also named first, using its English name. The less metallic is named second, using its English root plus *-ide*, as discussed before. These are not ionic compounds, so there are no charges that require balancing. However, this also means that more than one combination of the two elements is possible. Because more than one compound of the same two nonmetals could exist, *the number of atoms of each element present in the compound is indicated by the use of Greek prefixes* (See Table 4-3.) Table 4-4 illustrates the nomenclature of nonmetal–nonmetal

**TABLE 4-4** The Oxides of Nitrogen

| FORMULA                | NAME   |
|------------------------|--|
| $\text{N}_2\text{O}$   | dinitrogen monoxide (sometimes referred to as nitrous oxide) |
| $\text{NO}$            | nitrogen monoxide (sometimes referred to as nitric oxide)    |
| $\text{N}_2\text{O}_3$ | dinitrogen trioxide  |
| $\text{NO}_2$          | nitrogen dioxide   |
| $\text{N}_2\text{O}_4$ | dinitrogen tetroxide <sup>a</sup>                            |
| $\text{N}_2\text{O}_5$ | dinitrogen pentoxide <sup>a</sup>                            |

<sup>a</sup> The *a* is often omitted from *tetra* and *penta* with oxides for ease in pronunciation.

### OBJECTIVE FOR SECTION 4-5

Name binary molecular (nonmetal–nonmetal) compounds using proper Greek prefixes.



Chemical names are familiar to us in many common drugs and cleansers.

**TABLE 4-3**

### Greek Prefixes

| NUMBER | PREFIX |
|--------|--------|
| 1      | mono-  |
| 2      | di-    |
| 3      | tri-   |
| 4      | tetra- |
| 5      | penta- |
| 6      | hexa-  |
| 7      | hepta- |
| 8      | octa-  |
| 9      | nona-  |
| 10     | deca-  |

\*With few exceptions, in organic compounds containing C, H, and other elements, the C is written first followed by H and then other elements that are present.



Nitrogen dioxide contributes to the brownish haze in polluted air.

compounds with the six oxides of nitrogen. Notice that if there is only one atom of the nonmetal written first, *mono-* is not used. However, if there is only one of the second nonmetal, *mono-* is used. (Notice that the second *o* in *mono* is dropped in *monoxide* for ease in pronunciation.) The Stock method is rarely applied to the naming of nonmetal–nonmetal compounds because it can be ambiguous in some cases. For example, both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  could be named nitrogen(IV) oxide.

Several of these compounds are known only by their common names, such as water ( $\text{H}_2\text{O}$ ), methane ( $\text{CH}_4$ ), and ammonia ( $\text{NH}_3$ ).

According to the rules, compounds such as  $\text{TiO}_2$  and  $\text{UF}_6$  should be named by the Stock method—for example, titanium(IV) oxide and uranium(VI) fluoride, respectively. Sometimes, however, we hear them named in the same manner as nonmetal–nonmetal binary compounds (i.e., titanium dioxide and uranium hexafluoride). The rationale for the latter names is that when the charge on the metal exceeds +3, the compound has properties more typical of a molecular nonmetal–nonmetal binary compound than an ionic one. For example,  $\text{UF}_6$  is a liquid at room temperature, whereas true ionic compounds are all solids under these conditions. In any case, in this text we will identify all metal–nonmetal binary compounds by the Stock method regardless of their properties and confine the use of Greek prefixes to the nonmetal–nonmetal compounds.

### EXAMPLE 4-7

#### Naming Binary Molecular Compounds

What are the names of (a)  $\text{SeBr}_4$  and (b)  $\text{B}_2\text{O}_3$ ? What are the formulas of (c) dichlorine trioxide and (d) sulfur hexafluoride?

#### PROCEDURE

Check in the periodic table for the location of all the elements involved. Note that they are all nonmetals, meaning that these are examples of binary molecular compounds. Use the Greek prefixes and the ending *-ide* in the names.

#### SOLUTION

(a) selenium tetrabromide      (b) diboron trioxide      (c)  $\text{Cl}_2\text{O}_3$       (d)  $\text{SF}_6$

#### ANALYSIS

These are some of the easiest types of compounds to deal with. The prefixes essentially do all the work for you. The real chore comes in identifying these as binary molecular compounds in the first place.

#### SYNTHESIS

Sometimes formulas can be very confusing. In Chapter 2 (Figure 2-13) we discussed the difference between  $\text{NO}_2$  (nitrogen dioxide) and  $\text{NO}_2^-$  (the nitrite ion). Another case involves  $\text{SO}_3$  and  $\text{SO}_3^{2-}$ . How would you expect these two to differ from each other?  $\text{SO}_3$  is a binary molecular compound named sulfur trioxide. It is a molecular compound made from one sulfur and three oxygen atoms. It is a gas at room temperature.  $\text{SO}_3^{2-}$  is the sulfite anion. It is not a compound in and of itself. It cannot stand alone; instead, it needs to be combined with a charge-balancing cation, such as  $\text{Na}^+$ . It would then form the solid ionic compound, sodium sulfite ( $\text{Na}_2\text{SO}_3$ ).

### ASSESSING THE OBJECTIVE FOR SECTION 4-5

**EXERCISE 4-5(a) KNOWLEDGE:** What are the Greek prefixes for the following numbers?

(a) one      (b) four      (c) six      (d) ten

**EXERCISE 4-5(b) ANALYSIS:** What are the formulas of the following compounds?

(a) carbon tetrachloride      (c) sulfur dioxide  
(b) phosphorus pentabromide      (d) carbon monoxide

**EXERCISE 4-5(c) ANALYSIS:** What are the names of the following compounds?

- (a)  $\text{SiS}_2$     (b)  $\text{P}_2\text{O}_5$     (c)  $\text{BF}_3$     (d)  $\text{AsH}_3$

For additional practice, work chapter problems 4-43, 4-44, 4-45, and 4-46.

## 4-6 NAMING ACIDS

### OBJECTIVE FOR SECTION 4-6

Name and write the formulas of acids.



**LOOKING AHEAD!** We have one last category of compounds. These involve most of the anions listed in Figure 4-6 and Table 4-2 when combined with hydrogen. Since hydrogen is not a metal, these are molecular compounds in the pure state. However, many of these compounds have an important property when present in water. This special property allows us to give them special names, and we will do so in this section. ■

When hydrogen is combined with an anion such as  $\text{Cl}^-$ , the formula of the resulting compound is  $\text{HCl}$ . The fact that  $\text{HCl}$  is a gas, not a hard solid, at room temperature indicates that  $\text{HCl}$  is molecular rather than ionic. When dissolved in water, however, the  $\text{HCl}$  is ionized by the water molecules to form  $\text{H}^+$  ions and  $\text{Cl}^-$  ions. This ionization is illustrated as



Most of the hydrogen compounds formed from the anions in Figure 4-6 and Table 4-2 behave in a similar manner, at least to some extent. *This common property of forming  $\text{H}^+$  in aqueous solution is a property of a class of compounds called acids.* Acids are important enough to earn their own nomenclature. The chemical nature of acids is discussed in more detail in Chapters 5 and 13.

### 4-6.1 Binary Acids

The acids formed from the anions listed in Figure 4-6 are composed of hydrogen plus one other element, so they are called **binary acids**. These compounds can be named in two ways. In the pure state, the hydrogen is named like a metal with only one charge (+1). That is,  $\text{HCl}$  is named *hydrogen chloride*, and  $\text{H}_2\text{S}$  is named *hydrogen sulfide*. When dissolved in water, however, these compounds are generally referred to by their acid names. The acid name is obtained by dropping the word *hydrogen*, adding the prefix *hydro-* to the anion root, and changing the *-ide* ending to *-ic* followed by the word *acid*. Both types of names are illustrated in Table 4-5. Polyatomic anions that have an *-ide* ending are also named in the same manner as the binary acids. For example, the acid formed by the cyanide ion ( $\text{CN}^-$ ) has the formula  $\text{HCN}$  and is named hydrocyanic acid.

The following hydrogen compounds of anions listed in Figure 4-6 are not generally considered to be binary acids:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{PH}_3$ .

**TABLE 4-5** Binary Acids

| ANION           | FORMULA OF ACID      | COMPOUND NAME     | ACID NAME          |
|-----------------|----------------------|-------------------|--------------------|
| $\text{Cl}^-$   | $\text{HCl}$         | hydrogen chloride | hydrochloric acid  |
| $\text{F}^-$    | $\text{HF}$          | hydrogen fluoride | hydrofluoric acid  |
| $\text{I}^-$    | $\text{HI}$          | hydrogen iodide   | hydroiodic acid    |
| $\text{S}^{2-}$ | $\text{H}_2\text{S}$ | hydrogen sulfide  | hydrosulfuric acid |

TABLE 4-6 Oxyacids

| ANION                              | NAME OF ANION | FORMULA OF ACID                   | NAME OF ACID    |
|------------------------------------|---------------|-----------------------------------|-----------------|
| $\text{C}_2\text{H}_3\text{O}_2^-$ | acetate       | $\text{HC}_2\text{H}_3\text{O}_2$ | acetic acid     |
| $\text{CO}_3^{2-}$                 | carbonate     | $\text{H}_2\text{CO}_3$           | carbonic acid   |
| $\text{NO}_3^-$                    | nitrate       | $\text{HNO}_3$                    | nitric acid     |
| $\text{PO}_4^{3-}$                 | phosphate     | $\text{H}_3\text{PO}_4$           | phosphoric acid |
| $\text{ClO}_2^-$                   | chlorite      | $\text{HClO}_2$                   | chlorous acid   |
| $\text{ClO}_4^-$                   | perchlorate   | $\text{HClO}_4$                   | perchloric acid |
| $\text{SO}_3^{2-}$                 | sulfite       | $\text{H}_2\text{SO}_3$           | sulfurous acid  |
| $\text{SO}_4^{2-}$                 | sulfate       | $\text{H}_2\text{SO}_4$           | sulfuric acid   |

### 4-6.2 Oxyacids

The acids formed by combination of hydrogen with most of the polyatomic anions in Table 4-2 are known as **oxyacids** because they are formed from oxyanions. To name an oxyacid, we use the root of the anion to form the name of the acid. If the name of the oxyanion ends in *-ate*, it is changed to *-ic* followed by the word *-acid*. If the name of the anion ends in *-ite*, it is changed to *-ous* plus the word *-acid*. Most hydrogen compounds of oxyanions do not exist in the pure state as do the binary acids. Generally, only the acid name is used in the naming of these compounds. For example,  $\text{HNO}_3$  is called nitric acid, not hydrogen nitrate. Development of the acid name from the anion name is shown for some anions in Table 4-6.

In summary, acids are named as follows:

| Ending on anion | Change   | Anion example         | Acid Name                |
|-----------------|--|-----------------------|--------------------------|
| <i>-ide</i>     | add <i>hydro-</i> and<br>change ending to <i>-ic</i> | brom- <i>ide</i>      | <i>hydro-bromic acid</i> |
| <i>-ite</i>     | change ending to <i>-ous</i>                         | hypochlor- <i>ite</i> | hypochlorous acid        |
| <i>-ate</i>     | change ending to <i>-ic</i>                          | perchlor- <i>ate</i>  | perchloric acid          |

#### EXAMPLE 4-8

##### Naming Acids

Name the following acids:  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , and  $\text{HClO}$ .

##### PROCEDURE

Identify the type of acid and the typical ending of the anion (*-ide*, *-ate*, or *-ite*). Change the ending as appropriate and add the word *acid* to the name.

##### SOLUTION

| ACID                             | ANION                       | ANION NAME   | ACID NAME                |
|----------------------------------|-----------------------------|--------------|--------------------------|
| $\text{H}_2\text{Se}$            | $\text{Se}^{2-}$            | selenide     | <u>hydroselenic acid</u> |
| $\text{H}_2\text{C}_2\text{O}_4$ | $\text{C}_2\text{O}_4^{2-}$ | oxalate      | <u>oxalic acid</u>       |
| $\text{HClO}$                    | $\text{ClO}^-$              | hypochlorite | <u>hypochlorous acid</u> |

#### EXAMPLE 4-9

##### Writing Formulas of Acids

Give formulas for the following: permanganic acid, dichromic acid, and acetic acid.



**PROCEDURE**

Pay attention to the ending for each acid. Decide from what anion the acid is derived. Add enough hydrogens to that anion to balance the charge.

**SOLUTION**

| ACID NAME        | ANION NAME   | ANION                              | ACID                              |
|------------------|--------------|------------------------------------|-----------------------------------|
| permanganic acid | permanganate | $\text{MnO}_4^-$                   | $\text{HMnO}_4$                   |
| dichromic acid   | chromate     | $\text{Cr}_2\text{O}_7^{2-}$       | $\text{H}_2\text{Cr}_2\text{O}_7$ |
| acetic acid      | acetate      | $\text{C}_2\text{H}_3\text{O}_2^-$ | $\text{HC}_2\text{H}_3\text{O}_2$ |

**ANALYSIS**

It helps to have a few models on which to base the naming patterns. Many people are aware that HCl is hydrochloric acid and that  $\text{H}_2\text{SO}_4$  is sulfuric acid. These are among the most common of all acids. Use the principles of similarity to name other acids that resemble these in much the same fashion. HBr then becomes hydrobromic acid and  $\text{HBrO}_3$  becomes bromic acid.

**SYNTHESIS**

The hydrogen in a pure acid is not present as a positive ion. It forms a covalent bond to the anion. Since hydrogen is nearer the metal–nonmetal borderline, it is more metallic and is written first. When acids are present in aqueous (water) solutions, however, they do form positive hydrogen ions. This is what makes them distinctive compounds. Hydrogen can be present in compounds as a negative ion, however. What is it called when the hydrogen is negatively charged? A hydride (just as  $\text{Cl}^-$  would be called a chloride). In a molecule like acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , hydrogen is written in two separate locations. The first hydrogen is an acidic one. The next three are neutral, part of the covalent polyatomic anion. Consider the following three compounds: NaH, HI, and  $\text{CH}_4$ . These represent three different situations for hydrogen. NaH is a typical ionic compound where the hydrogen exists as a  $-1$  anion. HI is an acid that forms  $\text{H}^+$  and  $\text{I}^-$  ions in aqueous solution.  $\text{CH}_4$  is a typical molecular compound where the hydrogen is covalently bonded to the carbon. The hydrogens do not ionize in water, nor are they present as anions. We will learn more about this in Chapter 9.

**ASSESSING THE OBJECTIVE FOR SECTION 4-6**

**EXERCISE 4-6(A) KNOWLEDGE:** What changes are made to the name of an acidic compound whose anion would normally end in the following?

- (a) *-ide*    (b) *-ite*    (c) *-ate*

**EXERCISE 4-6(B) ANALYSIS:** What are the formulas of the following compounds?

- (a) acetic acid    (b) nitrous acid    (c) hydroiodic acid

**EXERCISE 4-6(C) ANALYSIS:** What are the names of the following compounds?

- (a)  $\text{H}_3\text{PO}_4$     (b)  $\text{HClO}$     (c)  $\text{HCN}$

**EXERCISE 4-6(D) SYNTHESIS:** Classify each compound as being an acid, a binary molecular compound, a binary ionic compound with either a representative or a variable cation, or an ionic compound with a polyatomic ion.

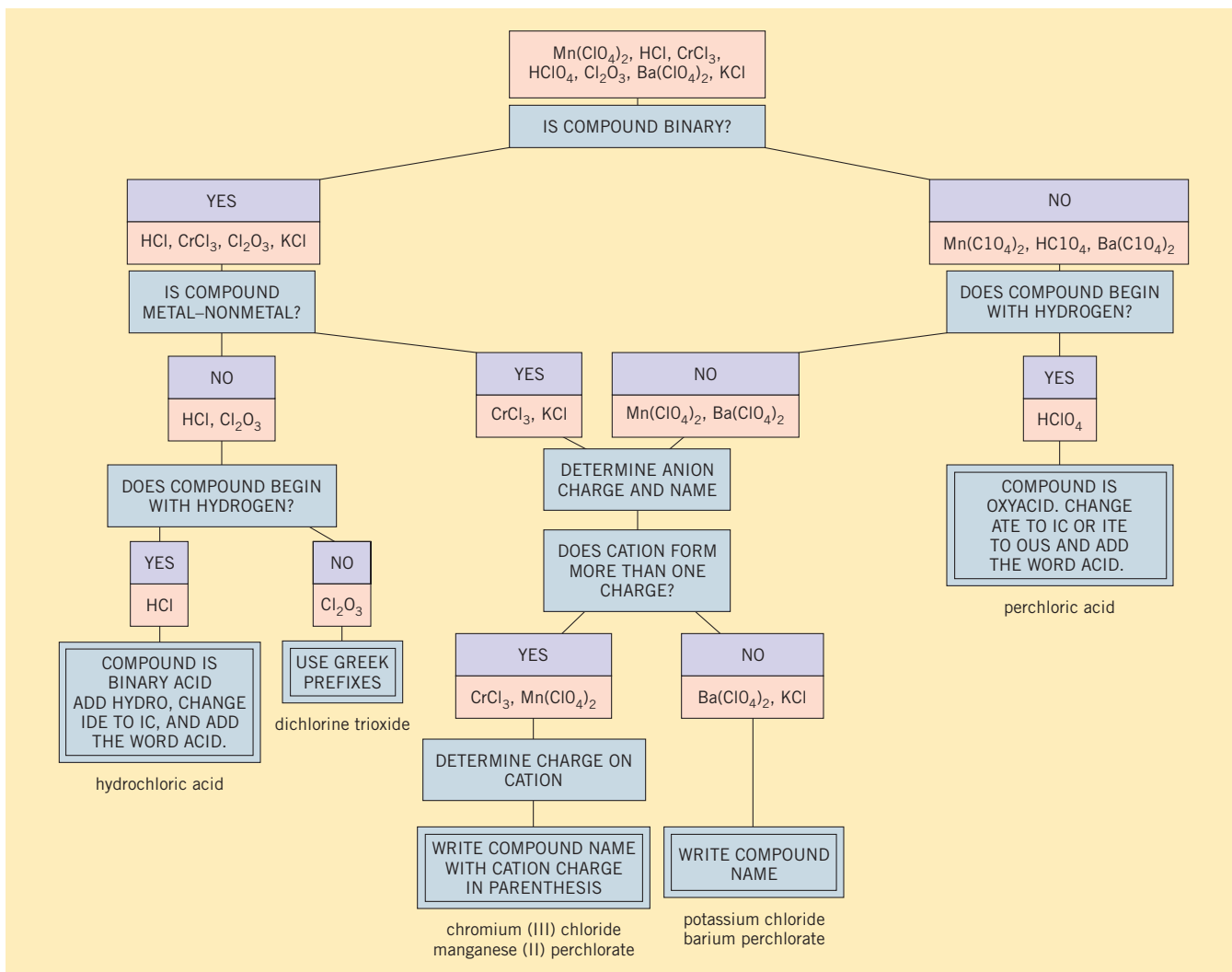
- (a)  $\text{SeBr}_4$     (c)  $\text{HNO}_3$     (e)  $\text{CS}_2$     (g)  $\text{K}_3\text{N}$   
 (b)  $\text{PbO}$     (d)  $\text{Mg}(\text{OH})_2$     (f)  $\text{AgNO}_3$     (h)  $\text{HF}$

For additional practice, work chapter problems 4-47 and 4-48.

**PART B SUMMARY****KEY TERMS**

- 4-3.2** Metals that have more than one charge are named by the **Stock method** or the **classical method**. p. 119
- 4-4.1** Most polyatomic anions are **oxyanions**. p. 122
- 4-5.2** Binary molecular compounds are named with the use of **Greek prefixes**. p. 125
- 4-6** **Acids** are compounds that produce in  $\text{H}^+$  ion in aqueous solution. p. 127
- 4-6.1** **Binary acids** contain hydrogen combined with a monatomic anion. p. 127
- 4.6.2** **Oxyacids** contain hydrogen combined with an oxyanion. p. 128

## SUMMARY CHART



## CHAPTER SUMMARY

There is no more important time-saving device for the chemist than the **periodic table**, which demonstrates in table form the **periodic law** for the elements. One important function of the periodic table is that it shows a clear boundary between elements that are classified as **metals** and **nonmetals**. Some metals and nonmetals have intermediate characteristics and may be referred to as **metalloids**.

Horizontal rows are known as **periods**, and vertical columns are known as **groups**. Although there are four categories of elements in the table, the category that we will emphasize in the text is the **main group** or **representative elements**. This category includes some named groups such as the **alkali metals**, the **alkaline earth metals**, and the **halogens**. The other three categories are the **noble gases**, the **transition metals**, and the **inner transition metals**. The last category includes the **lanthanides** and the **actinides**.

All three physical states are found among the elements at the reference temperature of 25°C, or **room temperature**.

Some of the nonmetals also exist as molecules rather than individual atoms at the reference temperature.

Our first important use of the periodic table is to aid us in **chemical nomenclature** by determining the type of chemical compound we are attempting to name. For example, binary compounds containing a metal and a nonmetal are named differently from those composed of two nonmetals. Also, all metals form cations, but some form only one charge and others form more than one. In using the **Stock method** of nomenclature, we need the periodic table to tell us which metals are in the latter group. The **classical method** is still used in the medical field. In addition to the binary compounds, we discussed the naming of **salts** containing **oxyanions**. Binary molecular compounds are named using **Greek prefixes** rather than the Stock method. Finally, a class of hydrogen compounds called **acids** (both **binary** and **oxyacids**) was discussed as a special group of molecular compounds.

| SECTION | YOU SHOULD BE ABLE TO...  | OBJECTIVES         |                    |                                |
|---------|---|--------------------|--------------------|--------------------------------|
|         |   | EXAMPLES           | EXERCISES          | CHAPTER PROBLEMS               |
| 4-1     | Describe the origins of the periodic table.   |                    | 1a, 1b             |                                |
| 4-2     | Using the periodic table, identify a specific element as a metal or nonmetal and give its period, group number, the name of the group if appropriate, and its physical state. |                    | 2a, 2b, 2c, 2d     | 3, 4, 6, 7, 9, 11, 14, 15      |
| 4-3     | Write and name ionic compounds involving a metal and nonmetal using IUPAC conventions.  | 4-1, 4-2, 4-3, 4-4 | 3a, 3b, 3c, 3d, 6d | 18, 19, 20, 21, 22, 23, 24, 25 |
| 4-4     | Write and name compounds containing polyatomic ions using IUPAC conventions.  | 4-5, 4-6           | 4a, 4b, 4c, 6d     | 32, 33, 34, 35, 36, 38, 40     |
| 4-5     | Name binary molecular (nonmetal–nonmetal) compounds using proper Greek prefixes.  | 4-7                | 5a, 5b, 5c, 6d     | 41, 43, 44, 45, 46             |
| 4-6     | Name and write the formulas of acids.   | 4-8, 4-9           | 6a, 6b, 6c, 6d     | 47, 48, 49, 50                 |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**4-1(a)** The periodic table was first displayed by Dimitri Mendeleev in the year 1869. Elements are grouped vertically into families that share the same chemical properties. Metals are lustrous and malleable. Nonmetals are dull and brittle.

**4-1(b)** Mendeleev chose to focus on chemical properties rather than physical properties, and he was not afraid to shift things around when those properties didn't line up. He also correctly assumed that not all elements had been discovered at that time, so left spaces in his table to be filled in later.

**4-2(a)** Of the two general classifications of elements, nickel is a metal and sulfur is a nonmetal. Some borderline elements such as germanium are sometimes referred to as metalloids. In the periodic table, elements are ordered according to increasing atomic number so that families of elements fall into vertical columns. Of the four general categories of elements, calcium is a representative element, nickel is a transition metal, and xenon is a noble gas. An element in Group IIA, such as calcium, is also known as an alkaline earth metal. A solid nonmetal that is composed of diatomic molecules is in the group known as the halogens. Metals are all solids except for mercury.

**4-2(b)** (a) transition metal, Cu, solid, metal, fourth period, Group IB (b) noble gas, Ar, gas, nonmetal, third period, Group VIIIA (c) representative element, Ba, solid, metal, sixth period, Group IIA (d) representative element, Br, liquid, nonmetal, fourth period, Group VIIA (e) inner transition metal, U, solid, metal, seventh period, no group number

**4-2(c)** (a) calcium (b) bromine (c) boron (d) cadmium (e) oxygen

**4-2(d)** 118: noble gas, gas, seventh period, VIIIA, nonmetal  
119: representative element, solid, eighth period, IA, metal

## PART B

## EXERCISES

**4-3(a)** Co and Sn

**4-3(b)** (a) lithium oxide (d) magnesium nitride  
(b) chromium(III) iodide (e) nickel(II) phosphide  
(c) lead(II) sulfide

**4-3(c)** (a)  $\text{AlI}_3$  (b)  $\text{Fe}_2\text{O}_3$  (c)  $\text{SnBr}_4$  (d)  $\text{Ca}_3\text{N}_2$

**4-3(d)**  $\text{MX}$ ,  $\text{MX}_2$ ,  $\text{MX}_3$ ,  $\text{M}_2\text{X}$ ,  $\text{M}_2\text{X}_3$ ,  $\text{M}_3\text{X}$ ,  $\text{M}_3\text{X}_2$

**4-4(a)** (a) nitrite (b) hydroxide (c) acetate  
(d) phosphate (e) bisulfate

**4-4(b)** (a)  $\text{Ni}(\text{CN})_2$  (b)  $\text{Al}_2(\text{SO}_3)_3$  (c)  $\text{Mg}(\text{HCO}_3)_2$   
(d)  $\text{Fe}(\text{ClO}_4)_3$  (e)  $(\text{NH}_4)_3\text{PO}_4$

**4-4(c)** (a) barium hydroxide (b) lithium dihydrogen phosphate  
(c) silver(I) hypochlorite (d) potassium chromate  
(e) cobalt(III) carbonate

**4-5(a)** (a) mono (b) tetra (c) hexa (d) deca

**4-5(b)** (a)  $\text{CCl}_4$  (b)  $\text{PBr}_5$  (c)  $\text{SO}_2$  (d) CO

**4-5(c)** (a) silicon disulfide (b) diphosphorus pentoxide  
(c) boron trifluoride (d) arsenic trihydride

**4-6(a)** (a) *-ide* → *hydro-* *-ic acid*  
(b) *-ite* → *-ous acid* (c) *-ate* → *-ic acid*

**4-6(b)** (a)  $\text{HC}_2\text{H}_3\text{O}_2$  (b)  $\text{HNO}_2$  (c) HI

**4-6(c)** (a) phosphoric acid (c) hydrocyanic acid  
(b) hypochlorous acid

**4-6(d)** (a) binary molecular compound (b) ionic compound with a variable cation  
(c) acid (with an oxyanion)  
(d) ionic compound with a representative cation and a polyatomic anion  
(e) binary molecular compound (f) ionic compound with a variable cation and a polyatomic anion  
(g) ionic compound with a representative cation (h) acid (binary)

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## The Periodic Table (SECTION 4-2)

**4-1.** How is an active metal different from a noble metal?

**4-2.** How many elements would be in the seventh period if it were complete?

**4-3.** Which of the following elements are halogens?

- (a) O<sub>2</sub>            (c) I<sub>2</sub>            (e) Li            (g) Br<sub>2</sub>  
 (b) P<sub>4</sub>            (d) N<sub>2</sub>            (f) H<sub>2</sub>

**4-4.** Which of the following elements are alkaline earth metals?

- (a) Sr            (c) B            (e) Na  
 (b) C            (d) Be            (f) K

**4-5.** Classify the following elements into one of the four main categories of elements.

- (a) Fe            (c) Pm            (e) Xe            (g) In  
 (b) Te            (d) La            (f) H

**4-6.** Classify the following elements into one of the four main categories of elements.

- (a) Se            (c) Ni            (e) Zn            (g) Er  
 (b) Ti            (d) Sr            (f) I

**4-7.** Which of the following elements are transition metals?

- (a) In            (c) Ca            (e) Pd            (g) Ag  
 (b) Ti            (d) Xe            (f) Tl

## Physical States of the Elements (SECTION 4-2)

**4-8.** What is the most common physical state of the elements at room temperature? Which are more common, metals or nonmetals?

**4-9.** Which metals, if any, are gases at room temperature? Which metals, if any, are liquids? Which nonmetals, if any, are liquids at room temperature?

**4-10.** Referring to Figure 4-5, tell which of the following are gases at room temperature.

- (a) Ne            (c) B            (e) Br            (g) Na  
 (b) S            (d) Cl            (f) N

**4-11.** Referring to Figure 4-5, tell which of the following elements exist as diatomic molecules under normal conditions.

- (a) N            (c) Ar            (e) H            (g) Xe  
 (b) C            (d) F            (f) B            (h) Hg

**4-12.** Referring to Figure 4-4, tell which of the following elements are metals.

- (a) Ru            (c) Hf            (e) Ar            (g) Se  
 (b) Sn            (d) Te            (f) B            (h) W

**4-13.** Which, if any, of the elements in problem 4-12 can be classified as a metalloid?

**4-14.** Identify the following elements using the information in Figures 4-4 and 4-5.

- (a) a nonmetal, monatomic gas in the third period

- (b) a transition metal that is a liquid  
 (c) a diatomic gas in Group VA  
 (d) the second metal in the second period  
 (e) the only member of a group that is a metal

**4-15.** Identify the following elements using the information in Figures 4-4 and 4-5.

- (a) a nonmetal, diatomic liquid  
 (b) the last element in the third period  
 (c) a nonmetal, diatomic solid  
 (d) the only member of a group that is a nonmetal

**4-16.** What would be the atomic number and group number of the next nonmetal after element 112? (Assume that the border between metals and nonmetals continues as before.)

**4-17.** What is the atomic number of the metal farthest to the right in the periodic table that would appear after element 112?

## Metal–Nonmetal Binary Compounds

## (SECTION 4-3)

**4-18.** Name the following compounds.

- (a) LiF            (c) Sr<sub>3</sub>N<sub>2</sub>            (e) AlCl<sub>3</sub>  
 (b) BaTe            (d) BaH<sub>2</sub>

**4-19.** Name the following compounds.

- (a) CaI<sub>2</sub>            (c) BeSe            (e) RaS  
 (b) FrF            (d) Mg<sub>3</sub>P<sub>2</sub>

**4-20.** Give formulas for the following compounds.

- (a) rubidium selenide            (d) aluminum carbide  
 (b) strontium hydride            (e) beryllium fluoride  
 (c) radium oxide

**4-21.** Give formulas for the following compounds.

- (a) potassium hydride            (c) potassium phosphide  
 (b) cesium sulfide            (d) barium telluride

**4-22.** Name the following compounds using the Stock method.

- (a) Bi<sub>2</sub>O<sub>5</sub>            (c) SnS<sub>2</sub>            (e) TiC  
 (b) SnS            (d) Cu<sub>2</sub>Te

**4-23.** Name the following compounds using the Stock method.

- (a) CrI<sub>3</sub>            (c) IrO<sub>4</sub>            (e) NiCl<sub>2</sub>  
 (b) TiCl<sub>4</sub>            (d) MnH<sub>2</sub>

**4-24.** Give formulas for the following compounds.

- (a) copper(I) sulfide            (d) nickel(II) carbide  
 (b) vanadium(III) oxide            (e) chromium(VI) oxide  
 (c) gold(I) bromide

**4-25.** Give formulas for the following compounds.

- (a) yttrium(III) hydride            (c) bismuth(V) fluoride  
 (b) lead(IV) chloride            (d) palladium(II) selenide

**4-26.** From the magnitude of the charges on the metals, predict which of the compounds in problems 4-22 and 4-24 may be molecular compounds.

**4-27.** From the magnitude of the charges on the metals, predict which of the compounds in problems 4-23 and 4-25 may be molecular compounds.

### Compounds with Polyatomic Ions (SECTION 4-4)

**4-28.** Which of the following is the chlorate ion?

- (a)  $\text{ClO}_2^-$       (c)  $\text{ClO}_3^-$       (e)  $\text{ClO}_3^+$   
 (b)  $\text{ClO}_4^-$       (d)  $\text{Cl}_3\text{O}^-$

**4-29.** Which of the following ions have a  $-2$  charge?

- (a) sulfate      (c) chlorite      (e) sulfite  
 (b) nitrite      (d) carbonate      (f) phosphate

**4-30.** What are the name and formula of the most common polyatomic cation?

**4-31.** Which of the following oxyanions contain four oxygen atoms?

- (a) nitrate      (d) sulfite      (g) carbonate  
 (b) permanganate      (e) phosphate  
 (c) perchlorate      (f) oxalate

**4-32.** Name the following compounds. Use the Stock method where appropriate.

- (a)  $\text{CrSO}_4$       (d)  $\text{RbHCO}_3$       (g)  $\text{Bi}(\text{OH})_3$   
 (b)  $\text{Al}_2(\text{SO}_3)_3$       (e)  $(\text{NH}_4)_2\text{CO}_3$   
 (c)  $\text{Fe}(\text{CN})_2$       (f)  $\text{NH}_4\text{NO}_3$

**4-33.** Name the following compounds. Use the Stock method where appropriate.

- (a)  $\text{Na}_2\text{C}_2\text{O}_4$       (c)  $\text{Fe}_2(\text{CO}_3)_3$   
 (b)  $\text{CaCrO}_4$       (d)  $\text{Cu}(\text{OH})_2$

**4-34.** Give formulas for the following compounds.

- (a) magnesium permanganate  
 (b) cobalt(II) cyanide  
 (c) strontium hydroxide  
 (d) thallium(I) sulfite  
 (e) iron(III) oxalate  
 (f) ammonium dichromate  
 (g) mercury(I) acetate [The mercury(I) ion exists as  $\text{Hg}_2^{2+}$ .]

**4-35.** Give formulas for the following compounds.

- (a) zirconium(IV) phosphate  
 (b) sodium cyanide  
 (c) thallium(I) nitrite  
 (d) nickel(II) hydroxide  
 (e) radium hydrogen sulfate  
 (f) beryllium phosphate  
 (g) chromium(III) hypochlorite

**4-36.** Complete the following table. Write the appropriate anion at the top and the appropriate cation to the left. Write the formulas and names in other blanks as is done in the upper-left-hand box.

|                     |  |                              |   |
|---------------------|--|------------------------------|---|
| <b>Cation/Anion</b> | $\text{HSO}_3^-$                                   | _____                        | _____                                   |
| $\text{NH}_4^+$     | $\text{NH}_4\text{HSO}_3$<br>ammonium<br>bisulfite | _____                        | _____                                   |
| _____               | _____  | $\text{CoTe}$<br>_____(name) | _____                                   |
| _____               | _____  | _____                        | _____(formula)<br>aluminum<br>phosphate |

**4-37.** Complete the following table. Write the appropriate anion at the top and the appropriate cation to the left. Write the formulas and names in other blanks as is done in the upper-left-hand box.

|                     |  |                             |                    |
|---------------------|--|-----------------------------|--------------------|
| <b>Cation/Anion</b> | _____                                      | $\text{C}_2\text{O}_4^{2-}$ | _____              |
| _____               | _____(formula)<br>thallium(I)<br>hydroxide | _____                       | _____              |
| $\text{Sr}^{2+}$    | _____                                      | _____                       | _____              |
| _____               | _____                                      | _____                       | TiN<br>_____(name) |

**4-38.** Give the systematic name for each of the following.

| <i>Common Name</i>      | <i>Formula</i>           |
|-------------------------|--------------------------|
| (a) table salt          | $\text{NaCl}$            |
| (b) baking soda         | $\text{NaHCO}_3$         |
| (c) marble or limestone | $\text{CaCO}_3$          |
| (d) lye                 | $\text{NaOH}$            |
| (e) chile saltpeter     | $\text{NaNO}_3$          |
| (f) sal ammoniac        | $\text{NH}_4\text{Cl}$   |
| (g) alumina             | $\text{Al}_2\text{O}_3$  |
| (h) slaked lime         | $\text{Ca}(\text{OH})_2$ |
| (i) caustic potash      | $\text{KOH}$             |

**4-39.** The perzenate ion has the formula  $\text{XeO}_6^{4-}$ . Write formulas of compounds of perzenate with the following.

- (a) calcium      (b) potassium      (c) aluminum

**\*4-40.** Name the following compounds. In these compounds, an ion is involved that is not in Table 4-2. However, the name can be determined by reference to other ions of the central element or from ions in Table 4-2 in which the central atom is in the same group.

- (a)  $\text{PH}_4\text{F}$       (c)  $\text{Co}(\text{IO}_3)_3$       (e)  $\text{AlPO}_3$   
 (b)  $\text{KBrO}$       (d)  $\text{CaSiO}_3$       (f)  $\text{CrMoO}_4$

### Nonmetal–Nonmetal Binary Compounds

#### (SECTION 4-5)

**4-41.** The following pairs of elements combine to form binary compounds. Which element should be written and named first?

- (a) Si and S      (c) H and Se      (e) H and F  
 (b) F and I      (d) Kr and F      (f) H and As



**4-42.** The following pairs of elements combine to make binary compounds. Which element should be written and named first?

- (a) S and P (c) O and Br  
(b) O and S (d) As and Cl

**4-43.** Name the following.

- (a) CS<sub>2</sub> (c) P<sub>4</sub>O<sub>10</sub> (e) SO<sub>3</sub> (g) PCl<sub>5</sub>  
(b) BF<sub>3</sub> (d) Br<sub>2</sub>O<sub>3</sub> (f) Cl<sub>2</sub>O (h) SF<sub>6</sub>

**4-44.** Name the following.

- (a) PF<sub>3</sub> (c) ClO<sub>2</sub> (e) SeCl<sub>4</sub>  
(b) I<sub>2</sub>O<sub>3</sub> (d) AsF<sub>5</sub> (f) SiH<sub>4</sub>

**4-45.** Write the formulas for the following.

- (a) tetraphosphorus hexoxide (d) dichlorine heptoxide  
(b) carbon tetrachloride (e) sulfur hexafluoride  
(c) iodine trifluoride (f) xenon dioxide

**4-46.** Write formulas for the following.

- (a) xenon trioxide  
(b) sulfur dichloride  
(c) dibromine monoxide  
(d) carbon disulfide  
(e) diboron hexahydride (also known as diborane)

### Naming Acids (SECTION 4-6)

**4-47.** Name the following acids.

- (a) HCl (c) HClO (e) HIO<sub>4</sub>  
(b) HNO<sub>3</sub> (d) HMnO<sub>4</sub> (f) HBr

**4-48.** Write formulas for the following acids.

- (a) hydrocyanic acid (d) carbonic acid  
(b) hydroselenic acid (e) hydroiodic acid  
(c) chlorous acid (f) acetic acid

**4-49.** Write formulas for the following acids.

- (a) oxalic acid (c) dichromic acid  
(b) nitrous acid (d) phosphoric acid

**\*4-50.** Refer to the ions in problems 4-39 and 4-40. Write the acid names for the following.

- (a) HBrO (c) H<sub>3</sub>PO<sub>3</sub> (e) H<sub>4</sub>XeO<sub>6</sub>  
(b) HIO<sub>3</sub> (d) HMnO<sub>4</sub>

**\*4-51.** Write the formulas and the names of the acids formed from the arsenite (AsO<sub>3</sub><sup>3-</sup>) ion and the arsenate (AsO<sub>4</sub><sup>3-</sup>) ion.

### General Problems

**4-52.** A gaseous compound is composed of two oxygens and one chlorine. It has been used to kill anthrax spores in contaminated buildings. Write the formula of the compound and give its name.

**4-53.** The halogen (A<sub>2</sub>) with the lowest atomic number forms a compound with another halogen (X<sub>2</sub>) that is a liquid at room temperature. The compound has the formula A<sub>5</sub>X or XA<sub>5</sub>. Write the correct formula with the actual elemental symbols and the name.

**4-54.** A metal that has only a +2 ion and is the third member of the group forms a compound with a nonmetal that has a -2 ion and is in the same period. What are the formula and name of the compound?

**4-55.** The only gas in a certain group forms a compound with a metal that has only a +3 ion. The compound contains one ion of each element. What are the formula and name of the compound? What are the formula and name of the compound the gas forms with a Ti<sup>2+</sup> ion?

**4-56.** An alkali metal in the fourth period forms a compound with the phosphide ion. What are the formula and name of the compound?

**4-57.** A transition metal ion with a charge of +2 has 25 electrons. It forms a compound with a nonmetal that has only a -1 ion. The anion has 36 electrons. What are the formula and name of the compound?

**4-58.** The lightest element forms a compound with a certain metal in the third period that has a +2 ion and with a nonmetal in the same period that has a -2 ion. What are the formulas and names of the two compounds?

**4-59.** The thiosulfate ion has the formula S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. What are the formula and name of the compound formed between the thiosulfate ion and an Rb ion; an Al ion; an Ni<sup>2+</sup> ion; and a Ti<sup>4+</sup> ion? What are the formula and name of the acid formed from the thiosulfate ion?

**4-60.** Name the following compounds: NiI<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, Sr(ClO<sub>3</sub>)<sub>2</sub>, H<sub>2</sub>Te, As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, and SnC<sub>2</sub>O<sub>4</sub>.

**4-61.** Name the following compounds: SiO<sub>2</sub>, SnO<sub>2</sub>, MgO, Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, HClO<sub>2</sub>, BaSO<sub>4</sub>, and HI.

**4-62.** Give formulas for the following compounds: tin(II) hypochlorite, chromic acid, xenon hexafluoride, barium nitride, hydrofluoric acid, iron(III) carbide, and lithium phosphate.

**4-63.** Which of the following is composed of a metal that can have one charge and a polyatomic ion?

- (a) H<sub>2</sub>CO<sub>3</sub> (c) B<sub>2</sub>O<sub>3</sub> (e) Rb<sub>2</sub>C<sub>2</sub>O<sub>4</sub>  
(b) Ca<sub>2</sub>C (d) V(NO<sub>3</sub>)<sub>3</sub>

**4-64.** Which of the following is composed of a metal that can have more than one charge and a monatomic anion?

- (a) Ti(ClO<sub>4</sub>)<sub>2</sub> (c) Cu<sub>2</sub>Se (e) MgCrO<sub>4</sub>  
(b) Mg<sub>2</sub>S (d) H<sub>2</sub>Se

**4-65.** The peroxide ion has the formula O<sub>2</sub><sup>2-</sup>. What are the formulas of compounds formed with Rb, Mg, Al, and Ti<sup>4+</sup>? What is the formula of the acid for this anion? What is the name of this compound as a pure compound and as an acid?

**4-66.** The cyanamide ion has the formula CN<sub>2</sub><sup>2-</sup>. What are the formulas of compounds formed with Li, Ba, Sc<sup>3+</sup>, and Sn<sup>4+</sup>? What is its formula as an acid? What is the name of this compound as a pure compound and as an acid?

**4-67.** Give the formulas of the following common compounds.

- (a) sodium carbonate (d) aluminum nitrate  
(b) calcium chloride (e) calcium hydroxide  
(c) potassium perchlorate (f) ammonium chloride

**4-68.** Give the names of the following common compounds.

- (a)  $\text{TiCl}_4$                       (d)  $\text{Mg}(\text{OH})_2$                       (g)  $\text{NaClO}_4$   
 (b)  $\text{NH}_4\text{NO}_3$                       (e)  $\text{HNO}_3$   
 (c)  $\text{LiH}$                               (f)  $\text{H}_2\text{SO}_4$

**4-69.** Nitrogen is found in five ions mentioned in this chapter. Write the formulas and names of these ions.

**4-70.** Carbon is found in six ions mentioned in this chapter. Write the formulas and names of these ions.

**4-71.** Which of the following is the correct name for  $\text{Cr}_2(\text{CO}_3)_3$ ?

- (a) dichromium tricarbonat  
 (b) chromium carbonate  
 (c) chromium(II) carbonate  
 (d) chromium(III) tricarbonat  
 (e) chromium(III) carbonate

**4-72.** Which of the following is the correct name for  $\text{SiCl}_4$ ?

- (a) sulfur tetrachloride                      (d) sulfur chloride  
 (b) silicon tetrachloride                      (e) silicon chloride  
 (c) silicon(IV) chloride

**4-73.** Which of the following is the correct name for  $\text{Ba}(\text{ClO}_2)_2$ ?

- (a) barium dichlorite                      (d) barium chlorite(II)  
 (b) barium(II) chlorite                      (e) barium chlorate  
 (c) barium chlorite

**4-74.** Which of the following is the correct name for  $\text{H}_2\text{CrO}_4$ ?

- (a) hydrogen(I) chromate                      (d) dichromic acid  
 (b) hydrogen chromate                      (e) dihydrogen chromate  
 (c) chromic acid                              (f) chromous acid

## STUDENT WORKSHOP

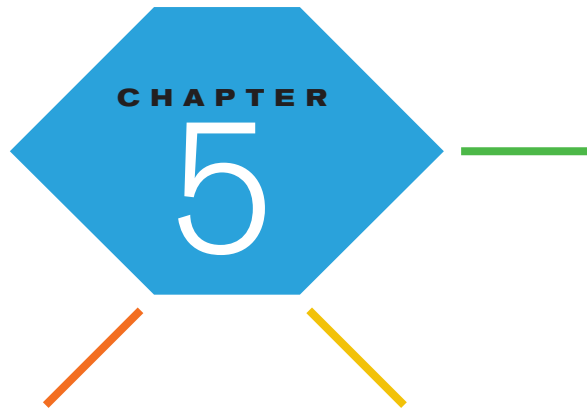
### A new Periodic Table

**Purpose:** To create a Table that illustrates the relationships in properties between elements. (Work in groups of three or four. Estimated time: 40 min.)

- Cut heavy cardstock into 18 equal-sized squares, approximately 2 in. per side. Onto each of them, transfer the data from one line in the following table.

| Melting Point | Boiling Point | Density | Mass | Formula with Cl  | Formula with O                |
|---------------|---------------|---------|------|------------------|-------------------------------|
| -272          | -269          | 0.18    | 4    | None             | None                          |
| -259          | -253          | 0.09    | 1    | XCl              | X <sub>2</sub> O              |
| -249          | -246          | 0.90    | 20   | None             | None                          |
| -220          | -188          | 1.70    | 19   | None             | X <sub>2</sub> O              |
| -218          | -183          | 1.43    | 16   | None             | None                          |
| -210          | -196          | 1.25    | 14   | XCl <sub>3</sub> | Multiple                      |
| -189          | -186          | 1.78    | 40   | None             | None                          |
| -101          | -35           | 3.21    | 36   | None             | Multiple                      |
| 44            | 280           | 1.82    | 31   | XCl <sub>3</sub> | Multiple                      |
| 98            | 553           | 0.97    | 23   | XCl              | X <sub>2</sub> O              |
| 113           | 445           | 2.07    | 32   | Multiple         | Multiple                      |
| 180           | 1347          | 0.53    | 7    | XCl              | X <sub>2</sub> O              |
| 650           | 1107          | 1.74    | 24   | XCl <sub>2</sub> | XO                            |
| 660           | 2467          | 2.70    | 27   | XCl <sub>3</sub> | X <sub>2</sub> O <sub>3</sub> |
| 1278          | 2970          | 1.85    | 9    | XCl <sub>2</sub> | XO                            |
| 1410          | 2355          | 2.33    | 28   | XCl <sub>4</sub> | XO <sub>2</sub>               |
| 2300          | 2550          | 2.34    | 11   | XCl <sub>3</sub> | X <sub>2</sub> O <sub>3</sub> |
| 3500          | 4827          | 2.62    | 12   | XCl <sub>4</sub> | XO, XO <sub>2</sub>           |

- Arrange the cards into rows and columns using whatever information seems relevant. Try to use at least one property for your rows and one for your columns to establish a pattern.
- Be prepared to discuss your arrangement and give justifications for it. Have any other patterns emerged other than the two that you used to establish rows and columns?



# Chemical Reactions



In the rain forest a cycle of life occurs. Green leaves, powered by sunlight, maintain life. The decay of dead trees returns the ingredients for life to the air and earth.

## PART A

### THE REPRESENTATION OF CHEMICAL CHANGES AND THREE TYPES OF CHANGES

#### 5-1 Chemical Equations

#### 5-2 Combustion, Combination, and Decomposition Reactions



#### MAKING IT REAL

*Life Where the Sun Doesn't Shine—  
Chemosynthesis*

## PART B

### IONS IN WATER AND HOW THEY REACT

#### 5-3 The Formation of Ions in Water

#### 5-4 Single-Replacement Reactions

#### 5-5 Double-Replacement Reactions—Precipitation



#### MAKING IT REAL

*Hard Water and Water Treatment*

#### 5-6 Double-Replacement Reactions—Neutralization

**SETTING THE STAGE** The weather seems to be crazy lately. More violent storms, record floods, melting at the poles, and even severe droughts seem to be happening regularly. Indeed, the past 15 years or so have been the warmest on record. All of this may be related to what we call global warming. Most scientists agree that the surface of the planet is warming, and at least part of that is due to the increase in carbon dioxide in the atmosphere.

Carbon dioxide is naturally removed from the atmosphere by the oceans and ocean life and also by trees and other vegetation. In a complex series of chemical reactions called *photosynthesis*, green leaves use energy from the sun, carbon dioxide, and water to produce carbohydrates (carbon, hydrogen, and oxygen compounds) along with elemental oxygen. These compounds can then undergo a type of chemical reaction called *combustion*. In this reaction, the carbon compounds from trees or fossil fuels (coal, oil, and natural gas) combine with oxygen in the air to re-form carbon dioxide and water and release the heat energy that originated from the sun. This fascinating cycle of chemical reactions maintains life on this beautiful planet.

The problem is that things have gotten out of balance in the past 150 years since the Industrial Revolution. There is considerably more combustion going on in our world than photosynthesis, so the level of carbon dioxide in the atmosphere is definitely increasing. Carbon dioxide is a gas that traps heat in the atmosphere much as heat is trapped inside a closed automobile on a sunny day. This is referred to as the greenhouse effect. The existence of over 6 billion people on our globe, all burning fuel and needing space at the expense of forests, assures that the balance will remain in favor of combustion.

Photosynthesis and combustion are only two types of chemical changes. In fact, the atoms of the elements combine, separate, and recombine in millions of ways, all indicating unique chemical changes. The rusting of iron, the decay of a fallen tree in the forest, the formation of muscle in our bodies, the cooking of food—all of these everyday, common occurrences are chemical changes.

Many of the more important chemical reactions on this planet occur in a water (aqueous) medium. Water has a unique ability to hold ionic and polar compounds in solution. Much of the chemistry that occurs in our bodies is a result of the interaction of these compounds circulating in our bloodstream. So it seems appropriate to take a deeper look at the particular chemistry that occurs in aqueous solution.

In Part A, we will introduce the chemical equation, how it is balanced, and three simple types of reactions. Types of reactions are extended in Part B to include the many and important types of reactions that occur in water.

**PART A**  
**THE REPRESENTATION OF**  
**CHEMICAL CHANGES AND**  
**THREE TYPES OF CHANGES**

**SETTING A GOAL**

- You will begin to use the symbolic language of chemistry by writing balanced chemical equations for several identifiable reaction types.

**OBJECTIVES**

- 5-1 (a)** Write a chemical equation from a word description of the reaction. **(b)** Balance a simple chemical equation by inspection.
- 5-2** Classify certain chemical reactions as being combustion, combination, or decomposition reactions.

▶ **OBJECTIVES FOR**  
**SECTION 5-1**

- (a)** Write a chemical equation from a word description of the reaction.  
**(b)** Balance a simple chemical equation by inspection.

## 5-1 CHEMICAL EQUATIONS

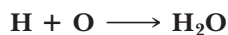


**LOOKING AHEAD!** The main rocket thruster of the space shuttle uses a simple but powerful chemical reaction. Hydrogen combines with oxygen to form water and a lot of heat energy. The way chemical reactions such as this are symbolized is the topic of this section. ■

### 5-1.1 Constructing an Equation

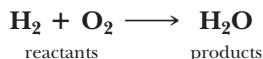
A **chemical equation** is the representation of a chemical reaction using the symbols of elements and the formulas of compounds. In the following discussion, we will focus on the matter that undergoes a change in the reaction. In Chapter 7, we will include the heat energy involved.

We will build the chemical equation that represents the reaction in the space shuttle one step at a time. First, let's represent with symbols the reaction of hydrogen combining with oxygen to form water.



In a chemical equation, *the original reacting species are shown to the left of the arrow and are called the reactants. The species formed as a result of the reaction are to the right of the arrow and are called the products.* In this format, note that the phrase *combines with* (or *reacts with*) is represented by a plus sign (+). When there is more than one reactant or product, the symbols or formulas on each side of the equation are separated by a +. The word *produces* (or *yields*) may be represented by an arrow ( $\longrightarrow$ ). Note in Table 5-1 that there are other representations for the yield sign, depending on the situation.

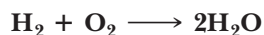
The chemical equation shown above tells us only about the elements involved. However, we know more information than just the elements involved. First, if an element exists as molecules under normal conditions, then the formula of the molecule is shown. Recall from Chapter 4 that both hydrogen and oxygen exist as diatomic molecules under normal conditions. Including this information, the equation is



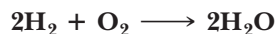
An important duty of a chemical equation is to demonstrate faithfully the law of conservation of mass, which states that *mass can be neither created nor destroyed*. In Dalton's atomic theory, this law was explained for chemical reactions. He suggested that reactions are simply rearrangements of the same number of atoms. A close look at the equation above shows that there are two oxygen atoms on the left but only one on the right. To conform to the law of conservation of mass, an equation must be



balanced. A **balanced equation** has the same number and type of atoms on both sides of the equation. An equation is balanced by introducing **coefficients**. Coefficients are whole numbers in front of the symbols or formulas. The equation in question is balanced in two steps. If we introduce a 2 in front of the  $\text{H}_2\text{O}$ , we have equal numbers of oxygen atoms, but the number of hydrogen atoms is now unbalanced.

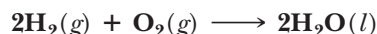


This problem can be solved rather easily. Simply return to the left and place a coefficient of 2 in front of the  $\text{H}_2$ . The equation is now completely balanced.



Note that equations cannot be balanced by changing or adjusting the subscripts of the elements or compounds. For example, the original equation could seem to be balanced in one step if the  $\text{H}_2\text{O}$  were changed to  $\text{H}_2\text{O}_2$ . However,  $\text{H}_2\text{O}_2$  is a compound known as hydrogen peroxide. This is a popular anti-septic but not the same as water.

Finally, the physical states of the reactants and products under the reaction conditions are sometimes added in parentheses after the formula for each substance. Hydrogen and oxygen are gases, and water is a liquid at room temperature. Using the proper letters shown in Table 5-1, we have the balanced chemical equation in proper form.



Note that if we describe this reaction in words, we have quite a bit to say. “Two molecules of gaseous hydrogen react with one molecule of gaseous oxygen to produce two molecules of liquid water.”



A powerful chemical reaction blasts the space shuttle into Earth orbit.

**TABLE 5-1** Symbols in the Chemical Equation

| SYMBOL                       | USE   |
|------------------------------|---|
| +                            | Between the symbols and/or formulas of reactants or products  |
| $\longrightarrow$            | Means “yields” or “produces”; separates reactants from products   |
| =                            | Same as arrow   |
| $\rightleftharpoons$         | Used for reversible reactions in place of a single arrow (see Chapter 14)   |
| (g)                          | Indicates a gaseous reactant or product   |
| $\uparrow$                   | Sometimes used to indicate a gaseous product  |
| (s)                          | Indicates a solid reactant or product   |
| $\downarrow$                 | Sometimes used to indicate a solid product  |
| (l)                          | Indicates a liquid reactant or product  |
| (aq)                         | Indicates that the reactant or product is in aqueous solution (dissolved in water)  |
| $\xrightarrow{\Delta}$       | Indicates that heat must be supplied to reactants before a reaction occurs  |
| $\xrightarrow{\text{MnO}_2}$ | An element or compound written above the arrow is a <i>catalyst</i> ; a catalyst speeds up a reaction but is not consumed in the reaction. It may also indicate the solvent, such as water. |

### 5-1.2 Rules for Balancing Equations

Properly balanced equations are a necessity when we consider the quantitative aspects of reactants and products, as we will do in Chapter 7. Before we consider some guidelines in balancing equations, there are three points to keep in mind concerning balanced equations.

1. The subscripts of a compound are fixed; they cannot be changed to balance an equation.
2. The coefficients used should be the smallest whole numbers possible.
3. The coefficient multiplies all of the number of atoms in the formula. For example,  $2\text{K}_2\text{SO}_3$  indicates the presence of four atoms of K, two atoms of S, and six atoms of O.

In this chapter, equations will be balanced by *inspection*. Certainly, many complex equations are extremely tedious to balance by this method, but such equations will be discussed in Chapter 14, where more systematic methods can be employed. The following rules are helpful in balancing simple equations by inspection.

1. In general, it is easiest to consider balancing elements other than hydrogen or oxygen first. Look to the compound on either side of the equation that contains the greatest number of atoms of an element other than oxygen or hydrogen. Balance the element in question on the other side of the equation.
2. If polyatomic ions appear unchanged on both sides of the equation, consider them as single units.
3. Balance all other elements except hydrogen and oxygen, except those that appear as free elements (not as part of a compound).
4. Balance hydrogen or oxygen next. Choose the one that is present in the fewer number of compounds first. (Usually, that is hydrogen.)
5. Finally, balance any element that is by itself.
6. Check to see that the atoms of all elements are balanced. The final balanced equation should have the smallest whole-number ratio of coefficients.

Sometimes fractional coefficients (e.g.,  $3/2$ ) are used initially, especially with regard to balancing  $\text{O}_2$ . In this case, multiply the whole equation through by the denominator (usually 2) to clear the fraction and produce only whole numbers. (This is illustrated in Example 5-3.)

#### EXAMPLE 5-1

##### Balancing a Simple Equation

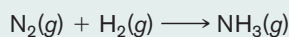
Ammonia is an important industrial commodity that is used mainly as a fertilizer. It is manufactured from its constituent elements. Write a balanced chemical equation from the following word equation: "nitrogen gas reacts with hydrogen gas to produce ammonia gas."

##### PROCEDURE

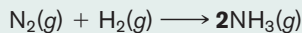
Refer to Table 5-1 for the proper symbols. Apply the rules above as needed.

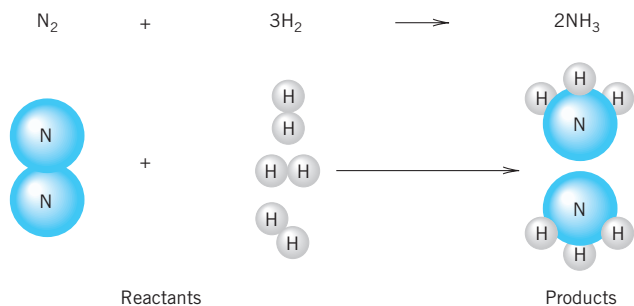
##### SOLUTION

The unbalanced chemical equation using the proper formulas of the elements and compound is



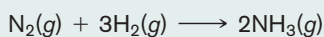
First consider the  $\text{N}_2$  molecule, since it has the most atoms of an element other than hydrogen or oxygen. Balance the N's on the other side by adding a coefficient of **2** in front of the  $\text{NH}_3$ .





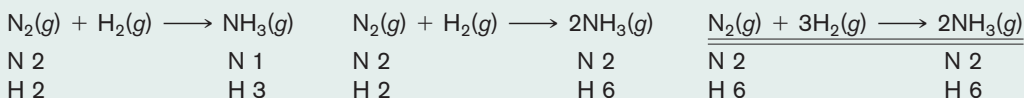
**FIGURE 5-1 Nitrogen Plus Hydrogen Yields Ammonia** In a chemical reaction, the atoms are simply rearranged into different molecules.

Now consider the hydrogens. We have “locked in” six hydrogen atoms on the right, so we will need six on the left. By adding a coefficient of **3** in front of the  $H_2$ , we have completed the balancing of the equation. (See Figure 5-1.)



### ANALYSIS

Many first-time students prefer to keep what is called an atom inventory during the course of balancing. In this way, they can see what coefficients are needed and how the addition of one coefficient changes the number of atoms of other elements. In each of the three equations in the solution, write underneath it the number of N atoms and the number of H atoms present on both the reactant side of the equation and the product side.



Notice that in the final solution, the number of atoms on both the reactant and the product side must be identical. This technique can be abandoned once you become proficient in balancing reactions.

### SYNTHESIS

Deciding on the proper order in which to balance the elements is the difference between smoothly solving a problem and having to attempt the same problem several times before success is achieved. In what order should the atoms in the following equation be checked and balanced?

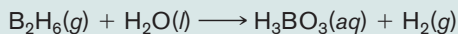


Balance lead first, then oxygen, hydrogen, and finally chlorine. The chlorine is last, because it is in its free state,  $Cl_2$ . The lead is first, since it is not hydrogen or oxygen. Now, why choose the oxygen second and the hydrogen third? Because the oxygen is bonded to the lead in  $PbO_2$ . Once we know the correct number of reactant lead atoms, we also know the correct number of reactant oxygen atoms and can predict the coefficient needed on the product side.

## EXAMPLE 5-2

### Balancing an Equation

Boron hydrogen compounds are being examined as a possible way to produce hydrogen for automobiles that will run on fuel cells. Although  $B_2H_6$  is not the compound that will be used (i.e., it ignites spontaneously in air), the following equation illustrates how boron–hydrogen compounds react with water to produce hydrogen. Balance the following equation.

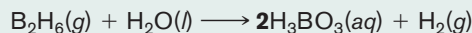


### PROCEDURE

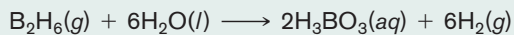
Decide in what order the atoms should be balanced. Change coefficients in front of one molecule at a time and notice the effect on the other atoms in that molecule.

**SOLUTION**

First consider the  $B_2H_6$  molecule, since it has the most atoms of an element other than hydrogen or oxygen. Balance the B by adding a coefficient of **2** in front of the  $H_3BO_3$  on the right.



Next, we notice that oxygen is in the fewer number of compounds, so we balance it next. Since there are 6 oxygen atoms in  $2H_3BO_3$ , place a **6** before the  $H_2O$  on the left. Finally, balance hydrogen. There are 18 on the left that are “locked in.” Thus we need a **6** in front of the  $H_2$  to have 18 hydrogens on the right. A quick check confirms that we have a balanced equation.

**ANALYSIS**

You may run into a case where you can't seem to balance the equation, no matter what combination of coefficients you use. Or perhaps you find yourself continually spiraling through the equation again and again as the numbers get larger and larger. Most chemical reactions balance with relatively small whole numbers. If there is a problem, it very well may be that one or more of your formulas are incorrect. You may have transcribed the problem inaccurately or written a wrong formula yourself. Rechecking formulas would be a logical place to restart.

**SYNTHESIS**

Technically, the coefficients should be the smallest set of whole numbers possible. Therefore  $4A + 6B \longrightarrow 2C + 8D$  should reduce to  $2A + 3B \longrightarrow C + 4D$ . It *is*, however, acceptable to use fractions when balancing, and they can be quite useful for several types of problems whose solutions might not be apparent otherwise. These fractions shouldn't be interpreted as a fraction of a molecule, and if the equation is being used to determine how many molecules of each type react together, then any equation with fractions should be cleared to whole numbers. See Example 5-3 in Section 5-2.1 for this type of problem.

**ASSESSING THE OBJECTIVES FOR SECTION 5-1**

**EXERCISE 5-1(a) KNOWLEDGE:** Fill in the blanks.

A chemical reaction is represented with symbols and formulas by means of a chemical \_\_\_\_\_. The arrow in an equation separates the \_\_\_\_\_ on the left from the \_\_\_\_\_ on the right. To conform to the law of conservation of mass, an equation must be \_\_\_\_\_. This is accomplished by introducing \_\_\_\_\_ in front of formulas rather than changing subscripts in a formula.

**EXERCISE 5-1(b) ANALYSIS:** Write unbalanced chemical equations for the following.

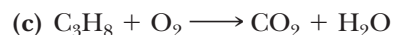
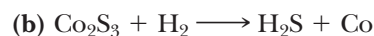
- Lithium and oxygen react to form lithium oxide.
- Aluminum and sulfuric acid yield aluminum sulfate and hydrogen.
- Copper reacts with nitric acid to produce copper(II) nitrate, nitrogen monoxide, and water.

**EXERCISE 5-1(c) ANALYSIS:** In what order should the atoms in the following equations be balanced?

- $H_3BCO + H_2O \longrightarrow B(OH)_3 + CO + H_2$
- $NH_3 + O_2 \longrightarrow NO + H_2O$
- $I_2 + Na_2S_2O_3 \longrightarrow NaI + Na_2S_4O_6$

**EXERCISE 5-1(d) ANALYSIS:** Balance the following reactions.

- $Cr + O_2 \longrightarrow Cr_2O_3$



**EXERCISE 5-1(e) SYNTHESIS:** Write a balanced equation from the following descriptions.

- (a) Ammonium carbonate decomposes into gaseous ammonia, carbon dioxide, and steam.
- (b) Ammonia reacts with chlorine trifluoride to form nitrogen gas, chlorine gas, and hydrogen fluoride.

For additional practice, work chapter problems 5-2, 5-4, 5-10, and 5-11.

## 5-2 COMBUSTION, COMBINATION, AND DECOMPOSITION REACTIONS

### OBJECTIVE FOR SECTION 5-2

Classify certain chemical reactions as being combustion, combination, or decomposition reactions.

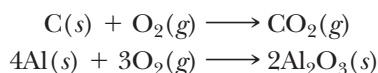


**LOOKING AHEAD!** All the millions of known chemical changes can be represented by balanced equations. Many of these chemical reactions have aspects in common, so they can be grouped into specific classifications. In the remainder of this chapter, we do this with five basic types of reactions. We will notice that each type has a characteristic chemical equation. These five types are not the only ways that reactions can be grouped. In later chapters we will find other convenient classifications that will suit our purpose at that time. The first three types are the simplest and will be considered in this section. ■

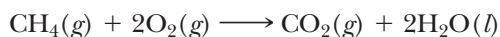
Fire is certainly dramatic evidence of the occurrence of a chemical reaction. What we see as fire is the hot, glowing gases of a combustion reaction. The easiest way to put out a fire is to deprive the burning substance of a reactant (oxygen) by dousing it with water or carbon dioxide from a fire extinguisher. The reaction of elements or compounds with oxygen is the first of three types of reactions that we will discuss in this section.

### 5-2.1 Combustion Reactions

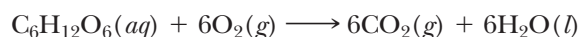
One of the most important types of reactions that we may refer to in the future is known as a **combustion reaction**. This type of reaction refers specifically to the reaction of an element or compound with elemental oxygen ( $\text{O}_2$ ). Combustion usually liberates a lot of heat energy and is accompanied by a flame. It is typically referred to as “burning.” When elements undergo combustion, generally only one product (the oxide) is formed. Examples are the combustion of carbon and aluminum shown here.



When compounds undergo combustion, however, two or more combustion products are formed. When carbon–hydrogen or carbon–hydrogen–oxygen compounds undergo combustion in an excess of oxygen, the combustion products are carbon dioxide and water. (Combustion reactions involving carbon–hydrogen or carbon–hydrogen–oxygen compounds are balanced in the order C, H, O).



The metabolism of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ , blood sugar) occurs in our bodies to produce the energy to sustain our life. It is also a combustion reaction that occurs at a steady, controlled rate.





When insufficient oxygen is present (as in the combustion of gasoline,  $C_8H_{18}$ , in an automobile engine), some carbon monoxide (CO) also forms. This incomplete combustion reaction is shown below.



### EXAMPLE 5-3

#### Balancing a Combustion Equation

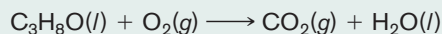
Most fuels are composed of carbon and hydrogen, and some may also contain oxygen. When they react with oxygen gas (burn), they form as products carbon dioxide gas and water. Write a balanced equation showing the burning of liquid rubbing alcohol ( $C_3H_8O$ ).

#### PROCEDURE

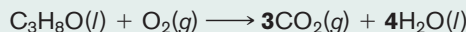
First, represent the names of the species involved as reactants and products with formulas and indicate their physical states. Remember that oxygen gas is diatomic. Then balance the atoms in the order of C, H, and O. Use fractions where necessary, and scale up.

#### SOLUTION

The unbalanced equation is written as follows:



Now, balance carbon. Place a coefficient of **3** in front of  $CO_2$  to balance the carbons in  $C_3H_8O$ . Next, balance the 8 hydrogen atoms in  $C_3H_8O$  by adding a coefficient of **4** in front of  $H_2O$ .



Notice that there are 10 oxygen atoms on the right. On the left 1 oxygen is in  $C_3H_8O$ , so 9 are needed from  $O_2$ . To get an odd number of oxygen atoms from  $O_2$ , we need to use a fractional coefficient, in this case  $\frac{9}{2}$  (i.e.,  $\frac{9}{2} \times 2 = 9$ ).



Finally, we need to clear the fraction so that all coefficients are whole numbers. Multiply the whole equation through by 2 and do a quick check.



#### ANALYSIS

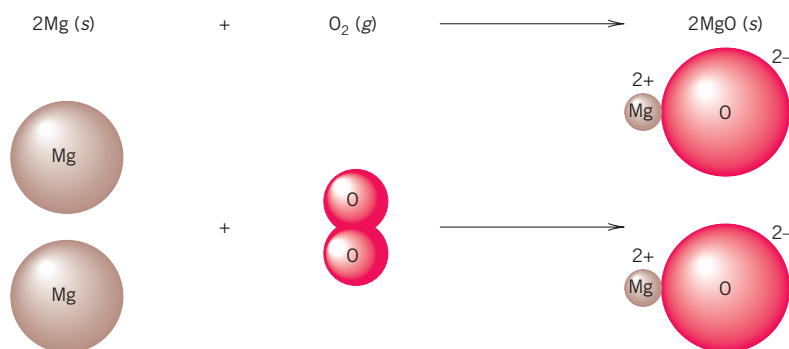
Generally, in a combustion reaction, the total number of oxygen atoms on the product side of an equation will be odd or even. If the number is odd, as in the above example, the use of a fraction makes the balancing easier. The fraction will be some half value ( $3/2$ ,  $7/2$ ,  $9/2$ , etc.). Afterwards, simply double each coefficient to arrive at the appropriate balanced equation. If the number of oxygen atoms is even, it is even easier. A whole number is all that is required to balance things from the start.

#### SYNTHESIS

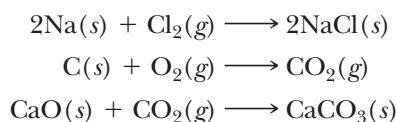
During any combustion reaction, oxygen combines with the elements present in the fuel. In cleaner-burning fuels, containing only carbon and hydrogen, and possibly oxygen, the only products of *complete* combustion are carbon dioxide and water. When there isn't enough oxygen present (such as in a poorly performing combustion engine), incomplete combustion results, with products containing fewer oxygen atoms than are optimal. This typically means CO (carbon monoxide—a deadly gas) and C (in the form of smoke, soot, or ash). When dirtier fuels are used, ones containing contaminants such as high-sulfur coal, the oxygen combines with these elements, too, to form by-products.  $SO_2$  is the unpleasant result of combustion of sulfur-containing compounds. Combustion at high enough temperatures in the presence of nitrogen in the air can lead to the formation of nitrogen oxides, such as NO and  $NO_2$ , which themselves have deleterious health effects.

### 5-2.2 Combination Reactions

The chemical properties of an element describe how it does, or in some cases does not, combine with other elements or compounds. One type of reaction, known as a **combination reaction**, concerns *the formation of one compound from two or more elements and/or simpler compounds*. For example, an important chemical property of the metal magnesium is that it reacts with elemental oxygen to form magnesium oxide. (See Figure 5-2.) The synthesis (i.e., production of a substance) of MgO is represented at the end of this paragraph by a balanced equation and an illustration of the magnesium and oxygen atoms in the reaction. Notice in the reaction that an ionic compound is formed from neutral atoms. The  $\text{Mg}^{2+}$  cation is smaller than the parent atom, while the  $\text{O}^{2-}$  anion is larger than the parent atom. The reason for this is discussed in Chapter 8. Since one of the reactants is elemental oxygen, this reaction can also be classified as a combustion reaction.

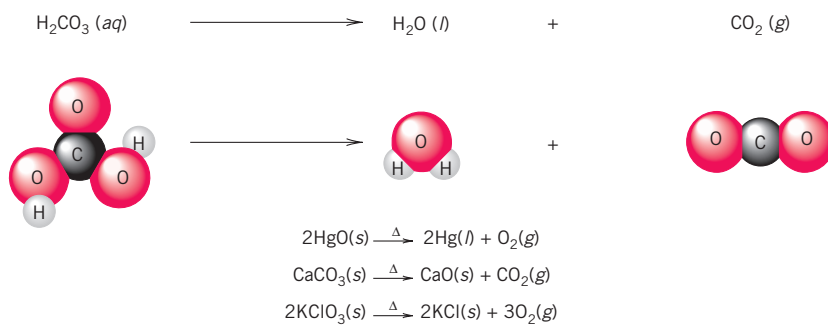


The following equations represent some other important combination reactions.



### 5-2.3 Decomposition Reactions

A chemical property of a compound may be its tendency to decompose into simpler substances. This type of reaction is simply the reverse of combination reactions. That is, one compound is decomposed into two or more elements or simpler compounds. Many of these reactions take place only when heat is supplied, which is indicated by a  $\Delta$  above the arrow. An example of this type of reaction is the decomposition of carbonic acid ( $\text{H}_2\text{CO}_3$ ). This **decomposition reaction** causes the fizz in carbonated beverages. The reaction is illustrated here and is followed by other examples. (See also Figure 5-3.)



**FIGURE 5-2** Combination or Combustion Reaction When magnesium burns in air, the reaction can be classified as either a combination or a combustion reaction.



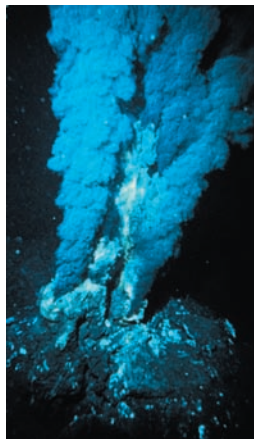
**FIGURE 5-3** Decomposition Reaction The fizz of carbonated water is the result of a decomposition reaction.

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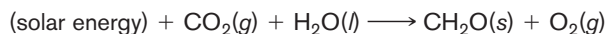
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## Life Where the Sun Doesn't Shine—Chemosynthesis



Miles deep in the ocean a phenomenal discovery profoundly changed the way we view the life forms on this planet and perhaps other planets far away. Previously, we understood life as totally dependent on energy from the sun. The chlorophyll in plants produces carbohydrates in a process known as *photosynthesis*, as illustrated below.

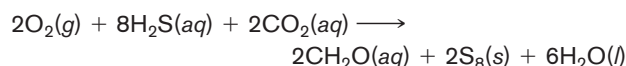
(Carbohydrates are represented by their simplest formula,  $\text{CH}_2\text{O}$ .)



We use these carbohydrates from plants, or animals that eat these plants, to sustain life. So our energy is indirectly solar energy.

In 1977, scientists in the research submarine *Alvin* were exploring the mile-deep ocean bottom near the Galapagos Islands in the Pacific. Suddenly, they came upon an unbelievable diversity of life that existed in scalding water ( $350^\circ\text{C}$ ). The colony of life extended from bacteria to giant clams, mussels, and tube worms 8 feet long. The *Alvin* had come upon ocean vents discharging huge amounts of hot water from deep in the Earth. The water was rich in minerals and chemicals.

One of those chemicals was hydrogen sulfide ( $\text{H}_2\text{S}$ ). This gas is very poisonous to surface life but turned out to be the main source of energy for the bacteria, which serve as the bottom of the food chain. These bacteria are able to produce carbohydrates with the chemical energy from hydrogen sulfide rather than the light energy from the sun. This process is called *chemosynthesis*. The equation illustrating this reaction to produce a carbohydrate is



In the late 1990s, even more startling discoveries were reported. Living bacteria have been found 3000 feet deep in the solid earth. These life-forms seem to use the chemical energy from  $\text{H}_2$  to maintain life. They do not even need  $\text{O}_2$ , which is produced as a by-product of photosynthesis, as was found in the chemosynthesis in the deep-sea vents.

Life is much more resilient than we ever thought. Because of these discoveries, many scientists feel much more confident that life could exist on other planets, especially Mars.

Currently, we are intensely studying the conditions on that planet. Recent discoveries of the presence of large amounts of water at the poles and buried beneath the surface of Mars have heightened expectations. The Mars explorers have more recently found that bodies of water once existed on the surface of this planet.

### ASSESSING THE OBJECTIVE FOR SECTION 5-2

**EXERCISE 5-2(a) KNOWLEDGE:** Label each statement as applying to a decomposition, combination, and/or combustion reaction.

- Oxygen is a reactant.
- There are two or more products.
- There are two or more reactants.
- The equation must be balanced.
- Reaction usually requires heating to occur.

**EXERCISE 5-2(b) ANALYSIS:** Label each of the following reactions as being an example of a combustion, combination, or decomposition reaction.

- $\text{Cu}(\text{OH})_2(s) \longrightarrow \text{CuO}(s) + \text{H}_2\text{O}(l)$
- $2\text{CH}_4\text{O}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$
- $\text{Ba}(s) + \text{F}_2(g) \longrightarrow \text{BaF}_2(s)$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{N}_2(g) + 4\text{H}_2\text{O}(g) + \text{Cr}_2\text{O}_3(s)$
- $\text{Na}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{NaOH}(aq)$

**EXERCISE 5-2(c) SYNTHESIS:** Represent each of the following word equations with a balanced chemical equation.

- (a) Disilane gas ( $\text{Si}_2\text{H}_6$ ) undergoes combustion to form solid silicon dioxide and water.
- (b) Solid aluminum hydride is formed by a combination reaction of its two elements.
- (c) When solid calcium bisulfite is heated, it decomposes to solid calcium oxide, sulfur dioxide gas, and water.

For additional practice, work chapter problems 5-16, 5-18, and 5-20.

## PART A SUMMARY

### KEY TERMS

- 5-1.1** Chemical reactions are represented by **chemical equations**. p. 138
- 5-1.1** **Reactants** and **products** in an equation are separated by an arrow. p. 138
- 5-1.1** Equations are **balanced** by use of **coefficients** in front of a compound or element. p. 139
- 5-2.1** **Combustion reactions** involve oxygen as a reactant. p. 143
- 5-2.2** **Combination reactions** have one product. p. 145
- 5-2.3** **Decomposition reactions** have one reactant. p. 145

### SUMMARY CHARTS

#### Sequence of Balancing Equations

- Most complex element  $\longrightarrow$  2. Any element (or polyatomic ion) other than H and O  $\longrightarrow$  3. Usually H next if present in the most species  $\longrightarrow$  4. Finally, balance O  $\longrightarrow$
5. Check

#### Three Types of Reactions

| Combustion                                       | Combination  | Decomposition                                 |
|--|--|---|
| $\text{O}_2$ is a reactant; oxides are products. | Elements and/or compounds combine to form one product. | One reactant forms elements and/or compounds. |

## PART B IONS IN WATER AND HOW THEY REACT

### SETTING A GOAL

- You will learn how ions are formed in aqueous solution and how these ions interact in two important types of chemical reactions.

### OBJECTIVES

- 5-3** Write the ions formed when ionic compounds or acids dissolve in water.
- 5-4** Given the activity series, complete several single-replacement reactions as balanced molecular, total ionic, and net ionic equations.
- 5-5 (a)** Given a table of solubility rules, determine whether a specific ionic compound is soluble or insoluble in water. **(b)** Write balanced molecular, total ionic, and net ionic equations for precipitation reactions.
- 5-6** Write balanced molecular, total ionic, and net ionic equations for neutralization reactions.

▶ **OBJECTIVE FOR SECTION 5-3**

Write the ions formed when ionic compounds or acids dissolve in water.

## 5-3 THE FORMATION OF IONS IN WATER



**LOOKING AHEAD!** Before we discuss some general types of reactions that occur in aqueous solution, we will examine how ions are formed in water. ■



**FIGURE 5-4 A Soluble Compound** Table salt dissolves as it is added to hot water.

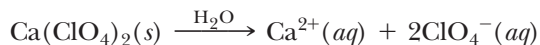
### 5-3.1 Salts in Aqueous Solution

When one adds a sprinkle of table salt (sodium chloride) to water, the salt soon disappears into the aqueous medium. We observe that the table salt is soluble in water. (See Figure 5-4.) On the other hand, if we add some chalk (calcium carbonate) to water, it slowly settles to the bottom of the container without apparent change. *When an appreciable amount of a substance dissolves in a liquid medium, we say that the substance is **soluble**. If very little or none of the substance dissolves, we say that the compound is **insoluble**.* The water and the table salt together make what is called a solution. A **solution** is a homogeneous mixture of a **solvent** (usually a liquid such as water) and a **solute** (a solid, a liquid, or even a gas).

In Chapters 3 and 4, we described table salt (NaCl) as an ionic compound composed of  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions in the solid state. When an ionic compound dissolves in water, in nearly all cases the compound is separated into individual ions. The solution of NaCl in water can be represented by the equation



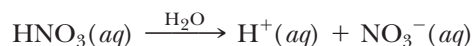
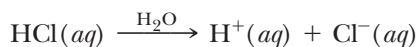
The  $\text{H}_2\text{O}$  shown above the arrow indicates the presence of water as a solvent. The solution of another ionic compound, calcium perchlorate, can be represented by the equation



Notice that all the atoms in the perchlorate ion remain together in solution as a complete entity. That is, they do not separate into chlorine and oxygen atoms. This is true for all of the polyatomic ions you've learned.

### 5-3.2 Strong Acids in Aqueous Solution

In Chapter 4, a class of compounds known as acids was introduced and named. These are molecular compounds, but like ionic compounds, they also produce ions when dissolved in water. In this case, the neutral molecule is "ionized" by the water molecules. (We will examine how this happens in a later chapter.) Acids are so named because *they all form the  $\text{H}^+(aq)$  ion when dissolved in water*. **Strong acids**, such as hydrochloric acid (HCl), *are completely ionized in water*. We will consider only the action of the six common strong acids (HCl, HBr, HI,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$ ) in water at this time. The solutions of the strong acids, hydrochloric and nitric acid, are illustrated by the equations





**EXAMPLE 5-4****Forming Ions in Aqueous Solution**

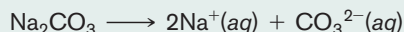
Write equations illustrating the solution of the following compounds in water: **(a)**  $\text{Na}_2\text{CO}_3$ , **(b)**  $\text{CaCl}_2$ , **(c)**  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , **(d)**  $\text{HClO}_4$ , and **(e)**  $\text{H}_2\text{SO}_4$ . (Although it is not exactly correct, consider sulfuric acid as completely separated into two  $\text{H}^+(\text{aq})$  ions in aqueous solution.)

**PROCEDURE**

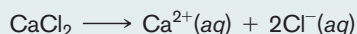
If necessary, refer to Table 4-2 or the periodic table for the charges on the ions.

**SOLUTION**

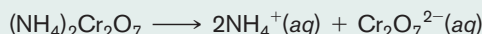
**(a)**  $\text{Na}_2\text{CO}_3$  is composed of  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  ions.



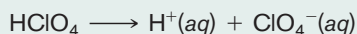
**(b)**  $\text{CaCl}_2$  is composed of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions.



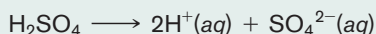
**(c)**  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is composed of  $\text{NH}_4^+$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions.



**(d)**  $\text{HClO}_4$  is a strong acid that produces  $\text{H}^+(\text{aq})$  and  $\text{ClO}_4^-$  ions.



**(e)**  $\text{H}_2\text{SO}_4$  is a strong acid that produces  $\text{H}^+(\text{aq})$  and  $\text{SO}_4^{2-}$  ions.

**ANALYSIS**

The meaning of the subscript again becomes crucial to your ability to perform this task. Distinguish between the 3 in  $\text{CO}_3^{2-}$  and the 3 in  $\text{FeCl}_3$ . In the carbonate ion, the subscript 3 is a part of the formula of the ion. You could almost consider it part of the “symbol” of carbonate. The symbol for chlorine is just Cl. Therefore, the subscript 3 in  $\text{FeCl}_3$  tells us how many ions of chloride there are. To show three ions of carbonate, the entire formula would have to be in parenthesis with a subscripted 3 on the outside.

**SYNTHESIS**

We will learn in Chapter 12 that the number of aqueous ions an ionic compound breaks into can affect some of that solution's properties. Order the following compounds by number of ions they'll form in solution:  $\text{Al}(\text{ClO}_3)_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Fe}_2(\text{SO}_4)_3$ . The correct order is  $\text{NH}_4\text{Cl}$  (with two),  $\text{Na}_2\text{CO}_3$  (three),  $\text{Al}(\text{ClO}_3)_3$  (four), and  $\text{Fe}_2(\text{SO}_4)_3$  (five).

**ASSESSING THE OBJECTIVE FOR SECTION 5-3**

**EXERCISE 5-3(a) ANALYSIS:** List the cations and the anions present when the following compounds dissolve in water.

**(a)**  $\text{HNO}_2$     **(b)**  $\text{K}_3\text{PO}_4$     **(c)**  $\text{NH}_4\text{NO}_3$     **(d)**  $\text{Zn}(\text{ClO}_4)_2$

**EXERCISE 5-3(b) ANALYSIS:** How many ions will the following species form when they dissolve in water?

**(a)**  $\text{MgBr}_2$     **(b)**  $\text{Na}_3\text{PO}_4$     **(c)**  $\text{Fe}(\text{NO}_3)_3$     **(d)**  $\text{KClO}_3$

**EXERCISE 5-3(c) SYNTHESIS:** Write the equations illustrating the formation of solutions of the following compounds.

**(a)**  $\text{Na}_2\text{SO}_4$     **(b)**  $\text{HNO}_3$     **(c)**  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$     **(d)**  $\text{Ca}(\text{OH})_2$

*For additional practice, work chapter problems 5-24, 5-25, and 5-26.*

### OBJECTIVE FOR SECTION 5-4

Given the activity series, complete several single-replacement reactions as balanced molecular, total ionic, and net ionic equations.

## 5-4 SINGLE-REPLACEMENT REACTIONS

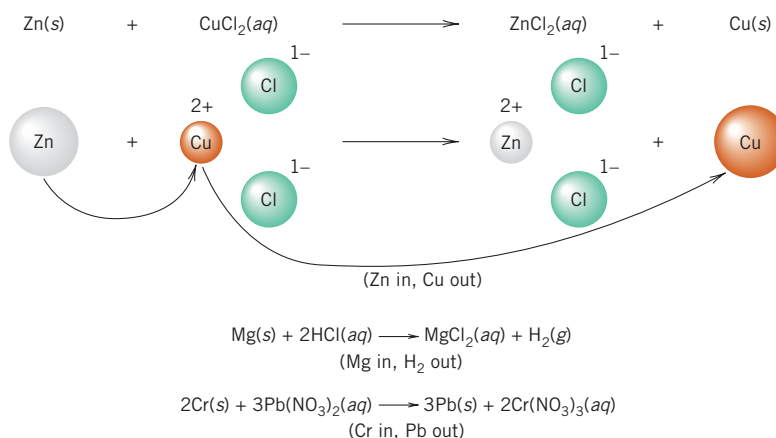


**LOOKING AHEAD!** Solutions containing metal cations may undergo chemical reactions when a solid sample of some other metal comes into contact with this solution. In this section, we will examine this type of reaction. ■



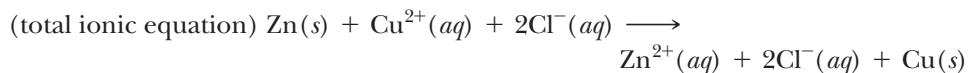
**FIGURE 5-5** Single-Replacement Reaction The formation of a layer of copper on a piece of zinc is a single-replacement reaction.

An interesting thing happens when we immerse a strip of zinc metal in a blue aqueous solution of a copper(II) salt. When we remove the zinc, it now looks as if it has changed into copper. Actually, what happened is that a coating of copper formed on the metal strip. Silver and gold will also form a coating on a strip of zinc immersed in solutions of compounds containing these metal ions. (See Figure 5-5.) These and similar reactions are known as **single-replacement reactions**. In this type of reaction, which most often occurs in aqueous solution, one free element substitutes for another already combined in a chemical compound. The replacement of zinc ions for the copper ions and the copper metal for the zinc metal is illustrated here; other examples follow.



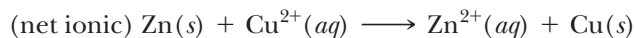
### 5-4.1 Types of Equations

The equation illustrating the replacement of Zn by Cu is known as the molecular form of the equation. *In a molecular equation, all reactants and products are shown as neutral compounds.* To represent the nature of soluble ionic compounds and strong acids in water, it is helpful to show the separate ions as they actually exist in aqueous solution. *When the cations and anions of a compound in solution are shown separately, the resulting equation is known as a total ionic equation.* It is illustrated as follows.



Notice that in this equation, the Cl<sup>-</sup> ions appear on both sides of the equation unchanged. Their role is to provide the anions needed to counteract the positive charge of the cations. The presence of the Cl<sup>-</sup> ions is certainly necessary because any compound, whether in the pure state or dispersed in solution, must be electrically neutral. However, they do not actually affect the chemical change that is occurring. *Ions that are in an identical state on both sides of a total ionic equation are called spectator ions.* If *spectator ions are subtracted from both sides of the equation, the remaining equation is known as the net ionic equation.* This equation focuses only on the species

that have undergone a change in the reaction. By subtracting the two  $\text{Cl}^-$  spectator ions from both sides of the equation we have the net ionic equation.



A reaction is spontaneous in one direction only, so the reverse reaction does not occur. That is, if we were to immerse a copper strip in a  $\text{ZnCl}_2$  solution, a coating of Zn would not form on the copper. (See Figure 5-6.)

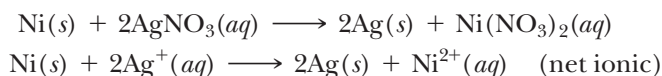
### 5-4.2 The Activity Series

Series of experiments performed on different metal–solution combinations allow us to compare the ability of one metal to replace the ions of other metals in solution. The **activity series** shown in Table 5-2 lists some common metals in decreasing order of their ability to replace metal ions in aqueous solution. (The metal cations present in solution are shown to the right of the metal.) The metal at the top (K) replaces all of the metal ions below it and is therefore the *most* reactive. The second metal replaces all below it, while its ions will be replaced only by K. In fact, K, Na, Mg, and Al are all so reactive that they react with water itself. (Aluminum *appears* unreactive with water because it is coated with  $\text{Al}_2\text{O}_3$ , which protects the metal from contact with water.) They replace other metal ions only when the solids are mixed, not when the ions are in water solution. The following balanced equation illustrates such a reaction.



The above reaction is known as the *thermite reaction* because it liberates so much heat that the iron formed is molten. As a result, this reaction has application in welding.

In the activity series  $\text{H}_2$  is treated as a metal and  $\text{H}^+(aq)$  (from one of the six strong acids) as its metal ion. The activity series can be used to predict which reactions are expected to occur. For example, notice in Table 5-2 that nickel is ranked higher than silver. This allows us to predict that elemental nickel metal replaces the  $\text{Ag}^+$  ion in solution. Thus, if we immerse a strip of nickel in a solution of aqueous  $\text{AgNO}_3$ , we find that a coating of silver forms on the nickel. The balanced molecular equation and net ionic equation illustrating this reaction are as follows. Note that the nitrate ion ( $\text{NO}_3^-$ ) is a spectator ion.



**FIGURE 5-6** Copper in a Zinc Sulfate Solution When a strip of copper is immersed in a zinc ion solution, no reaction occurs.

**TABLE 5-2** The Activity Series

|                | METAL        | METAL ION        |
|----------------|--------------|------------------|
| (most active)  | K            | $\text{K}^+$     |
|                | Na           | $\text{Na}^+$    |
|                | Mg           | $\text{Mg}^{2+}$ |
|                | Al           | $\text{Al}^{3+}$ |
|                | Zn           | $\text{Zn}^{2+}$ |
|                | Cr           | $\text{Cr}^{3+}$ |
|                | Fe           | $\text{Fe}^{2+}$ |
|                | Ni           | $\text{Ni}^{2+}$ |
|                | Sn           | $\text{Sn}^{2+}$ |
|                | Pb           | $\text{Pb}^{2+}$ |
|                | $\text{H}_2$ | $\text{H}^+$     |
|                | Cu           | $\text{Cu}^{2+}$ |
|                | Ag           | $\text{Ag}^+$    |
| (least active) | Au           | $\text{Au}^{3+}$ |

### EXAMPLE 5-5

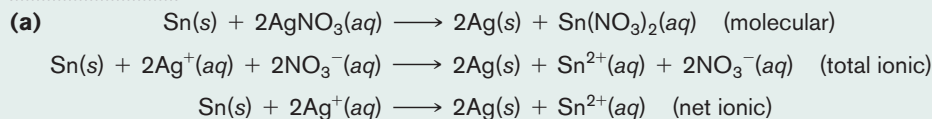
#### Predicting Spontaneous Single-Replacement Reactions

Consider the following two possible reactions. If a reaction does occur, write the balanced molecular, total ionic, and net ionic equations illustrating the reactions.

- A strip of tin metal is placed in an aqueous  $\text{AgNO}_3$  solution.
- A strip of silver metal is placed in an aqueous perchloric acid solution.

#### PROCEDURE

- Notice in the activity series that Sn is higher in the series than Ag. Therefore Sn replaces  $\text{Ag}^+$  ions from solution.
- In the activity series,  $\text{H}_2$  is higher than Ag. Therefore,  $\text{H}_2$  replaces  $\text{Ag}^+$ , but the reverse reaction, the replacement of  $\text{H}^+$  by Ag, does not occur.

**SOLUTION**

(b) No reaction occurs.

**ANALYSIS**

To say that a metal is reactive means that it has a tendency to exist as an ion, not a free metal. To say that a metal is stable means that it is more often found in its metallic, or free, state. So compare Al and Pb. Which is more reactive? Which is more likely to be found in its free state? Which will replace which in a single-replacement reaction? The aluminum is more reactive. The lead is more stable. Therefore, solid aluminum will switch places with, or replace, aqueous lead ion in a single replacement reaction. It's worth noting that Table 5-2 also reflects the ease with which metals are recovered in mining. You can proceed up the list from the bottom, and have a roughly accurate historical record of the order in which important metals were put into service by various cultures.

**SYNTHESIS**

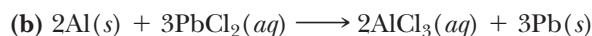
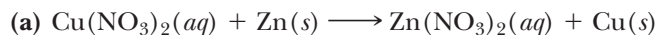
According to Table 5-2, which metals won't react with acid? Cu, Ag, and Au. How are the uses of these metals related to this chemical property? We use them to make metallic objects that we wouldn't want to corrode or dissolve. Obvious examples are coins, wiring, and jewelry. Why, then, is iron used so extensively in structural building? It is in the middle of the chart, and fairly reactive. It's because it is strong, abundant, and easy to mine and process. We then have to make allowances for the fact that we'll need to replace structures made from iron, and its alloy steel, on a regular basis because of the constant chemical corrosion that occurs.

**ASSESSING THE OBJECTIVE FOR SECTION 5-4**

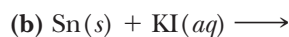
**EXERCISE 5-4(a) KNOWLEDGE:** Choose the metal that will replace the other one (as an ion) in solution.

(a) Ag or Ni    (b) Al or Cu    (c) Cr or Mg    (d) Sn or acid

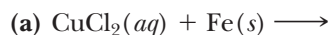
**EXERCISE 5-4(b) ANALYSIS:** Given the following molecular equations, write the total and the net ionic equations for the reactions:



**EXERCISE 5-4(c) ANALYSIS:** Complete balanced molecular equations for the following reactants.



**EXERCISE 5-4(d) SYNTHESIS:** Write total and net ionic equations for the following reactants.



*For additional practice, work chapter problems 5-28, 5-30, and 5-31.*

## 5-5 DOUBLE-REPLACEMENT REACTIONS—PRECIPITATION



**LOOKING AHEAD!** In a single-replacement reaction, only cations are involved. In a double-replacement reaction, both cations and anions are involved. The driving force of these reactions is the formation of a product from the exchange of ions that is insoluble in water, is a molecular compound, or, in a few cases, is both.

The first type of double-replacement reaction, formation of a solid, is discussed in this section. ■

### OBJECTIVES FOR SECTION 5-5

(a) Given a table of solubility rules, determine whether a specific ionic compound is soluble or insoluble in water. (b) Write balanced molecular, total ionic, and net ionic equations for precipitation reactions.

### 5-5.1 Soluble and Insoluble Ionic Compounds

Marble statues have suffered the ravages of weather, for thousands of years in some cases. Marble, limestone, and chalk are essentially the same compound, calcium carbonate. Obviously, this ionic compound is insoluble in water. It formed when calcium ions ( $\text{Ca}^{2+}$ ) and carbonate ions ( $\text{CO}_3^{2-}$ ) present in some ancient sea came together to form a solid deposit. Before we look at this type of reaction, we should bring some order and guidelines to the determination of which ionic compounds are soluble in water and which are not. In Table 5-3, some rules for the solubility of compounds containing common anions are listed. Although this table focuses only on anions, it will help to know that compounds formed from cations of Group IA (i.e.,  $\text{Na}^+$ ,  $\text{K}^+$ ) and the  $\text{NH}_4^+$  ion are all water soluble regardless of the anion.

**TABLE 5-3** Solubility Rules for Some Ionic Compounds

| ANION   | SOLUBILITY RULE  |
|---|--|
| <b>Mostly Soluble</b>   |  |
| $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$                            | All cations form <i>soluble</i> compounds except $\text{Ag}^+$ , $\text{Hg}_2^{2+}$ , and $\text{Pb}^{2+}$ . ( $\text{PbCl}_2$ and $\text{PbBr}_2$ are slightly soluble.)            |
| $\text{NO}_3^-$ , $\text{ClO}_4^-$ , $\text{C}_2\text{H}_3\text{O}_2^-$ | All cations form <i>soluble</i> compounds. ( $\text{KClO}_4$ and $\text{AgC}_2\text{H}_3\text{O}_2$ are slightly soluble.)   |
| $\text{SO}_4^{2-}$  | All cations form <i>soluble</i> compounds except $\text{Pb}^{2+}$ , $\text{Ba}^{2+}$ , and $\text{Sr}^{2+}$ . ( $\text{Ca}^{2+}$ and $\text{Ag}^+$ form slightly soluble compounds.) |
| <b>Mostly Insoluble</b>   |  |
| $\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$                                 | All cations form <i>insoluble</i> compounds except Group IA metals and $\text{NH}_4^+$ .   |
| $\text{S}^{2-}$   | All cations form <i>insoluble</i> compounds except Group IA and IIA metals and $\text{NH}_4^+$ .   |
| $\text{OH}^-$   | All cations form <i>insoluble</i> compounds except Group IA metals, $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$ , and $\text{NH}_4^+$ . [ $\text{Ca}(\text{OH})_2$ is slightly soluble.]     |

### EXAMPLE 5-6

#### Predicting Whether an Ionic Compound Is Soluble

Use Table 5-3 to predict whether the following compounds are soluble or insoluble.

- (a)  $\text{NaI}$     (b)  $\text{CdS}$     (c)  $\text{Ba}(\text{NO}_3)_2$     (d)  $\text{SrSO}_4$

#### PROCEDURE

Apply the solubility rules to the anion. Check to see that the cation is mentioned as an exception.



**SOLUTION**

- (a) According to Table 5-3, all alkali metal (Group IA) compounds of the anions listed are soluble. Therefore, Nal is soluble.
- (b) All  $S^{2-}$  compounds are insoluble except those formed with Group IA and IIA metals and  $NH_4^+$ . Since Cd is in Group IIB, it is not one of the exceptions. CdS is insoluble.
- (c) All  $NO_3^-$  compounds are soluble. Therefore, Ba(NO<sub>3</sub>)<sub>2</sub> is soluble.
- (d) The  $Sr^{2+}$  ion is one of the exceptions to soluble  $SO_4^{2-}$  compounds. Therefore, SrSO<sub>4</sub> is insoluble.

**ANALYSIS**

In order for an ionic compound to be insoluble, both the cation and the anion have to form at least some insoluble compounds. If either of them forms only soluble compounds, then the specific compounds containing these cations or anions are soluble (with the noted exceptions). Consider the following compounds:  $NH_4Cl$ ,  $Na_3PO_4$ ,  $Fe(NO_3)_3$ , and  $Cu(OH)_2$ . In  $NH_4Cl$ ,  $Cl^-$  is a listed soluble anion, and  $NH_4^+$  is one of the universally soluble cations. Clearly the compound is soluble. In the case of  $Na_3PO_4$ , the presence of  $Na^+$  (a soluble cation) overrides the presence of the typically insoluble  $PO_4^{3-}$ . Just the reverse is true in  $Fe(NO_3)_3$ , where the presence of the soluble  $NO_3^-$  makes the compound soluble.  $Cu(OH)_2$ , however, is insoluble, since the  $Cu^{2+}$  ion is not one of the exceptions.

**SYNTHESIS**

Occasionally it is useful to remove a particular cation or anion from solution by formation of a solid compound containing that ion. What anion could you add to a solution containing  $Zn^{2+}$  to make it insoluble? There are several possibilities. Anything in the lower half of Table 5-3 would work to precipitate the zinc— $S^{2-}$ , for example. This leads us to the discussion of these types of reactions.

**5-5.2 Formation of a Precipitate**

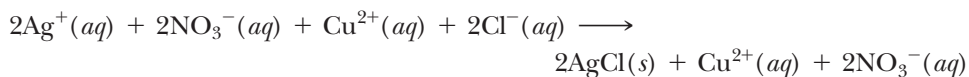
What happens when we mix solutions containing soluble ionic compounds? It depends. If we mix a solution of  $CuCl_2$  (green) and  $KNO_3$  (clear), we simply have a mixture of the four ions in solution, as illustrated in Figure 5-7. No cation is associated with a particular anion.

Now let's consider a case of two solutions, one containing the soluble compound  $CuCl_2$  and the other containing the soluble compound  $AgNO_3$ . When we mix these two solutions, something obviously occurs. The mixture immediately becomes cloudy, and eventually a white solid settles to the bottom of the container. *The solid that is formed by the reaction is called a precipitate* of the insoluble compound,  $AgCl$ . In fact, whenever  $Ag^+$  and  $Cl^-$  are mixed into the same solution, they come together to form solid  $AgCl$ . This leaves the  $Cu^{2+}$  (which forms a blue color) and the  $NO_3^-$  ions in solution, since  $Cu(NO_3)_2$  is soluble. (See Figure 5-8.)

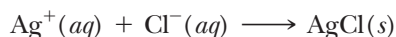
*The formation of a precipitate by mixing solutions of two soluble compounds is known as a precipitation reaction.* This is one of two types of **double-replacement reactions** where the two cations involve exchange anions. The reaction is illustrated by the following molecular equation.



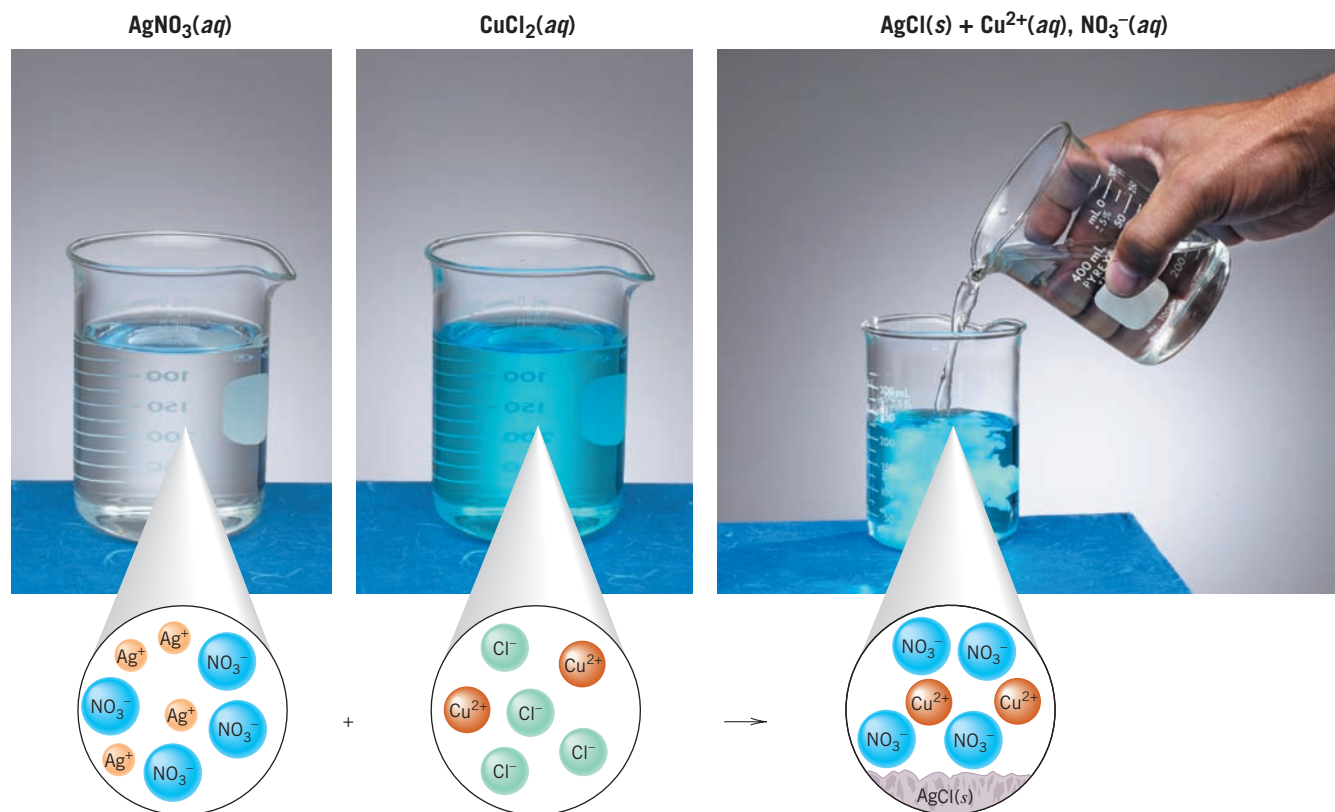
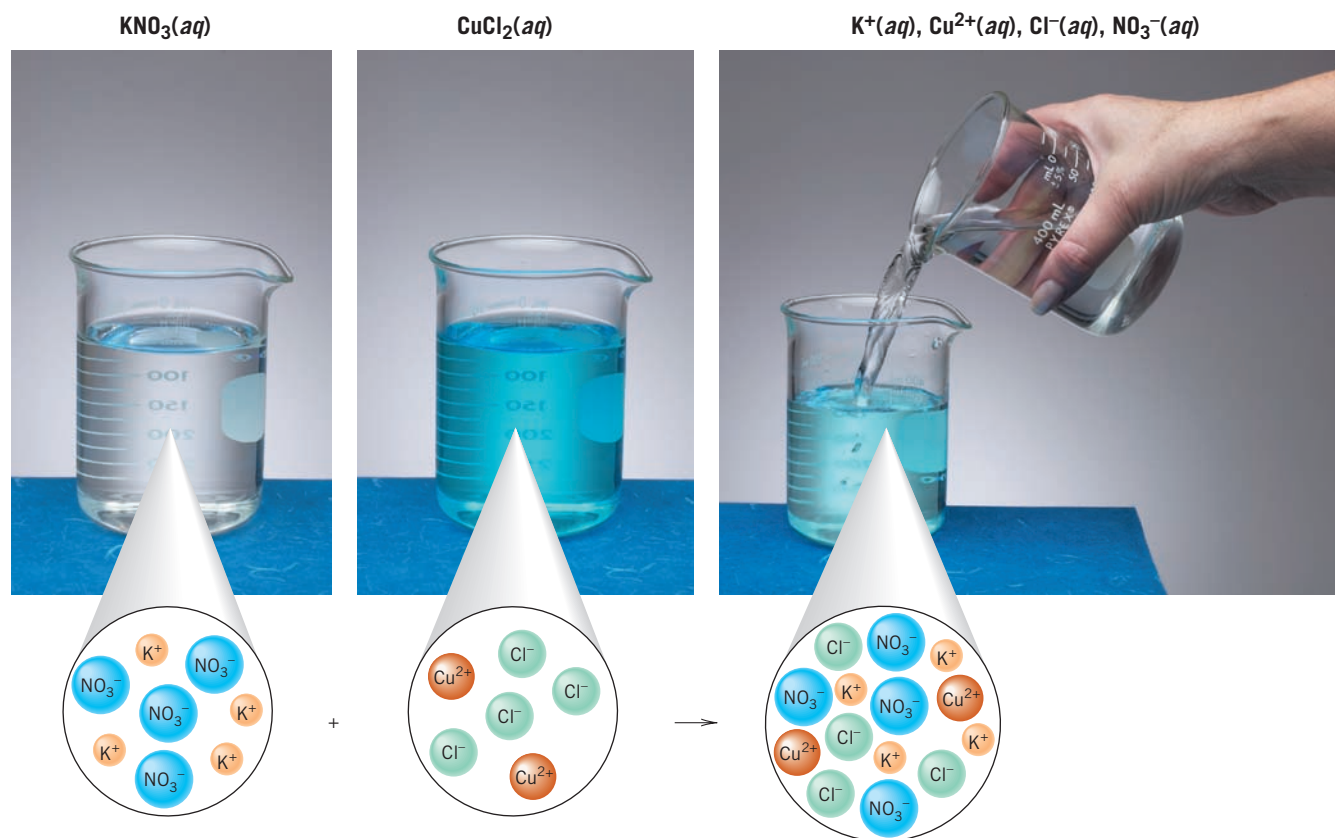
In the total ionic equation, the soluble ionic compounds are represented as separate ions on both sides of the equation, but the solid precipitate (i.e.,  $AgCl$ ) is shown as a neutral compound since the two ions come together to produce the solid.



Notice that there are two spectator ions,  $Cu^{2+}$  and  $NO_3^-$ . After spectator ions are subtracted from the equation, we have the net ionic equation for the reaction.



As in the single-replacement reactions discussed previously, the net ionic equation focuses on the driving force for the reaction, which is the formation of solid  $AgCl$  from two soluble compounds.



There are some very practical applications of precipitation reactions in industry as well as in the laboratory. Our example is of particular value. Silver is actually used more in the development of photographs and film than in jewelry and coins. It is obviously worthwhile to recover this precious metal from film negatives whenever possible. Silver metal in film can be dissolved in aqueous nitric acid to form the water-soluble compound  $\text{AgNO}_3$ . [This is not a single-replacement reaction (which by itself would not work) but involves the nitrate ion in a more complex reaction.] Although the solution contains many other dissolved substances, addition of a soluble compound containing the  $\text{Cl}^-$  ion (e.g.,  $\text{NaCl}$ ) leads to the formation of solid  $\text{AgCl}$ , as shown in Figure 5-8. As you notice from Table 5-3, very few other cations form precipitates with  $\text{Cl}^-$ , so this is a reaction more or less specific to removing  $\text{Ag}^+$  from aqueous solution. The  $\text{AgCl}$  can then be filtered from the solution and silver metal eventually recovered.

In other precipitation reactions, we may want to recover the soluble compound and discard the insoluble compound. In such a case, we would remove the precipitate by filtration and then recover the soluble compound by boiling away the solvent water.

### 5-5.3 Rules for Writing Precipitation Reactions

By careful use of Table 5-3, we can predict the occurrence of many precipitation reactions. To accomplish this, we follow this procedure:

1. Write the compounds produced in the reaction by “switching partners,” changing subscripts as necessary to make sure that the compounds have the correct formulas based on the ions’ charges (which do not change).
2. Examine Table 5-3 to determine whether one of these compounds is insoluble. Label the soluble chemicals (*aq*) for *aqueous* and the insoluble ones (*s*) for *solid*.
3. If one of the two new compounds is insoluble in water, a precipitation reaction occurs and we can write the equation illustrating the reaction.

The following examples illustrate the use of Table 5-3 to predict and write precipitation reactions.

#### EXAMPLE 5-7

##### Writing a Possible Precipitation Reaction

A solution of  $\text{Na}_2\text{CO}_3$  is mixed with a solution of  $\text{CaCl}_2$ . Predict what happens. If a precipitate forms, write the balanced molecular, total ionic, and net ionic equations.

##### PROCEDURE

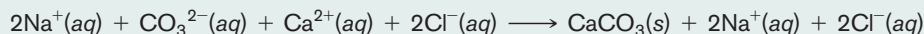
Follow the steps outlined above.

##### SOLUTION

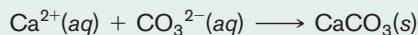
The four ions involved are  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$ . The combinations of the  $\text{Na}^+$  and  $\text{Cl}^-$  and the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  produce the compounds  $\text{NaCl}$  and  $\text{CaCO}_3$ . If both of these compounds are soluble, no reaction occurs. In this case, however, reference to Table 5-3 indicates that  $\text{CaCO}_3$  is insoluble. Thus, a reaction occurs that we can illustrate with a balanced reaction written in molecular form.



The equation written in total ionic form is



Note that the  $\text{Na}^+$  and the  $\text{Cl}^-$  ions are spectator ions. Elimination of the spectator ions on both sides of the equation leaves the net ionic equation.



(This would be an example of the formation of limestone in an ancient sea.)

**ANALYSIS**

Working as many of these types of problems as possible is the key to seeing the patterns that develop. Typically, the anion of one of the reactants will combine with the cation of the second to form the insoluble product. A quick glance at the anions present will give you an idea of the likelihood that they will form an insoluble compound. Then analyze the cation of the other reactant. Will it combine with the first anion to precipitate? Consider  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Li}_3\text{PO}_4$ . Do we expect an insoluble product to form? Of the two anions, the phosphate is the one likely to form a precipitate. The cation of the first compound,  $\text{Ni}^{2+}$ , is not in the Group IA column, so it, too, is a good candidate. We'd expect the product of the two, nickel(II) phosphate, to be a precipitate.

**SYNTHESIS**

Can you go further and find a compound that would react with a given reactant? What compound (and there are several) would form a precipitate with  $\text{KOH}$ ? Here it is the anion that likely will precipitate. Let's pick a cation that will do the job.  $\text{Cu}^{2+}$  would work. Now we need an anion that will ensure the  $\text{Cu}^{2+}$  to be initially soluble. Nitrate, chloride, and acetate fit the bill.  $\text{Cu}(\text{NO}_3)_2$ , for one, would dissolve in water and then form a precipitate with  $\text{KOH}$ . Following that same reasoning, any of these would also work:  $\text{FeCl}_3$ ,  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ ,  $\text{NiSO}_4$ , and many others. Consider the following example.

**EXAMPLE 5-8****Writing a Possible Precipitation Reaction**

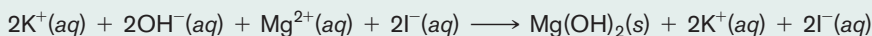
A solution of  $\text{KOH}$  is mixed with a solution of  $\text{MgI}_2$ . Predict what happens. If a precipitate forms, write the balanced molecular, total ionic, and net ionic equations.

**SOLUTION**

The four ions involved are  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{I}^-$ . An exchange of ions in the reactants produces the compounds  $\text{KI}$  and  $\text{Mg}(\text{OH})_2$ . Reference to Table 5-3 indicates that  $\text{Mg}^{2+}$  forms an insoluble compound with  $\text{OH}^-$ . Therefore, a precipitation reaction does occur and is illustrated with the following molecular equation.



The total ionic equation is



Elimination of spectator ions gives the net ionic equation.

**ANALYSIS**

When writing the total ionic equation, simply go through your equation to all the ionic compounds or acids labeled "aqueous" and break them apart into their ions. Any other chemical, labeled as "solid," "liquid," or "gas," should be written exactly the same way it was in the molecular equation.

**SYNTHESIS**

It is almost always the case that the combination of the four possible ions from a double-replacement reaction will at most form one insoluble chemical. In several cases, *no* insoluble chemical forms and there is no reaction (see the next example). By studying Table 5-3, particularly the exceptions, can you come up with a combination of two soluble compounds that will react to form two insoluble products? There are very few choices. Notice that  $\text{Ba}(\text{OH})_2$  is soluble, whereas most hydroxides are insoluble. Furthermore,  $\text{BaSO}_4$  is insoluble, whereas most sulfates are soluble. Does that give you an idea? As an example, how about combining solutions of  $\text{Ba}(\text{OH})_2(aq)$  and  $\text{CuSO}_4(aq)$ ?

**EXAMPLE 5-9****Writing a Possible Precipitation Reaction**

A solution of  $\text{KBr}$  is mixed with a solution of  $\text{Sr}(\text{ClO}_4)_2$ . Predict what happens. If a precipitate forms, write the balanced molecular, total ionic, and net ionic equations.

**SOLUTION**

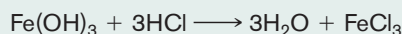
The four ions involved are  $K^+$ ,  $Br^-$ ,  $Sr^{2+}$ , and  $ClO_4^-$ . An exchange of ions produces the compounds  $KClO_4$  and  $SrBr_2$ . Both of these compounds are soluble, so no reaction occurs. The solution contains a mixture of these four ions.

**ANALYSIS**

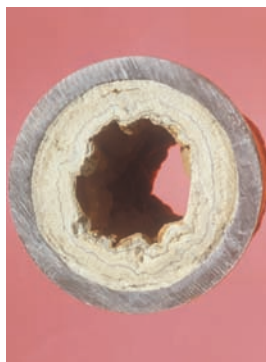
Visually, what would we expect to see in these examples? In the case of the precipitation reactions, we initially begin with two clear, though not necessarily colorless, solutions. Upon mixing, a cloudiness appears due to particles that should eventually settle to the bottom of the reaction vessel. For this last reaction, the two solutions are simply mixed together into one large vessel; they look essentially the same as before mixing. If one solution was colored, the combination might appear to be a lighter hue, but this is just due to diluting. It doesn't indicate a chemical reaction.

**SYNTHESIS**

The following reaction works, for reasons to be discussed in the following section. What would you predict to be the visual indication of a reaction?



According to the solubility rules,  $Fe(OH)_3$  is a solid.  $HCl$  and  $FeCl_3$  are in aqueous solutions.  $H_2O$  is, of course, a liquid. So we are starting off with a solid and aqueous solution, and ending with a mixture of a soluble salt in water. Therefore, upon the addition of hydrochloric acid, we should see our solid “disappear,” as its soluble product dissolves in water.

**Hard Water and Water Treatment**

Hard water is water that contains significant concentrations of  $Fe^{3+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ . These are picked up when rainwater filters down through soil rich in these ions. Most areas of the country, other than the South, East Coast, and Pacific Northwest, suffer from very hard water. Hard water has a strong tendency to form insoluble

compounds with the compounds found in soap. This reduces the soap's ability to clean by forming an insoluble residue that deposits on sinks, tubs, dishes, and clothes. This leaves them gray, gritty, and dingy. Insoluble carbonates may also precipitate within water pipes and water heaters, forming what is called scale. Scale reduces water flow, insulates the water in heaters from the heat source, and lowers the lifetime of the plumbing.

The hard water part of this problem can be reduced by using detergents with added softening agents. These compounds remain soluble despite the presence of the hard ions, making lathering and cleaning more effective. The installation of a water-softening system in a house also

solves the problem of hard water. This system exchanges the soft soluble cation  $Na^+$  for the hard ions that form precipitates in the water. (Recall that sodium compounds are all soluble.) This must be done to preserve the total charge, so it takes two sodium ions to remove one calcium or one magnesium ion, and three sodium ions to remove one iron ion [e.g.,  $3Na^+(aq)$  has the same total charge as one  $Fe^{3+}$ ]. However, the large amount of sodium added to the water can make it unhealthy, especially for those on a low-sodium diet. So water-softening systems are installed only on pipes leading to showers and other cleaning devices. Typically the kitchen and bathroom sinks receive the harder, but healthier, water.

Municipalities in areas that have hard water try to reduce the problem by removing some of the ions at the source before the water goes to commercial and residential areas. They do this by adding  $CaO$  and  $Na_2CO_3$  to the water. These compounds cause the hard ions to precipitate at the site as their insoluble hydroxide or carbonate salts. These salts are then allowed to settle out of the water and are periodically removed.

Each treatment option described relies on chemists and engineers understanding the chemical reactions that lead to the problems caused, and then employing other reactions, based on solubility, that allow them to alleviate the problem.



## ASSESSING THE OBJECTIVES FOR SECTION 5-5

**EXERCISE 5-5(a) KNOWLEDGE:** Do the following refer to soluble or insoluble compounds?

- (a) It forms a precipitate.
- (b) It is labeled “(aq)”.
- (c) It dissolves in water.
- (d) Its formation is the driving force in the reaction.

**EXERCISE 5-5(b) ANALYSIS:** Label the following as being soluble (aq) or insoluble (s).

- (a)  $(\text{NH}_4)_2\text{SO}_4$     (b)  $\text{Sn}(\text{OH})_2$     (c)  $\text{Pb}(\text{NO}_3)_2$     (d)  $\text{Fe}_2(\text{SO}_4)_3$

**EXERCISE 5-5(c) ANALYSIS:** Determine whether the following reactants will form a precipitate.

- (a)  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$     (b)  $\text{AlBr}_3$  and  $\text{NaOH}$     (c)  $(\text{NH}_4)_2\text{S}$  and  $\text{CaI}_2$

**EXERCISE 5-5(d) ANALYSIS:** Write the balanced molecular formula, complete with the state symbols (aq) and (s), for the following reactants.

- (a)  $\text{CrI}_3(\text{aq}) + \text{Li}_3\text{PO}_4(\text{aq}) \longrightarrow$   
 (b)  $\text{Cs}_2\text{CO}_3(\text{aq}) + \text{FeBr}_3(\text{aq}) \longrightarrow$

**EXERCISE 5-5(e) SYNTHESIS:** A solution of  $\text{AgNO}_3$  is mixed with a solution of  $\text{K}_2\text{S}$ . Write the molecular, total ionic, and net ionic equations illustrating the reaction.

For additional practice, work chapter problems 5-34, 5-37, 5-39, 5-44, and 5-46.

## 5-6 DOUBLE-REPLACEMENT REACTIONS—NEUTRALIZATION

## ▶ OBJECTIVE FOR SECTION 5-6

Write balanced molecular, total ionic, and net ionic equations for neutralization reactions.



**LOOKING AHEAD!** In a second type of double-replacement reaction, the ions combine to form a molecular compound. Although there are several examples of this, we will focus on the formation of the simple molecular compound water. This is discussed next. ■

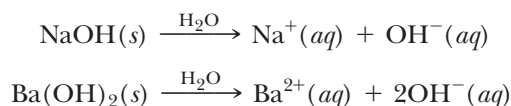
## 5-6.1 Strong Acids and Strong Bases

Strong acids and bases are two compounds that can be difficult, if not dangerous, to handle. They are very corrosive and can cause severe burns. (See Figure 5-9.) When carefully mixed together in the right proportions, however, they become harmless. The corrosive properties of both are neutralized. In Section 4-6 we defined a class of compounds known as strong acids. They are characterized by their complete ionization in water to form  $\text{H}^+(\text{aq})$  and an anion. A second class of compounds, **strong bases**, dissolve in water to form the hydroxide ion  $[\text{OH}^-(\text{aq})]$ . Unlike acids, these compounds are ionic in the solid state and the ions are simply separated in the aqueous solution as in any soluble ionic compound. The strong bases are hydroxides formed by the Group IA and IIA metal ions (except for  $\text{Be}^{2+}$ ). Examples



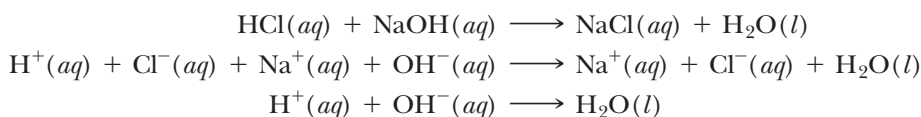
**FIGURE 5-9 Strong Acids and Bases** Containers of these compounds usually include a warning about their corrosive properties.

include sodium hydroxide (lye) and barium hydroxide. Their solution in water is illustrated by the following equations.

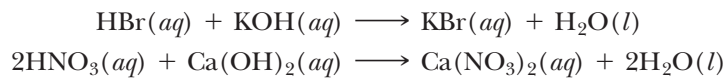


## 5-6.2 Neutralization Reactions

When solutions of strong acids and bases are mixed, the  $\text{H}^+(aq)$  from the acid combines with the  $\text{OH}^-(aq)$  from the base to form the molecular compound water. *The reaction of an acid and a base is known as a neutralization reaction.* The neutralization of hydrochloric acid and sodium hydroxide is illustrated below with the molecular, total ionic, and net ionic equations. The ionic compound remaining in solution, NaCl, is known as salt. *A salt is formed from the cation of the base and the anion of the acid.* If the salt is soluble, its ions are spectator ions and are subtracted from the equation to form the net ionic equation.



Unlike precipitation reactions, the net ionic equation for all neutralization reactions between strong acids and strong bases is the same. The driving force for these reactions is the formation of water, a molecular compound, from two ions. The balanced molecular equations for two additional neutralization reactions follow.



The interactions of other types of acids and bases, known as weak acids and bases, are somewhat more involved and are discussed in more detail in Chapter 13.

### EXAMPLE 5-10

#### Writing Neutralization Reactions

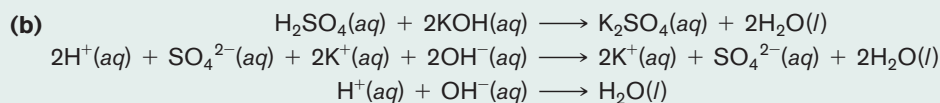
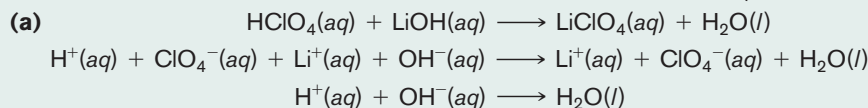
Write the molecular, total ionic, and net ionic equations for the neutralization of (a)  $\text{HClO}_4$  and  $\text{LiOH}$  and (b)  $\text{H}_2\text{SO}_4$  and  $\text{KOH}$ .

#### PROCEDURE

Follow the steps outlined in Section 5-5.3. Water is a product in neutralization reactions and should be labeled with an  $(l)$  and not ionized.

#### SOLUTION

To balance the equations, one should make sure that there is one  $\text{H}^+(aq)$  for each  $\text{OH}^-(aq)$ . Another way is to write the formula of the salt formed and then balance the number of reactant cations (from the base) and reactant anions (from the acid).



#### ANALYSIS

The water that is produced in the reaction is in addition to the water used as a solvent to dissolve the reactants. So, unlike a precipitation reaction, where the formation of the solid shows us that there is an obvious reaction occurring, neutralization

reactions are harder to recognize in the lab. There are many times where no discernible physical change occurs. If the concentrations of reactants are high enough, a significant amount of heat can be produced in the neutralization process and the solution's temperature will rise. Alternately, you can follow the course of the reaction with chemical indicators that change color as the reactants are neutralized, or the reaction can be followed by electrical meters. Beyond that, it's just our knowledge of the chemistry of the reaction that tells us that anything is occurring.

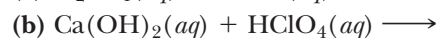
### SYNTHESIS

It will be useful in upcoming chapters to know the balancing coefficients for chemical reactions. Neutralization reactions provide us with a shortcut to determine the needed coefficients for the reactants. Every acid provides a given number of  $\text{H}^+$ 's. Every base provides a given number of  $\text{OH}^-$ 's. Together they'll combine in a 1-to-1 ratio to form water. So how many of the acid molecules and how many of the base molecules are needed to produce the same number of  $\text{H}^+$ 's and  $\text{OH}^-$ 's? Consider a reaction between  $\text{H}_3\text{PO}_4$  and  $\text{Ba}(\text{OH})_2$ . What will be the balancing coefficient in front of each molecule?

$\text{H}_3\text{PO}_4$  delivers  $3\text{H}^+$ .  $\text{Ba}(\text{OH})_2$  delivers  $2\text{OH}^-$ . Two acids and three bases will produce a total of six waters. The balancing coefficients are 2 and 3, respectively.

### ASSESSING THE OBJECTIVE FOR SECTION 5-6

**EXERCISE 5-6(a) ANALYSIS:** Write out the balanced molecular equation, complete with the state symbols (*aq*) and (*l*), for the following reactants.



**EXERCISE 5-6(b) SYNTHESIS:** Write the balanced molecular, total ionic, and net ionic equations illustrating the neutralization of nitric acid with strontium hydroxide.

*For additional practice, work chapter problems 5-55, 5-57, and 5-60.*

### PART B SUMMARY

#### KEY TERMS

- 5-3.1** Ionic compounds may be **soluble** or **insoluble** in water. p. 148
- 5-3.1** A **solution** is formed by a **solute** dissolving in a **solvent**. p. 148
- 5-3.2** **Strong acids** are completely ionized in aqueous solution. p. 148
- 5-4** A **single-replacement reaction** involves the exchange of a free metal for a different metal ion. p. 150
- 5-4.1** Reactions in aqueous solution can be represented by **molecular** and **total ionic equations**. p. 150
- 5-4.1** When **spectator ions** are subtracted out, a **net ionic equation** results. p. 150
- 5-4.2** The **activity series** relates the ability of a metal to replace other metal ions. p. 151
- 5-5.2** A **precipitate** is a solid formed from solution. p. 154
- 5-5.2** A **precipitation reaction** is a type of **double-replacement reaction**. p. 154
- 5-6.1** **Strong bases** are ionic compounds that produce the hydroxide ion in solution. p. 159
- 5-6.2** A **neutralization reaction** is a second type of double-replacement reaction that produces a **salt** and water. p. 160

#### SUMMARY CHART

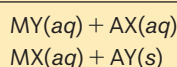
##### Three More Types of Reactions

##### Single Replacement

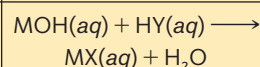


##### Double Replacement

##### Precipitation



##### Neutralization

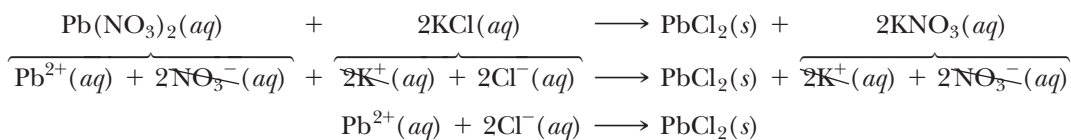


## CHAPTER SUMMARY

A concise statement of a chemical property is relayed by the **chemical equation**. With symbols, formulas, and other abbreviations, a sizable amount of chemical information can be communicated. This includes the elements or compounds involved as **reactants** and **products**, their physical states, and the number of molecules of each compound involved in the reaction. When the numbers of atoms of each element are made the same on both sides of the equation by use of **coefficients**, the equation is said to be **balanced**.

In this chapter, we considered five different types of reactions that can be conveniently represented by equations. Each type has a general equation that characterizes that kind of reaction. The first three types discussed in this chapter are **combustion reactions**, **combination reactions**, and **decomposition reactions**.

In addition to these three types of reactions, two other types usually involve reactions that occur in an aqueous solution. When a substance (a **solute**) is dispersed by a liquid (a **solvent**), it forms a homogeneous mixture known as a **solution**. Substances that dissolve in water are said to be **soluble** and those that do not are **insoluble**. Soluble ionic compounds are separated into their individual ions in aqueous solution.



In **single-replacement reactions**, a metal exchanges places with the cation of a different metal. The ability of metals to replace other metal ions can be compared and ranked in the **activity series**. Hydrogen, although not a metal, is usually included in this series.

**Double-replacement reactions** involve the exchange of ions between two soluble compounds. In a **precipitation reaction**, the two ions combine to form a solid ionic compound known as a **precipitate**, which separates from the solution. In a **neutralization reaction**, the two ions form a molecular compound.

In neutralization reactions, **strong acids** [molecular compounds that dissolve in water to form  $\text{H}^+(aq)$  ions] react with **strong bases** [ionic compounds that dissolve in water to form  $\text{OH}^-(aq)$  ions]. The reaction produces water and a **salt**.

Single- and double-replacement reactions can be illustrated by three types of equations. In a **molecular equation**, all species are represented as neutral compounds. In a **total ionic equation**, soluble ionic compounds and strong acids are represented as separate ions. If the **spectator ions** (those ions that are not directly involved in the reaction) are removed, the result is a **net ionic equation**. The three types of equations for a typical precipitation reaction are shown below.

## OBJECTIVES

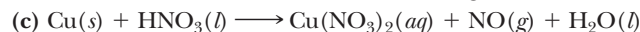
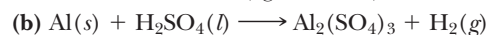
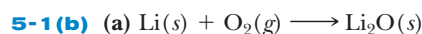
| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES      | EXERCISES      | CHAPTER PROBLEMS                   |
|---------|---|---------------|----------------|------------------------------------|
| 5-1     | Write a chemical equation from a word description of the reaction.  | 5-1           | 1a, 1b, 1e, 2c | 10, 11, 12, 13                     |
|         | Balance a simple chemical equation by inspection.   | 5-1, 5-2, 5-3 | 1c, 1d         | 2, 3, 4, 5                         |
| 5-2     | Classify certain chemical reactions as being combustion, combination, or decomposition reactions.                                     | 5-3           | 2a, 2b, 2c     | 14, 15, 16, 18, 19, 20, 21, 22, 23 |
| 5-3     | Write the ions formed when ionic compounds or acids dissolve in water.  | 5-4           | 3a, 3b, 3c     | 24, 25, 26, 27                     |
| 5-4     | Given the activity series, complete several single-replacement reactions as balanced molecular, total ionic, and net ionic equations. | 5-5           | 4a, 4b, 4c, 4d | 28, 29, 30, 33                     |
| 5-5     | Given a table of solubility rules, determine whether a specific ionic compound is soluble or insoluble in water.                      | 5-6           | 5a, 5b, 5c     | 34, 35, 40, 42                     |
|         | Write balanced molecular, total ionic, and net ionic equations for precipitation reactions.   | 5-7, 5-8, 5-9 | 5d, 5e         | 44, 45, 46, 47, 48, 49             |
| 5-6     | Write balanced molecular, total ionic, and net ionic equations for neutralization reactions.  | 5-10          | 6a, 6b         | 55, 56, 57, 58                     |

## ANSWERS TO ASSESSING THE OBJECTIVES

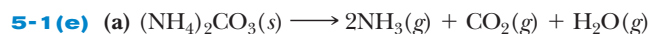
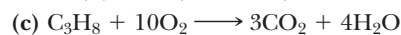
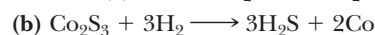
## PART A

## EXERCISES

**5-1(a)** A chemical reaction is represented with symbols and formulas by means of a chemical equation. The arrow in an equation separates the reactants on the left from the products on the right. To conform to the law of conservation of mass, an equation must be balanced. This is accomplished by introducing coefficients in front of formulas rather than changing subscripts in a formula.

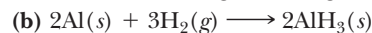
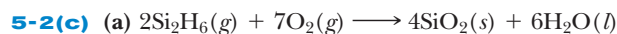


**5-1(c)** (a) B, C, O, H (b) N, H, N(again), O (c) S, O, Na, I



**5-2(a)** (a) combination, combustion (b) decomposition, combustion (c) combination, combustion (d) all reactions (e) decomposition

**5-2(b)** (a) decomposition (b) combustion (c) combination (d) decomposition (e) combination

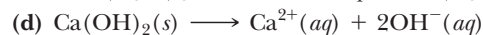
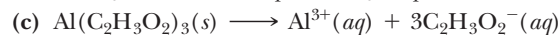
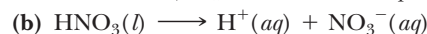


## PART B

## EXERCISES

**5-3(a)** (a)  $\text{H}^+$  and  $\text{NO}_2^-$  (b)  $\text{K}^+$  and  $\text{PO}_4^{3-}$  (c)  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (d)  $\text{Zn}^{2+}$  and  $\text{ClO}_4^-$

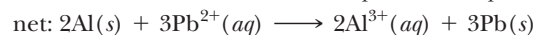
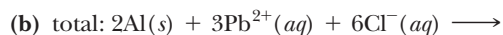
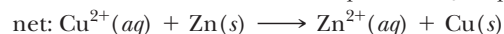
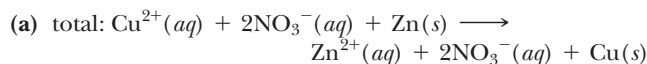
**5-3(b)** (a) three (b) four (c) four (d) two



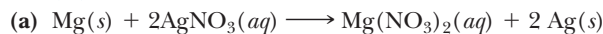
**5-4(a)** (a) Ni replaces Ag (b) Al replaces Cu

(c) Mg replaces Cr (d) Sn replaces H

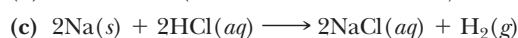
## 5-4(b)



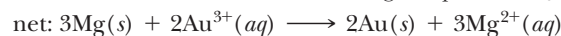
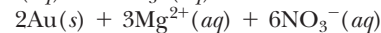
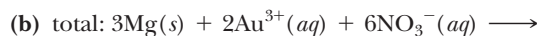
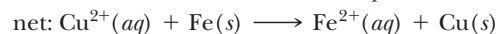
## 5-4(c)



(b) no reaction (Sn is less reactive than K)



## 5-4(d)

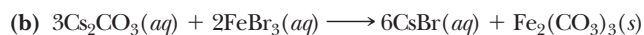
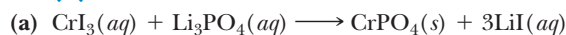


**5-5(a)** (a) insoluble (b) soluble (c) soluble (d) insoluble

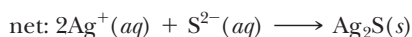
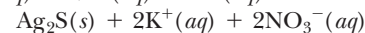
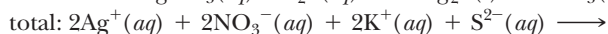
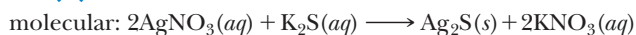
**5-5(b)** (a) soluble (b) insoluble (c) soluble (d) soluble

**5-5(c)** (a) No. Both the  $\text{K}^+$  and the  $\text{Na}^+$  will produce soluble products. (b) Yes.  $\text{Al}(\text{OH})_3$  is insoluble. (c) Yes.  $\text{CaS}$  is insoluble.

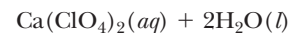
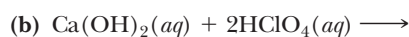
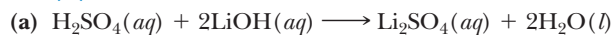
## 5-5(d)



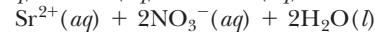
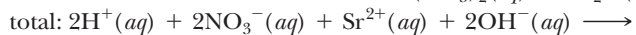
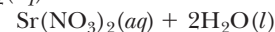
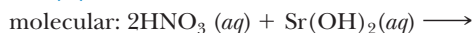
## 5-5(e)



## 5-6(a)



## 5-6(b)





## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## Chemical Equations (SECTION 5-1)

**5-1.** The physical state of an element is included in a chemical equation. Each of the following compounds is a gas, a solid, or a liquid under normal conditions. Indicate the proper physical state by adding (g), (s), or (l) after the formula.

- |                                    |                      |                     |                     |
|------------------------------------|----------------------|---------------------|---------------------|
| (a) Cl <sub>2</sub>                | (d) H <sub>2</sub> O | (g) Br <sub>2</sub> | (j) Na              |
| (b) C                              | (e) P <sub>4</sub>   | (h) NaBr            | (k) Hg              |
| (c) K <sub>2</sub> SO <sub>4</sub> | (f) H <sub>2</sub>   | (i) S <sub>8</sub>  | (l) CO <sub>2</sub> |

**5-2.** Balance the following equations.

- (a)  $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$   
 (b)  $\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}$   
 (c)  $\text{H}_2\text{SO}_4 + \text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$   
 (d)  $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$

**5-3.** Balance the following equations.

- (a)  $\text{NaBr} + \text{Cl}_2 \longrightarrow \text{NaCl} + \text{Br}_2$   
 (b)  $\text{KOH} + \text{H}_3\text{AsO}_4 \longrightarrow \text{K}_2\text{HAsO}_4 + \text{H}_2\text{O}$   
 (c)  $\text{Ti} + \text{Cl}_2 \longrightarrow \text{TiCl}_4$   
 (d)  $\text{Al} + \text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2$

**5-4.** Balance the following equations.

- (a)  $\text{Al} + \text{H}_3\text{PO}_4 \longrightarrow \text{AlPO}_4 + \text{H}_2$   
 (b)  $\text{Ca}(\text{OH})_2 + \text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$   
 (c)  $\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$   
 (d)  $\text{C}_2\text{H}_6 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$

**5-5.** Balance the following equations.

- (a)  $\text{Ca}(\text{CN})_2 + \text{HBr} \longrightarrow \text{CaBr}_2 + \text{HCN}$   
 (b)  $\text{C}_3\text{H}_6 + \text{O}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$   
 (c)  $\text{P}_4 + \text{S}_8 \longrightarrow \text{P}_4\text{S}_3$   
 (d)  $\text{Cr}_2\text{O}_3 + \text{Si} \longrightarrow \text{Cr} + \text{SiO}_2$

**5-6.** Balance the following equations.

- (a)  $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2 + \text{NH}_3$   
 (b)  $\text{H}_2\text{S} + \text{O}_2 \longrightarrow \text{S} + \text{H}_2\text{O}$   
 (c)  $\text{Si}_2\text{H}_6 + \text{H}_2\text{O} \longrightarrow \text{Si}(\text{OH})_4 + \text{H}_2$   
 (d)  $\text{C}_2\text{H}_6 + \text{Cl}_2 \longrightarrow \text{C}_2\text{HCl}_5 + \text{HCl}$

**5-7.** Balance the following equations.

- (a)  $\text{Na}_2\text{NH} + \text{H}_2\text{O} \longrightarrow \text{NH}_3 + \text{NaOH}$   
 (b)  $\text{CaC}_2 + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$   
 (c)  $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow \text{XeO}_3 + \text{HF}$   
 (d)  $\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + \text{HCl}$

**5-8.** Balance the following equations.

- (a)  $\text{B}_4\text{H}_{10} + \text{O}_2 \longrightarrow \text{B}_2\text{O}_3 + \text{H}_2\text{O}$   
 (b)  $\text{SF}_6 + \text{SO}_3 \longrightarrow \text{O}_2\text{SF}_2$   
 (c)  $\text{CS}_2 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{SO}_2$   
 (d)  $\text{BF}_3 + \text{NaH} \longrightarrow \text{B}_2\text{H}_6 + \text{NaF}$

**5-9.** Balance the following equations.

- (a)  $\text{NH}_3 + \text{Cl}_2 \longrightarrow \text{NHCl}_2 + \text{HCl}$   
 (b)  $\text{PBr}_3 + \text{H}_2\text{O} \longrightarrow \text{HBr} + \text{H}_3\text{PO}_3$   
 (c)  $\text{Mg} + \text{Fe}_3\text{O}_4 \longrightarrow \text{MgO} + \text{Fe}$   
 (d)  $\text{Fe}_3\text{O}_4 + \text{H}_2 \longrightarrow \text{Fe} + \text{H}_2\text{O}$

**5-10.** Write balanced chemical equations from the following word equations. Include the physical state of each element or compound.

- (a) Sodium metal plus water yields hydrogen gas and an aqueous sodium hydroxide solution.  
 (b) Potassium chlorate when heated yields potassium chloride plus oxygen gas. (Ionic compounds are solids.)  
 (c) An aqueous sodium chloride solution plus an aqueous silver nitrate solution yields a silver chloride precipitate (solid) and a sodium nitrate solution.  
 (d) An aqueous phosphoric acid solution plus an aqueous calcium hydroxide solution yields water and solid calcium phosphate.

**5-11.** Write balanced chemical equations from the following word equations. Include the physical state of each element or compound.

- (a) Solid phenol (C<sub>6</sub>H<sub>6</sub>O) reacts with oxygen to form carbon dioxide gas and liquid water.  
 (b) An aqueous calcium hydroxide solution reacts with gaseous sulfur trioxide to form a precipitate of calcium sulfate and water.  
 (c) Lithium is the only element that combines with nitrogen at room temperature. The reaction forms lithium nitride.  
 (d) Magnesium dissolves in an aqueous chromium(III) nitrate solution to form chromium and a magnesium nitrate solution.

**5-12.** Nickel(II) nitrate is prepared by heating nickel metal with liquid dinitrogen tetroxide. In addition to the nitrate, gaseous nitrogen monoxide is formed. Write the balanced equation.

**5-13.** One of the steps in the production of iron involves the reaction of Fe<sub>3</sub>O<sub>4</sub> with carbon monoxide to produce FeO and carbon dioxide. Write the balanced equation.

### Combustion, Combination, and Decomposition Reactions (SECTION 5-2)

**5-14.** Which reactions in problems 5-2 and 5-4 can be classified as a combustion, a combination, or a decomposition reaction?

**5-15.** Which reactions in problems 5-3 and 5-5 can be classified as either a combustion, a combination, or a decomposition reaction?

**5-16.** Write combustion reactions when the following compounds react with excess oxygen.

- (a)  $C_7H_{14}(l)$       (c)  $C_4H_{10}O(l)$   
 (b)  $LiCH_3(s)$       (d)  $C_2H_5SH(g)$  (a product is  $SO_2$ )

**5-17.** Write combustion reactions when the following compounds react with excess oxygen.

- (a)  $C_2H_6O_2(l)$   
 (b)  $B_6H_{12}(g)$  [a product is  $B_2O_3(s)$ ]  
 (c)  $C_6H_{12}(l)$   
 (d)  $Pb(C_2H_5)_4(s)$  [a product is  $PbO_2(s)$ ]

**5-18.** Write combination reactions that occur when the metal barium reacts with the following nonmetals.

- (a) hydrogen                      (c) bromine  
 (b) sulfur                              (d) nitrogen

**5-19.** Write combination reactions that occur when the metal aluminum reacts with the following nonmetals.

- (a) hydrogen                      (c) iodine  
 (b) oxygen                              (d) nitrogen

**5-20.** Write decomposition reactions for the following compounds. Recall that ionic compounds are solids.

- (a)  $Ca(HCO_3)_2$  into calcium oxide, carbon dioxide, and water  
 (b)  $Ag_2O$  into its elements  
 (c)  $N_2O_3$  gas into nitrogen dioxide gas and nitrogen monoxide gas

**5-21.** Write decomposition reactions for the following compounds. Recall that ionic compounds are solids.

- (a) liquid  $SbF_5$  into fluorine and solid antimony trifluoride  
 (b)  $PtO_2$  into its elements  
 (c) gaseous  $BrF$  into bromine and gaseous bromine trifluoride

**5-22.** Write balanced equations by predicting the products of the following reactions. Include the physical state of each element or compound.

- (a) the combination of potassium and chlorine  
 (b) the combustion of liquid benzene ( $C_6H_6$ )  
 (c) the decomposition of gold(III) oxide into its elements by heating  
 (d) the combustion of propyl alcohol ( $C_3H_8O$ )  
 (e) the combination of phosphorus ( $P_4$ ) and fluorine gas to produce solid phosphorus pentafluoride

**5-23.** Write balanced equations by predicting the products of the following reactions. Include the physical state of each element or compound.

- (a) the combustion of liquid butane ( $C_4H_{10}$ )  
 (b) the decomposition of aqueous sulfurous acid to produce water and a gas  
 (c) the combination of sodium and oxygen gas to form sodium peroxide (the peroxide ion is  $O_2^{2-}$ )  
 (d) the decomposition of copper(I) oxide into its elements by heating

## Ions in Aqueous Solution (SECTION 5-3)

**5-24.** Write equations illustrating the solution of each of the following compounds in water.

- (a)  $Na_2S$                               (d)  $CaS$   
 (b)  $Li_2SO_4$                               (e)  $(NH_4)_2S$   
 (c)  $K_2Cr_2O_7$                               (f)  $Ba(OH)_2$

**5-25.** Write equations illustrating the solution of each of the following compounds in water.

- (a)  $Ca(ClO_3)_2$                               (c)  $AlCl_3$   
 (b)  $CsBr$                                       (d)  $Cs_2SO_3$

**5-26.** Write equations illustrating the solution of the following compounds in water.

- (a)  $HNO_3$                                       (b)  $Sr(OH)_2$

**5-27.** Write equations illustrating the solution of the following compounds in water.

- (a)  $LiOH$                                       (b)  $HI$

## Single-Replacement Reactions (SECTION 5-4)

**5-28.** If any of the following reactions occur spontaneously, write the balanced net ionic equation. If not, write "no reaction." (Refer to Table 5-2.)

- (a)  $Pb + Zn^{2+} \longrightarrow Pb^{2+} + Zn$   
 (b)  $Fe + H^+ \longrightarrow Fe^{2+} + H_2$   
 (c)  $Cu + Ag^+ \longrightarrow Cu^{2+} + Ag$   
 (d)  $Cr + Zn^{2+} \longrightarrow Cr^{3+} + Zn$

**5-29.** If any of the following reactions occur spontaneously, write the balanced net ionic equation. If not, write "no reaction." (Refer to Table 5-2.)

- (a)  $Pb + Sn^{2+} \longrightarrow Pb^{2+} + Sn$   
 (b)  $H_2 + Ni^{2+} \longrightarrow H^+ + Ni$   
 (c)  $Cr + Ni^{2+} \longrightarrow Cr^{3+} + Ni$   
 (d)  $H_2 + Au^{3+} \longrightarrow H^+ + Au$

**5-30.** In the following situations, a reaction may or may not take place. If it does, write the balanced molecular, total ionic, and net ionic equations illustrating the reaction. Assume all involve aqueous solutions.

- (a) Some iron nails are placed in a  $CuCl_2$  solution.  
 (b) Silver coins are dropped in a hydrochloric acid solution.  
 (c) A copper wire is placed in a  $Pb(NO_3)_2$  solution.  
 (d) Zinc strips are placed in a  $Cr(NO_3)_3$  solution.

**5-31.** In the following situations, a reaction may or may not take place. If it does, write the balanced molecular, total ionic, and net ionic equations illustrating the reaction. Assume all involve aqueous solutions.

- (a) A solution of nitric acid is placed in a tin can.  
 (b) Iron nails are placed in a  $ZnBr_2$  solution.  
 (c) A chromium-plated auto accessory is placed in an  $SnCl_2$  solution.  
 (d) A silver bracelet is placed in a  $Cu(ClO_4)_2$  solution.

**5-32.** When heated, sodium metal reacts with solid  $\text{Cr}_2\text{O}_3$ . Write the balanced molecular and the net ionic equations for this single-replacement reaction.

**5-33.** When heated, aluminum metal reacts with solid  $\text{PbO}$ . Write the balanced molecular and net ionic equations for this single-replacement reaction.

## Solubility and Precipitation Reactions

### (SECTION 5-4)

**5-34.** Referring to Table 5-3, determine which of the following compounds are insoluble in water.

- (a)  $\text{Na}_2\text{S}$  (d)  $\text{Ag}_2\text{S}$   
 (b)  $\text{PbSO}_4$  (e)  $(\text{NH}_4)_2\text{S}$   
 (c)  $\text{MgSO}_4$  (f)  $\text{HgI}_2$

**5-35.** Referring to Table 5-3, determine which of the following compounds are insoluble in water.

- (a)  $\text{NiS}$  (d)  $\text{Rb}_2\text{SO}_4$   
 (b)  $\text{Hg}_2\text{Br}_2$  (e)  $\text{CaS}$   
 (c)  $\text{Al}(\text{OH})_3$  (f)  $\text{BaCO}_3$

**5-36.** Write the formulas of the precipitates formed when  $\text{Ag}^+$  combines with the following anions.

- (a)  $\text{Br}^-$  (b)  $\text{CO}_3^{2-}$  (c)  $\text{PO}_4^{3-}$

**5-37.** Write the formulas of the precipitates formed when  $\text{Pb}^{2+}$  combines with the following anions.

- (a)  $\text{SO}_4^{2-}$  (b)  $\text{PO}_4^{3-}$  (c)  $\text{I}^-$

**5-38.** Write the formulas of the precipitates formed when  $\text{CO}_3^{2-}$  combines with the following cations.

- (a)  $\text{Cu}^{2+}$  (b)  $\text{Cd}^{2+}$  (c)  $\text{Cr}^{3+}$

**5-39.** Write the formulas of the precipitates formed when  $\text{OH}^-$  combines with the following cations.

- (a)  $\text{Ag}^+$  (b)  $\text{Ni}^{2+}$  (c)  $\text{Co}^{3+}$

**5-40.** Which of the following chlorides is insoluble in water? (Refer to Table 5-3.)

- (a)  $\text{NaCl}$  (c)  $\text{AlCl}_3$   
 (b)  $\text{Hg}_2\text{Cl}_2$  (d)  $\text{BaCl}_2$

**5-41.** Which of the following sulfates is insoluble in water? (Refer to Table 5-3.)

- (a)  $\text{K}_2\text{SO}_4$  (c)  $\text{SrSO}_4$   
 (b)  $\text{ZnSO}_4$  (d)  $\text{MgSO}_4$

**5-42.** Which of the following phosphates is insoluble in water? (Refer to Table 5-3.)

- (a)  $\text{K}_3\text{PO}_4$  (c)  $(\text{NH}_4)_3\text{PO}_4$   
 (b)  $\text{Ca}_3(\text{PO}_4)_2$  (d)  $\text{Li}_3\text{PO}_4$

**5-43.** Which of the following hydroxides is insoluble in water? (Refer to Table 5-3.)

- (a)  $\text{Mg}(\text{OH})_2$  (c)  $\text{Ba}(\text{OH})_2$   
 (b)  $\text{CsOH}$  (d)  $\text{NaOH}$

**5-44.** Write the balanced molecular equation for any reaction that occurs when the following solutions are mixed. (Refer to Table 5-3.)

- (a)  $\text{KI}$  and  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  (d)  $\text{BaS}$  and  $\text{Hg}_2(\text{NO}_3)_2$   
 (b)  $\text{AgClO}_4$  and  $\text{KNO}_3$  (e)  $\text{FeCl}_3$  and  $\text{KOH}$   
 (c)  $\text{Sr}(\text{ClO}_4)_2$  and  $\text{Ba}(\text{OH})_2$

**5-45.** Write the balanced molecular equation for any reaction that occurs when the following solutions are mixed. (Refer to Table 5-3.)

- (a)  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{Na}_2\text{SO}_4$  (c)  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Na}_3\text{PO}_4$   
 (b)  $\text{NaClO}_4$  and  $\text{Pb}(\text{NO}_3)_2$  (d)  $\text{SrS}$  and  $\text{NiI}_2$

**5-46.** Write the total ionic and net ionic equations for any reactions that occurred in problem 5-44.

**5-47.** Write the total ionic and net ionic equations for any reactions that occurred in problem 5-45.

**5-48.** Write the total ionic equation and the net ionic equation for each of the following reactions.

- (a)  $\text{K}_2\text{S}(aq) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{PbS}(s) + 2\text{KNO}_3(aq)$   
 (b)  $(\text{NH}_4)_2\text{CO}_3(aq) + \text{CaCl}_2(aq) \longrightarrow$   
 $\text{CaCO}_3(s) + 2\text{NH}_4\text{Cl}(aq)$   
 (c)  $2\text{AgClO}_4(aq) + \text{Na}_2\text{CrO}_4(aq) \longrightarrow$   
 $\text{Ag}_2\text{CrO}_4(s) + 2\text{NaClO}_4(aq)$

**5-49.** Write the total ionic equation and the net ionic equations for each of the following reactions.

- (a)  $\text{Hg}_2(\text{ClO}_4)_2(aq) + 2\text{HBr}(aq) \longrightarrow$   
 $\text{Hg}_2\text{Br}_2(s) + 2\text{HClO}_4(aq)$   
 (b)  $2\text{AgNO}_3(aq) + (\text{NH}_4)_2\text{SO}_4(aq) \longrightarrow$   
 $\text{Ag}_2\text{SO}_4(s) + 2\text{NH}_4\text{NO}_3(aq)$   
 (c)  $\text{CuSO}_4(aq) + 2\text{KOH}(aq) \longrightarrow \text{Cu}(\text{OH})_2(s) + \text{K}_2\text{SO}_4(aq)$

**\*5-50.** Write the balanced molecular equations indicating how the following ionic compounds can be prepared by a precipitation reaction using any other ionic compounds. In some cases, the equation should reflect the fact that the desired compound is soluble and must be recovered by vaporizing the solvent water after removal of a precipitate.

- (a)  $\text{CuCO}_3$  (c)  $\text{Hg}_2\text{I}_2$  (e)  $\text{KC}_2\text{H}_3\text{O}_2$   
 (b)  $\text{PbSO}_4$  (d)  $\text{NH}_4\text{NO}_3$

## Neutralization Reactions (SECTION 5-5)

**5-51.** Which of the following is not a strong acid?

- (a)  $\text{HBr}$  (c)  $\text{HNO}_3$   
 (b)  $\text{HF}$  (d)  $\text{HClO}_4$

**5-52.** Which of the following is not a strong acid?

- (a)  $\text{HNO}_3$  (c)  $\text{H}_2\text{SO}_4$   
 (b)  $\text{HI}$  (d)  $\text{HNO}_2$

**5-53.** Which of the following is not a strong base?

- (a)  $\text{NaOH}$  (c)  $\text{Al}(\text{OH})_3$   
 (b)  $\text{Ba}(\text{OH})_2$  (d)  $\text{CsOH}$

**5-54.** Which of the following is not a strong base?

- (a)  $\text{Be}(\text{OH})_2$  (c)  $\text{LiOH}$   
 (b)  $\text{Ba}(\text{OH})_2$  (d)  $\text{KOH}$

**5-55.** Write balanced molecular equations for the neutralization reactions between the following compounds.

- (a)  $\text{HI}$  and  $\text{CsOH}$  (c)  $\text{H}_2\text{SO}_4$  and  $\text{Sr}(\text{OH})_2$   
 (b)  $\text{HNO}_3$  and  $\text{Ca}(\text{OH})_2$

**5-56.** Write balanced molecular equations for the neutralization reactions between the following compounds.

- (a)  $\text{Ca}(\text{OH})_2$  and  $\text{HI}$  (c)  $\text{HClO}_4$  and  $\text{Ba}(\text{OH})_2$   
 (b)  $\text{H}_2\text{SO}_4$  and  $\text{LiOH}$

**5-57.** Write the total ionic and net ionic equations for the reactions in problem 5-55.

**5-58.** Write the total ionic and net ionic equations for the reactions in problem 5-56.

**\*5-59.** Magnesium hydroxide is considered a strong base but has very low solubility in water. It is known as milk of magnesia and is used to neutralize stomach acid (HCl). Write the balanced molecular, total ionic, and net ionic equations illustrating this reaction. (Since magnesium hydroxide is a solid, the total and net ionic equations will be somewhat different.)

**\*5-60.** When calcium hydroxide is neutralized with sulfuric acid, the salt produced is insoluble in water. Write the balanced molecular, total ionic, and net ionic equations illustrating this reaction.

### General Problems

**5-61.** Write the balanced equations representing the combustion of propane gas ( $C_3H_8$ ), butane liquid ( $C_4H_{10}$ ), octane ( $C_8H_{18}$ ) in liquid gasoline, and liquid ethyl alcohol ( $C_2H_5OH$ ) found in alcoholic beverages.

**5-62.** In the combination reaction between sodium and chlorine and in the combustion reaction of magnesium, why could these also be considered electron exchange reactions?

**5-63.** Iron replaces gold ions in solution. Can you think of any practical application of this reaction?

**5-64.** Write balanced equations by predicting the products of the following reactions. Include the physical state of each element or compound.

- the combination of barium and iodine
- the neutralization of aqueous rubidium hydroxide with hydrobromic acid
- a single-replacement reaction of calcium metal with a nitric acid solution

- the combustion of solid naphthalene ( $C_{10}H_8$ )
- a precipitation reaction involving aqueous ammonium chromate and aqueous barium bromide
- the decomposition of solid aluminum hydroxide into solid aluminum oxide and gaseous water

**5-65.** Write the total ionic and net ionic equations for parts (b), (c), and (e) of problem 5-64.

**5-66.** Write balanced equations by predicting the products of the following reactions. Include the physical state of each element or compound.

- the decomposition of solid sodium azide ( $NaN_3$ ) into solid sodium nitride and nitrogen gas
- a precipitation reaction involving aqueous potassium carbonate and aqueous copper(II) sulfate
- the combustion of solid benzoic acid ( $C_7H_6O_2$ )
- a single-replacement reaction of iron metal and an aqueous gold(III) nitrate solution
- the combination of aluminum and solid sulfur ( $S_8$ )
- the neutralization of aqueous sulfuric acid with aqueous barium hydroxide

**5-67.** Write the total ionic and net ionic equations for parts (b), (d), and (f) of problem 5-66.

**5-68.** Consider a mixture of the following ions in aqueous solution:  $Na^+$ ,  $H^+$ ,  $Ba^{2+}$ ,  $ClO_4^-$ ,  $OH^-$ , and  $SO_4^{2-}$ . Write the net ionic equations for any reaction or reactions that occur between a cation and an anion.

**5-69.** Consider a mixture of the following ions in aqueous solution:  $NH_4^+$ ,  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Cl^-$ ,  $S^{2-}$ , and  $CO_3^{2-}$ . Write the net ionic equations for any reaction or reactions that occur between a cation and an anion.

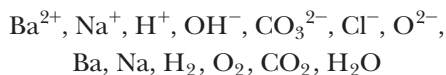
**5-70.** Consider a mixture of the following ions in aqueous solution:  $K^+$ ,  $Fe^{3+}$ ,  $Pb^{2+}$ ,  $I^-$ ,  $PO_4^{3-}$ , and  $S^{2-}$ . Write the net ionic equations for any reaction or reactions that occur between a cation and an anion.

## STUDENT WORKSHOP

### Chemical Reactions

**Purpose:** To write and balance several different classes of chemical reactions. (Work in groups of three or four. Estimated time: 20 min.)

Use the following ions, elements, and molecular compounds to write as many molecular equations as possible:

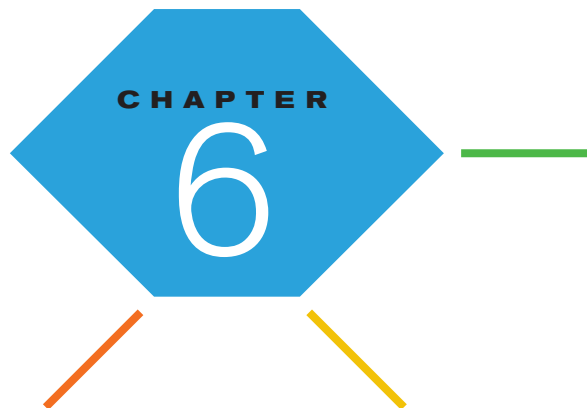


- Assign state symbols [(s), (l), (g), and (aq)] to all reactants and products.


- Balance the chemical reactions.
- Label each reaction by its type (decomposition, combination, combustion, single replacement, precipitation, neutralization).

Each group should be allowed to put one unique equation on the board. How many different reactions was the class able to come up with?





# Quantities in Chemistry

A photograph of a tractor pulling a large white tank and a plow through a field, kicking up dust. The image is partially obscured by a white circular glow on the right side.

**M**odern farming techniques require the addition of nitrogen to the soil. The composition of ammonia makes it ideal for delivering a large amount of nitrogen. The composition of compounds is a topic of this chapter.



**PART A**  
**THE MEASUREMENT OF  
MASSES OF ELEMENTS AND  
COMPOUNDS**

**6-1** Relative Masses of Elements

**6-2** The Mole and the Molar Mass of  
Elements

**6-3** The Molar Mass of Compounds

**PART B**  
**THE COMPONENT ELEMENTS  
OF COMPOUNDS**

**6-4** The Composition of Compounds



**MAKING IT REAL**

*Calcium in Our Diets—How Much Are You  
Getting?*

**6-5** Empirical and Molecular Formulas

**SETTING THE STAGE** The small size of the atom is difficult for our human minds to comprehend. For example, the period at the end of this sentence contains between  $10^{16}$  and  $10^{17}$  atoms of carbon. Obviously, such huge amounts are nearly impossible to count, even with a computer. So we count by weighing. Consider a related example. When we purchase a large quantity of small items such as nails, we certainly don't count them out one by one. In fact, we probably use a scale. This works because all the nails are about the same mass. So we buy them by the pound, knowing that 1 pound contains a specific number of nails. Since atoms of a specific element all weigh the same on average, we can do the same thing—we will weigh them. This leads us to a counting unit, specific to chemistry, that deals with a huge number of atoms.

Understanding the counting unit of chemistry will provide us with an important tool for specific calculations. For example, consider a very practical application in the use of fertilizers to provide the nitrogen that is essential for crops. Without fertilizers, it is estimated that two out of five us would not be alive today. Nature just does not supply enough fixed nitrogen to produce the crops to feed over 6 billion people. Two manufactured compounds that are widely used as a source of nitrogen for soil are ammonia ( $\text{NH}_3$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). The advantage of ammonia is that 100 kg of ammonia supplies 82 kg of nitrogen to the soil. Its disadvantage is that it is a gas and must be injected into the soil. Ammonium nitrate, an ionic compound, is a solid and can be spread on the surface. Its disadvantage is that it supplies only 35 kg of nitrogen for each 100 kg of fertilizer applied. The decision about which to use depends on cost, availability, and soil conditions. The mass of nitrogen in a given amount of each of these two compounds relates to its formula and to the relative masses of the elements in each compound, as we will discuss in this chapter.

In Part A, we will examine the main unit of mass and number as it relates to elements and compounds. We will use this information in Part B to examine the elemental composition of compounds.

**PART A**  
**THE MEASUREMENT OF**  
**MASSSES OF ELEMENTS AND**  
**COMPOUNDS**

**SETTING A GOAL**

- You will become proficient at working with the units of moles, mass, and numbers of atoms and molecules, and at converting between each of these.

**OBJECTIVES**

- 6-1** Calculate the masses of equivalent numbers of atoms of different elements.
- 6-2** Define the mole and relate this unit to numbers of atoms and to the atomic masses of the elements.
- 6-3** Perform calculations involving masses, moles, and number of molecules or formula units for compounds.

**OBJECTIVE FOR SECTION 6-1**

Calculate the masses of equivalent numbers of atoms of different elements.

**6-1 RELATIVE MASSES OF ELEMENTS**



**LOOKING AHEAD!** A good place to start is by looking at how the mass of an average atom of one element relates to the average mass of an atom of another element. From this we relate the masses of elements containing any equivalent numbers of atoms. ■

**6-1.1 The Mass of an Atom**

Each carbon atom in a tiny smudge of graphite is a specific isotope of carbon. Most of the atoms are  $^{12}\text{C}$ , which is used as the standard and is assigned a mass of exactly 12 amu. The masses of other carbon isotopes and the isotopes of any other element are calculated by comparison to  $^{12}\text{C}$ . Most elements occur in nature as mixtures of isotopes, so the atomic mass in the periodic table represents the weighted average mass of all isotopes of that element. In this chapter, we will treat the atoms of an element as if they were all identical, with the atomic mass representing the mass of this hypothetical “average” atom. The mass of individual atoms has, so far, been expressed in terms of the mass unit *amu* (atomic mass unit). This is valuable when comparing the masses of individual atoms, but it has no practical value in a laboratory situation. For example, the mass of one “average” carbon atom is 12.01 amu. This converts to grams as follows.

$$12.01 \text{ amu} = 1.994 \times 10^{-23} \text{ g}$$

Since even the best laboratory balance can detect no less than  $10^{-5}$  g, it is obvious that we need many atoms at a time to register on our scales. Because we can't work with individual atoms, we must “scale-up” the numbers of atoms so that the amounts are detectable with our laboratory instruments. In order to scale-up our measurements, we need an appropriate counting unit for atoms. To use this counting unit, however, we will not be able to actually count the number of atoms. In this case, we will weigh rather than count.

**6-1.2 Counting by Weighing**

Before we get into the calculations involving moles and molar mass, consider how a grocer may count by weighing. If we want to purchase a large number of lemons (e.g., 165) in a grocery store, it would be very tedious to actually count them one by one. It would be far easier and much quicker to use a weight scale to know that we have the desired number. If one average lemon has a mass of 145 g and we need 165 lemons, the following calculation tells us how much to weigh.

$$165 \text{ lemons} \times \frac{145 \text{ g}}{\text{lemon}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = \underline{23.9 \text{ kg}}$$

Now, suppose we want to measure the same number of apples. An average apple has a mass of 282 g, so we need the following mass of apples.

$$165 \text{ apples} \times \frac{282 \text{ g}}{\text{apple}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = \underline{46.5 \text{ kg}}$$

If we just want to have the same number of apples as lemons, we can use a shortcut that does not involve the actual number of fruit. Once we know the mass ratio of apples to lemons, we can easily convert an equivalent number of lemons to apples, and vice versa. The ratio of the masses can be expressed as follows.

$$\frac{282 \text{ g apple}}{145 \text{ g lemon}} \quad \text{and} \quad \frac{145 \text{ g lemon}}{282 \text{ g apple}}$$

*The mass ratio holds for any units of mass.* For example, there will be the same number of fruit in 282 pounds of apples and 145 pounds of lemons. Using the appropriate mass ratio expressed in kilograms rather than grams, we can make the previous calculation easier and not even be concerned with the actual number of fruit involved. The following calculation allows us to measure the same number of apples as there are lemons in 23.9 kg of lemons.

$$23.9 \text{ kg lemons} \times \frac{282 \text{ kg apple}}{145 \text{ kg lemon}} = \underline{46.5 \text{ kg apples}}$$

From this calculation, we would also know that there are the same number of fruit in 23.9 tons of lemons and 46.5 tons of apples.

Now, let's return to the world of atoms and apply the same principles. In many of the calculations that follow in this chapter, we do not need to know the *actual* number of atoms involved in a certain weighed amount, but we do need to know the *relative* numbers of atoms of different elements present. However, if we know the relative masses of the individual atoms, this is no problem. For example, if one helium atom has a mass of 4.00 amu and one carbon atom has a mass of 12.0 amu, their masses are in the following ratio.

$$\frac{4.00 \text{ amu He}}{12.0 \text{ amu C}}$$

In fact, any time helium and carbon are present in a 4.00:12.0 mass ratio *regardless of the units of mass*, we can conclude that the same number of atoms of each element is present. (See Table 6-1.) We can generalize this statement to all the elements. *When the masses of samples of any two elements are in the same ratio as that of their atomic masses, the samples have the same number of atoms.* Thus, if we wanted the same number of helium atoms as the number of atoms present in 45.0 g of carbon, we do not have to count or even know what the number is. The following calculation tells us what we want.

$$45.0 \text{ g C} \times \frac{4.00 \text{ g He}}{12.0 \text{ g C}} = 15.0 \text{ g He}$$

**TABLE 6-1** Mass Relation of C and He

| C        | He       | NUMBER OF ATOMS OF EACH ELEMENT PRESENT |
|----------|----------|---|
| 12.0 amu | 4.00 amu | 1                                       |
| 24.0 amu | 8.00 amu | 2                                       |
| 12.0 g   | 4.00 g   | $6.02 \times 10^{23}$                   |
| 24.0 g   | 8.00 g   | $1.20 \times 10^{24}$                   |
| 12.0 lb  | 4.00 lb  | $2.73 \times 10^{26}$                   |
| 24.0 ton | 8.00 ton | $1.09 \times 10^{30}$                   |

**EXAMPLE 6-1****Calculating the Relative Masses of Elements in a Compound**

The formula of the compound magnesium sulfide (MgS) indicates that there is one atom of Mg for every atom of S. What mass of sulfur is combined with 46.0 lb of magnesium?

**PROCEDURE**

From the atomic masses in the periodic table, note that one atom of magnesium has a mass of 24.31 amu and one atom of sulfur has a mass of 32.07 amu. Likewise, 24.31 lb of magnesium and 32.07 lb of sulfur have an equal number of atoms. This statement can be represented by two conversion factors, which we can use to change a mass of one element to an equivalent mass of the other.

$$(1) \quad \frac{24.31 \text{ lb Mg}}{32.07 \text{ lb S}} \quad (2) \quad \frac{32.07 \text{ lb S}}{24.31 \text{ lb Mg}}$$

Use factor (2) to convert the mass of Mg to an equivalent mass of S.

**SOLUTION**

$$46.0 \text{ lb Mg} \times \frac{32.07 \text{ lb S}}{24.31 \text{ lb Mg}} = \underline{60.7 \text{ lb S}}$$

Thus, 60.7 lb of sulfur has the same number of atoms as 46.0 lb of magnesium.

**ANALYSIS**

Again, let us stress that we are saying nothing about the actual number of atoms present. But we don't need to. Is it important to know that there are a million atoms or a million and ten? Not really. Just knowing that there are the same number of atoms is the most important thing chemically.

**SYNTHESIS**

Can this be done with compounds made up of atoms of three different elements? Consider sodium carbonate,  $\text{Na}_2\text{CO}_3$ . What would the ratio of the masses look like for this molecule? Since there are two sodium atoms, the total relative mass of sodium would be  $23 \times 2 = 46$ . The relative mass of oxygen would be  $16 \times 3 = 48$ . So any of these ratios or any of their inverses could be used to solve problems.

$$\frac{46 \text{ amu Na}}{12 \text{ amu C}} \quad \frac{46 \text{ amu Na}}{48 \text{ amu O}} \quad \frac{48 \text{ amu O}}{12 \text{ amu C}}$$

Also, any unit of mass could be put into the equation: pounds, grams, tons. Typically grams will be the most convenient.

**ASSESSING THE OBJECTIVE FOR SECTION 6-1**

**EXERCISE 6-1(a) KNOWLEDGE:** What mass of each of these elements has the same number of atoms as does 12.00 g of  $^{12}\text{C}$ ?

(a) Cl    (b) Na    (c) Pb

**EXERCISE 6-1(b) KNOWLEDGE:** What is the approximate ratio of masses of elements in the following compounds?

(a) SiC    (b) HF    (c)  $\text{SO}_2$

**EXERCISE 6-1(c) ANALYSIS:** A compound has the formula NO. What mass of oxygen is present in the compound for each 25.0 g of nitrogen?

**EXERCISE 6-1(d) ANALYSIS:** What mass of fluorine would combine with 8.50 g of Si to make  $\text{SiF}_4$ ?

**EXERCISE 6-1(e) SYNTHESIS:** If 15.0 g of Fe and 8.60 g of S combined to form FeS, would you use all of the reactants? Would anything be left over? How much?

*For additional practice, work chapter problems 6-4, 6-6, and 6-9.*

## 6-2 THE MOLE AND THE MOLAR MASS OF ELEMENTS

### ▶ OBJECTIVE FOR SECTION 6-2

Define the mole and relate this unit to numbers of atoms and to the atomic masses of the elements.



**LOOKING AHEAD!** From the previous discussion we can conclude that the atomic masses of the elements, regardless of the mass units, represent equal numbers of atoms. But what is this number and just how big is it? That will be discussed in this section. ■

### 6-2.1 The Definition of the Mole

We can easily deal with and weigh gram quantities of elements in a laboratory, but such masses represent an inconceivably large number of atoms. We are now ready for a counting unit that represents this huge number of atoms. *The number of atoms represented by the atomic mass of an element expressed in grams is a unit known as a mole.* (The SI symbol is **mol**.) The number that one mole represents is expressed in the following equality.

$$1.000 \text{ mol} = 6.022 \times 10^{23} \text{ objects or particles}$$

This number,  $6.022 \times 10^{23}$ , is referred to as **Avogadro's number** (named in honor of Amedeo Avogadro, 1776–1856, a pioneer investigator of the quantitative aspects of chemistry). Avogadro's number was determined experimentally by various methods. The formal definition of one mole concerns an isotope of carbon,  $^{12}\text{C}$ . *One mole is defined as the number of atoms in exactly 12 grams of  $^{12}\text{C}$ .* This number, of course, is Avogadro's number. *Thus the atomic mass of one mole of any element, expressed in grams, contains the same number of basic particles as there are in exactly 12 grams of  $^{12}\text{C}$ .* Avogadro's number is not an exact, defined number such as 12 in 1 dozen or 144 in 1 gross, but it is known to many more significant figures than the four (i.e., 6.022) that are shown and used in this text.

Many common counting units represent a number consistent with their use. For example, a baker sells a dozen doughnuts at a time because 12 is a practical number for that purpose. On the other hand, we buy a ream of computer paper, which contains 500 sheets. A ream of doughnuts and a dozen sheets of computer paper are not practical amounts to purchase for most purposes. Counting units of a dozen or a ream are of little use to a chemist because they don't include enough individual objects. For example, grouping  $10^{20}$  atoms into about  $10^{19}$  dozen atoms does us little good. The counting unit used by chemists needs to include an extremely large number of individual units in order to be practical. (See Figure 6-1.)

Although Avogadro's number is valuable to a chemist, its size defies the ability of the human mind to comprehend. For example, if an atom were the size of a marble and one mole of marbles were spread over the surface of Earth, our planet would



a dozen doughnuts



a ream of paper



a mole of sand particles

**FIGURE 6-1 Counting Units** One dozen, one ream, and one mole all have applications dependent on the amount needed.



be covered by a 50-mi-thick layer. Or, if the marbles were laid end to end and extended into outer space, they would reach past the farthest planets almost to the center of the galaxy. It takes light moving at 186,000 miles per second over 30,000 years to travel from Earth to the center of the galaxy. A new supercomputer can count all the people in the United States in one-quarter of a second, but it would take almost 2 million years for it to count one mole of people at the same rate. A glass of water, which is about 10 moles of water, contains more water molecules than there are grains of sand in the Sahara desert. That's difficult to imagine.

## 6-2.2 The Meaning of a Mole

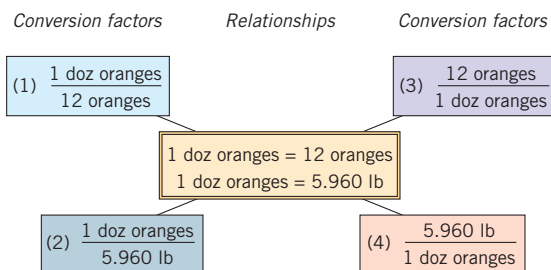
Note that one mole of a certain element implies two things.

1. *The atomic mass expressed in grams*, which is *different* for each element. This mass is known as the **molar mass of the element**. (Most of the measurements that we will use in the examples and exercises that follow are expressed to three significant figures. We will express the molar mass and Avogadro's number to four significant figures so that these factors will not limit the precision of the answer.) Thus, the mass of one mole of oxygen atoms is 16.00 g, the mass of one mole of helium atoms is 4.002 g, and the mass of one mole of uranium atoms is 238.0 g.
2. *Avogadro's number of atoms*, which is the *same* for all elements. (See Figure 6-2.)



**FIGURE 6-2 Moles of Elements** One mole of iron (the paper clips), copper, liquid mercury, and sulfur are shown. Each sample contains the same number of atoms (Avogadro's number) but has a different mass.

At this point, notice that we have established a relationship among a unit (mole), a number ( $6.022 \times 10^{23}$ ), and the mass of an element expressed in grams. It is now necessary for us to be able to convert among these three quantities. The mechanics of the conversions are not complex, however. So before we do some conversions involving atoms and so on, let's consider similar conversions involving an everyday object like a dozen oranges. In the following two calculations, assume that we are dealing with identical oranges that are weighed and sold by the dozen instead of individually. One dozen of these oranges has a mass of 5.960 lb, so we can consider this to be the "dozen mass" of oranges just as there is a "molar mass" for atoms of elements. The number in 1 dozen, however, is a much more manageable 12 rather than the  $6.022 \times 10^{23}$  in one mole. The relationships between mass of oranges and the number in 1 dozen can be summarized as follows. Notice that the four ratios that result can be used as conversion factors in calculations using the factor-label method introduced in Chapter 1.



## 6-2.3 Relationships among Dozens (the Unit), Number, and Mass

If we are asked to calculate how many dozens of oranges there are in 17.9 lb, we would need to convert from a mass (lb) to a unit (dozen). Factor (2) is used for this conversion, as follows.

$$17.9 \cancel{\text{ lb}} \times \frac{1 \text{ doz oranges}}{5.960 \cancel{\text{ lb}}} = \underline{3.00 \text{ doz oranges}}$$

In a second problem, if we are asked to calculate the mass of 142 oranges, we need to convert between mass in pounds and number of oranges. Since a direct conver-

sion is not given, the calculation can be done in two steps. We first convert the number of oranges to the dozen unit [factor (1)] and, in the second step, convert the dozen unit to mass [factor (4)]. The unit map appears as



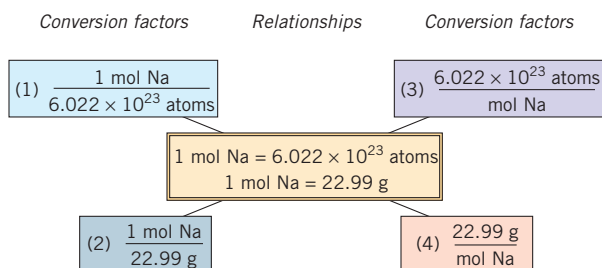
The calculation is as follows.

$$142 \text{ oranges} \times \frac{1 \text{ doz oranges}}{12 \text{ oranges}} \times \frac{5.960 \text{ lb}}{\text{doz oranges}} = \underline{70.5 \text{ lb}}$$

### 6-2.4 Relationships among Moles (the Unit), Number, and Mass

We are now ready to work very similar problems using moles, grams, and  $6.022 \times 10^{23}$  rather than dozens, pounds, and 12. If you're still a little uneasy with scientific notation, see Appendix C for a review.

In these problems, we will assume that the atoms are all identical, with the same size, shape, and mass. From the periodic table we find that the molar mass (the mass of  $6.022 \times 10^{23}$ ) of sodium atoms is 22.99 g. The two relationships just given can be either written as equalities or set up as ratios that can eventually be used as conversion factors.



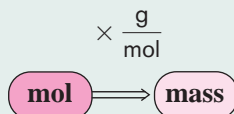
#### EXAMPLE 6-2

### Converting Moles to Mass

What is the mass of 3.00 mol of Na?

#### PROCEDURE

We need a conversion factor that converts units of moles to units of mass, or g. Thus, the conversion factor would have mole in the denominator and grams in the numerator. This is factor (4).



#### SOLUTION

$$3.00 \text{ mol Na} \times \frac{22.99 \text{ g}}{\text{mol Na}} = \underline{69.0 \text{ g}}$$

#### ANALYSIS

It's worth repeating that whenever you're solving a problem, the unit of the answer is the unit that belongs in the numerator of your conversion factor. If the unit in the denominator is not the one for which given information is provided, then a second conversion factor is needed, again with this new unit in the numerator. This process continues until you reach the unit with which you're starting.

#### SYNTHESIS

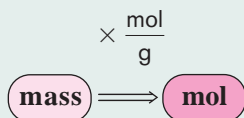
What would be the mass of the same amount of chlorine?  $3.00 \text{ mol Cl} \times 35.45 \text{ g/mol} = 106 \text{ g}$ . So there is the same number of moles, and therefore the same number of atoms, in 69.0 g of Na as there is in 106 g of Cl. If you were trying to make NaCl from its elements, you wouldn't use the same mass of each element. That would be a waste of sodium. You'd want to use about one and a half times as much chlorine. The larger the mass of each atom, the larger the mass needed to give you the same number of moles.

**EXAMPLE 6-3****Converting Mass to Moles**

How many moles are present in 34.5 g of Na?

**PROCEDURE**

This is the reverse of the previous problem, so we need a conversion factor that has grams in the denominator and mole in the numerator. This is factor (2).

**SOLUTION**

$$34.5 \text{ g} \times \frac{1 \text{ mol Na}}{22.99 \text{ g}} = \underline{\underline{1.50 \text{ mol Na}}}$$

**ANALYSIS**

Does this answer make sense? One mole is about 23 g and two moles would be double that mass, or 46 grams. Clearly the amount given is about halfway in between, so 1.50 mol is reasonable.

**SYNTHESIS**

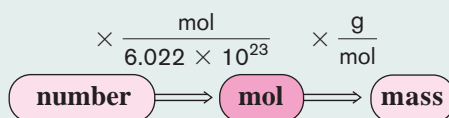
Consider what is reasonable for all your answers. Typical mass values are usually between 1.0 g and 100 g, masses that are easy to manipulate in the laboratory (there are plenty of exceptions, of course.) The numbers of moles are smaller than that, from a fraction of a mole to less than 10. For atoms (the next example), the numbers are around 20 powers of 10 or more greater than the number of moles.

**EXAMPLE 6-4****Converting Number to Mass**

What is the mass of  $1.20 \times 10^{24}$  atoms of Na?

**PROCEDURE**

In this conversion, a direct relationship between mass and number is not given. This requires a two-step conversion. In the first step, we convert the number of atoms to moles [factor (1)]; in the second step, we convert moles to mass [factor (4)].

**SOLUTION**

$$1.20 \times 10^{24} \text{ atoms Na} \times \frac{1 \text{ mol Na}}{6.022 \times 10^{23} \text{ atoms Na}} \times \frac{22.99 \text{ g}}{\text{mol Na}} = \underline{\underline{45.8 \text{ g}}}$$

**ANALYSIS**

Does this answer make sense? One mole ( $6.02 \times 10^{23}$  atoms) is about 23 g, and two moles ( $1.20 \times 10^{24}$  atoms) would be double that mass, or 46 grams. Clearly the answer should be around 46 g.

**SYNTHESIS**

What if we simplified the question and asked how many moles are in  $8.75 \times 10^{22}$  atoms of aluminum? The solution would be

$$8.75 \times 10^{22} \text{ atoms Al} \times \frac{1 \text{ mol Al}}{6.022 \times 10^{23} \text{ atoms Al}} = 0.145 \text{ mol}$$

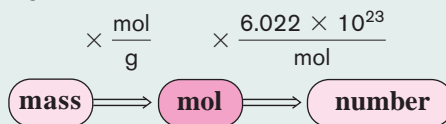
So, then, how many moles are present in  $8.75 \times 10^{22}$  atoms of iron? The same number. Since we are not considering grams, the different molar masses of aluminum and iron are not part of the calculation. It would be analogous to asking how many dozen roses are 24? How many dozen eggs are 24? 2 dozen in each case. There's 12 anything in 1 dozen and there's  $6.022 \times 10^{23}$  anything in one mole.

**EXAMPLE 6-5****Converting Mass to Number**

How many individual atoms are present in 11.5 g of Na?

**PROCEDURE**

This is the reverse of the previous problem and also requires a two-step conversion. We will convert grams to moles using factor (2) and then moles to number using factor (3).

**SOLUTION**

$$11.5 \text{ g} \times \frac{1 \text{ mol Na}}{22.99 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ atoms Na}}{\text{mol Na}} = \underline{\underline{3.01 \times 10^{23} \text{ atoms Na}}}$$

**ANALYSIS**

Always check to see that your answer makes sense. If you were asked to determine grams and the answer you calculated was  $3 \times 10^{23}$  g, is this likely? That is more than the mass of several moons in the solar system. On the other hand, if you were calculating the number of atoms and the calculator said 10.25, again, you would want to recheck how you set up the solution. Do the units cancel? Are the conversion factors correct? Was scientific notation entered into the calculator correctly? Any of these could lead to an answer that should send up red flags.

**SYNTHESIS**

Can you take these two-step analysis problems one more step? What if the element in question was a liquid, like mercury, and we wanted to know the number of atoms in 8.50 mL of Hg. What extra conversion factor is now needed? How would the problem be set up? What we need is a conversion between grams and mL. This is the density of mercury, as we discussed in Chapter 3. In the case of mercury, the factor is 13.5 g/mL. So the problem sets up:

$$\text{mL} \times \frac{\text{g}}{\text{mL}} \times \frac{\text{mol}}{\text{g}} \times \frac{\text{atoms}}{\text{mol}} = \text{atoms}$$

**ASSESSING THE OBJECTIVE FOR SECTION 6-2**

**EXERCISE 6-2(a) KNOWLEDGE:** What is needed for a conversion factor between grams and moles? Between molecules and moles?

**EXERCISE 6-2(b) ANALYSIS:** How many moles of vanadium atoms are represented by  $4.82 \times 10^{24}$  atoms? What is the mass of this number of atoms of vanadium?

**EXERCISE 6-2(c) SYNTHESIS:** Order these items by increasing mass.

- (a)  $4.55 \times 10^{22}$  atoms of Pb      (c) 0.280 moles of Ca  
(b) 8.50 g of C      (d)  $7.14 \times 10^{22}$  atoms of Zn

*For additional practice, work chapter problems 6-14, 6-16, 6-18, and 6-20.*

**6-3 THE MOLAR MASS OF COMPOUNDS**

**LOOKING AHEAD!** Using *moles* of atoms rather than individual atoms allows us to scale-up our measurements to convenient laboratory quantities. Most of the substances around us, however, are composed of compounds rather than free elements. In this section we will extend the concept of the mole from elements to compounds. ■

**OBJECTIVE FOR SECTION 6-3**

Perform calculations involving masses, moles, and number of molecules or formula units for compounds.

### 6-3.1 The Formula Weight of a Compound

Just as the mass of an automobile is the sum of the masses of all its component parts, the mass of a molecule is the sum of the masses of its component atoms. First, we will examine the masses of single molecules. The **formula weight** of a compound is determined from the number of atoms and the atomic mass (in amu) of each element indicated by a chemical formula. Recall that chemical formulas represent two types of compounds: molecular and ionic. The formula of a molecular compound represents a discrete molecular unit, whereas the formula of an ionic compound represents a formula unit, which is the whole-number ratio of cations to anions (e.g., one formula unit of  $\text{K}_2\text{SO}_4$  contains two  $\text{K}^+$  ions and one  $\text{SO}_4^{2-}$  ion). The following examples illustrate the calculation of the formula weight of a molecular compound (Example 6-6) and an ionic compound (Example 6-7).

#### EXAMPLE 6-6

##### Calculating the Formula Weight of a Molecular Compound

What is the formula weight of  $\text{CO}_2$ ?

##### PROCEDURE

Determine the number of atoms of each type. Multiply the number of atoms by their atomic masses, and add the totals together.

##### SOLUTION

| ATOM | NUMBER OF ATOMS IN MOLECULE |   | ATOMIC MASS |   | TOTAL MASS OF ATOMS IN MOLECULE |
|------|-----------------------------|---|-------------|---|---------------------------------|
| C    | 1                           | × | 12.01 amu   | = | 12.01 amu                       |
| O    | 2                           | × | 16.00 amu   | = | <u>32.00 amu</u>                |
|      |                             |   |             |   | 44.01 amu                       |

The formula weight of  $\text{CO}_2$  is

44.01 amu

#### EXAMPLE 6-7

##### Calculating the Formula Weight of an Ionic Compound

What is the formula weight of  $\text{Fe}_2(\text{SO}_4)_3$ ?

##### PROCEDURE

The same process holds for both molecular and ionic compounds.

##### SOLUTION

| ATOM | NUMBER OF ATOMS IN FORMULA UNIT |   | ATOMIC MASS |   | TOTAL MASS OF ATOMS IN FORMULA UNIT |
|------|---------------------------------|---|-------------|---|-------------------------------------|
| Fe   | 2                               | × | 55.85 amu   | = | 111.70 amu                          |
| S    | 3                               | × | 32.07 amu   | = | 96.21 amu                           |
| O    | 12                              | × | 16.00 amu   | = | <u>192.00 amu</u>                   |
|      |                                 |   |             |   | 399.91 amu                          |

The formula weight of  $\text{Fe}_2(\text{SO}_4)_3$  (to four significant figures) is

399.9 amu

##### ANALYSIS

In these multiplications we observe the rules for addition and subtraction for significant figures because the numbers of atoms are exact and the multiplication could be considered the same as addition. Therefore, the decimal place takes precedence over the number of significant figures.

##### SYNTHESIS

When we had single atoms, we were able to scale-up their individual masses from amu's to grams to accumulate a more usable quantity of matter. Will we be able to do the same thing with compounds? We will do this shortly.



### 6-3.2 The Formula Weight of Hydrates

Certain ionic compounds can have water molecules attached to their cations and/or anions. These compounds are known as *hydrates* and have some distinctive properties compared to their unhydrated (no-water) forms. For example,  $\text{CuSO}_4$  [copper(II) sulfate] is a pale-green solid, whereas  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  [copper(II) sulfate pentahydrate] is a dark-blue solid. The waters of hydration can usually be removed by heating the solid. The formula weight of a hydrate includes the mass of the water molecules. For example, the molar mass of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is calculated by summing the atomic masses of copper, sulfur, four oxygens, and five waters. That is,  $63.55 \text{ amu} (\text{Cu}) + 32.07 \text{ amu} (\text{S}) + (4 \times 16.00 \text{ amu}) (\text{O}) + (5 \times 18.02 \text{ amu}) (2\text{H} + \text{O}) = 249.7 \text{ amu}$ .

### 6-3.3 The Molar Mass of a Compound

The formula weights that we have calculated represent one molecule or one formula unit. Once again, we need to scale-up our numbers so that we have a workable amount that can be measured on a laboratory balance. Thus, we extend the definition of the mole to include compounds. *The mass of one mole ( $6.022 \times 10^{23}$  molecules or formula units) is referred to as the molar mass of the compound and is the formula weight expressed in grams.* As was the case with atoms of elements, the molar masses of various compounds differ, but the number of molecules or formula units remains the same. (See Figure 6-3.)



**FIGURE 6-3** Moles of Compounds One mole of white sodium chloride ( $\text{NaCl}$ ), blue copper sulfate hydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), yellow sodium chromate ( $\text{Na}_2\text{CrO}_4$ ), and water are shown. Each sample contains Avogadro's number of molecules or formula units.

#### EXAMPLE 6-8

##### Converting Moles to Mass and Number of Formula Units

- (a) What is the mass of 0.345 mol of  $\text{Al}_2(\text{CO}_3)_3$ ?  
 (b) How many individual ionic formula units does this amount represent?

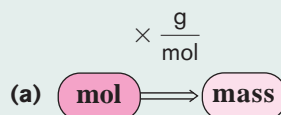
##### PROCEDURE

The problem is worked much like the examples in which we were dealing with moles of atoms rather than compounds. In this case, however, we need to find the molar mass of the compound, which is the formula weight expressed in grams. The units of molar mass are g/mol. The molar mass equals

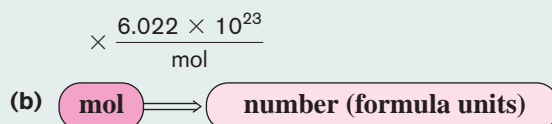
$$2\text{Al} + 3\text{C} + 9\text{O} = [(2 \times 26.98) + (3 \times 12.01) + (9 \times 16.00)] = 234.0 \text{ amu}$$

Thus, the molar mass is 234.0 g/mol.

The conversions are



and



##### SOLUTION

$$\text{(a) } 0.345 \text{ mol } \text{Al}_2(\text{CO}_3)_3 \times \frac{234.0 \text{ g}}{\text{mol } \text{Al}_2(\text{CO}_3)_3} = \underline{80.7 \text{ g}}$$

$$\text{(b) } 0.345 \text{ mol } \text{Al}_2(\text{CO}_3)_3 \times \frac{6.022 \times 10^{23} \text{ formula units}}{\text{mol } \text{Al}_2(\text{CO}_3)_3} = \underline{2.08 \times 10^{23} \text{ formula units}}$$

##### ANALYSIS

Most quantitative calculations use moles as the basis for their conversion. As a rule, if mass is mentioned in the problem, either in the given information or as the quantity to be calculated, that should be a tip-off that the molar mass of that compound or element is a necessary conversion for solving the problem. Any mention of molecule or atom indicates a sure bet that Avogadro's number,  $6.022 \times 10^{23}$  molecules/mol, is needed.

**SYNTHESIS**

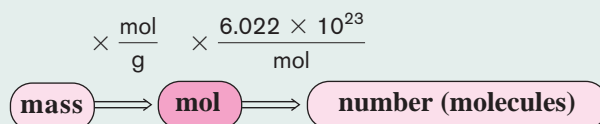
Looking ahead, then, are there other quantities that convert directly to moles? Volumes of gases and solutions both do. These will be explored in Chapters 10 and 12, respectively. In addition, reactants in an equation relate to each other by moles as well, as will be explored in Chapter 7. Clearly, the mole is a central concept for working quantitatively in chemistry, and the first step in many, many problems is to convert the given amount of material into moles.

**EXAMPLE 6-9****Converting Mass to Number of Molecules**

How many individual molecules are present in 25.0 g of  $\text{N}_2\text{O}_5$ ?

**PROCEDURE**

The formula weight of  $\text{N}_2\text{O}_5$  =  $[(2 \times 14.01) + (5 \times 16.00)] = 108.0$  amu. The molar mass is 108.0 g/mol. This is a two-step conversion as follows.

**SOLUTION**

$$25.0 \text{ g-N}_2\text{O}_5 \times \frac{1 \text{ mol}}{108.0 \text{ g-N}_2\text{O}_5} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = \underline{\underline{1.39 \times 10^{23} \text{ molecules}}}$$

**ANALYSIS**

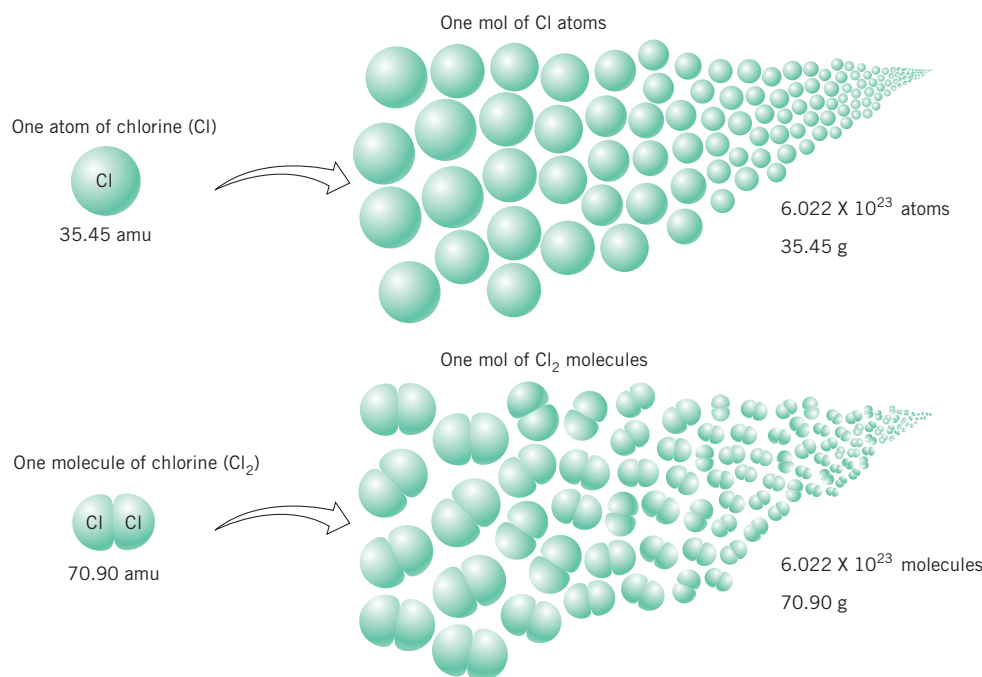
Building on the ideas in this example, notice that the question asks for number of molecules. Immediately realize the necessity of Avogadro's number. Then the given information notes the presence of 25.0 g of  $\text{N}_2\text{O}_5$ . Grams indicate molar mass, specifically of the  $\text{N}_2\text{O}_5$ . Having both these quantities is now sufficient for the solution to be put together.

**SYNTHESIS**

The terms *grams per mole* and *molecules per mole* sound very scientific, and the concept of the mole is difficult at first. Always remember that the mole is just a number of particles and, as such, is treated the same way as the term dozen (12), score (20) or grand (1000). The example above conceptually is no different from asking how many doughnuts are in 6 lb if a dozen doughnuts weighs 2 lb. Easy. At 2 lb per dozen, 6 lb is 3 doz doughnuts. 3 doz is 36. If you can make the same conceptual connections in the problems, they'll work much more easily.

The term *a mole of molecules* does sound confusing. It is somewhat unfortunate that the counting unit (mole) and the fundamental particle that is being counted (molecule) read so similarly. Try to remember that the *molecule* is the tiny, fundamental particle of a compound that is being counted. A *mole* is an incredibly large number of molecules (i.e.,  $6.022 \times 10^{23}$ ).

Another point of caution concerns nonmetal elements, such as chlorine ( $\text{Cl}_2$ ), that exist in nature as molecules rather than solitary atoms. For example, if we report the presence of "one mole of chlorine," it is not always obvious what is meant. Do we have one mole of chlorine atoms ( $6.022 \times 10^{23}$  atoms, 35.45 g) or one mole of chlorine molecules ( $6.022 \times 10^{23}$  molecules, 70.90 g)? Note that there are *two Cl atoms per molecule* and *two moles of Cl atoms per mole of  $\text{Cl}_2$  molecules*. (See Figure 6-4.) In future discussions, one mole of chlorine or any of the diatomic elements will refer to the molecules. Thus it is important to be specific in cases where we are using one mole of atoms. This situation is analogous to the difference between a dozen sneakers and a dozen pairs of sneakers. Both the mass and the actual number of the dozen pairs of sneakers are double those of a dozen sneakers.



**FIGURE 6-4 Atoms, Molecules, and Moles** A molecule is a discrete entity. A mole is a huge number of these entities.

**ASSESSING THE  
OBJECTIVE FOR  
SECTION 6-3**

**EXERCISE 6-3(a) KNOWLEDGE:** How many grams and how many formula units are in one mole of CaF<sub>2</sub>?

**EXERCISE 6-3(b) ANALYSIS:** Determine the answer, with the proper unit, of the following.

- (a) formula weight of magnesium nitride
- (b) molar mass of sulfur hexafluoride

**EXERCISE 6-3(c) ANALYSIS:** How many moles of Cl<sub>2</sub>O and how many individual molecules are present in 438 g of Cl<sub>2</sub>O?

**EXERCISE 6-3(d) SYNTHESIS:** Which of the possible iron chlorides [iron(II) chloride or iron(III) chloride] contains  $1.00 \times 10^{24}$  formula units in 269 g?

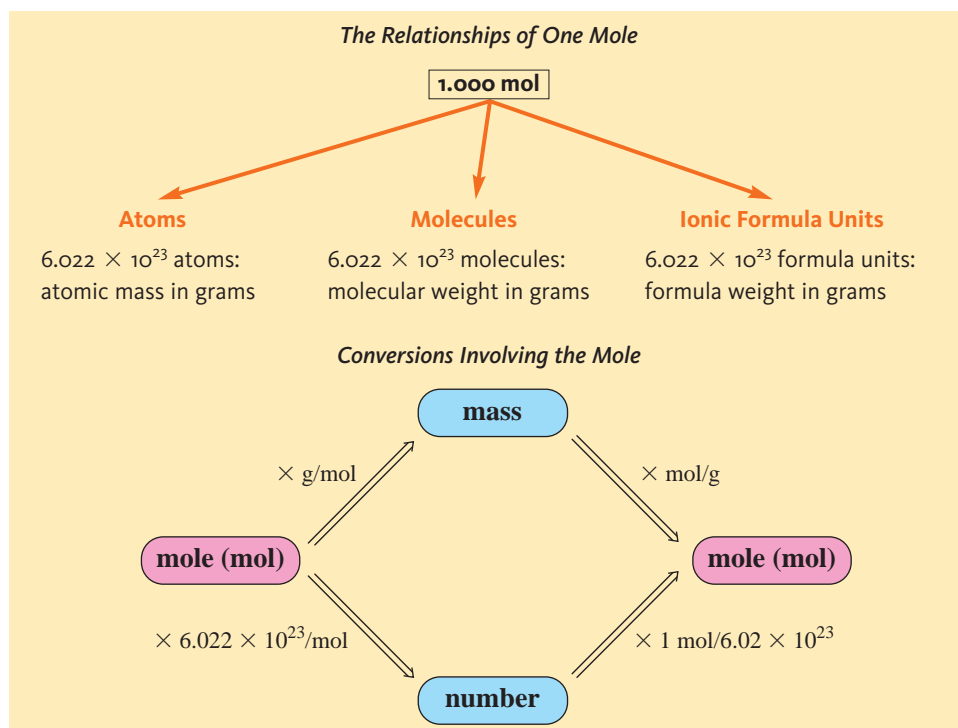
*For additional practice, work chapter problems 6-26, 6-30, and 6-31.*

**PART A  
SUMMARY**

**KEY TERMS**

- 6-2.1** The unit of quantity in chemistry is known as the **mole (mol)** and represents **Avogadro's number** of particles. p. 173
- 6-2.2** The **molar mass of an element** is the atomic weight in grams. p. 174
- 6-3.1** The **formula weight** of a compound is the sum of the atomic weights of its component atoms expressed in amu. p. 178
- 6-3.3** The **molar mass of a compound** is the formula weight expressed in grams. p. 179

## SUMMARY CHARTS



## PART B THE COMPONENT ELEMENTS OF COMPOUNDS

### SETTING A GOAL

- You will learn the relationship between the formula of a compound and its elemental composition.

### OBJECTIVES

- 6-4** Given the formula of a compound, determine the mole, mass, and percent composition of its elements.
- 6-5 (a)** Use percent or mass composition to determine the empirical formula of a compound. **(b)** Given the molar mass of a compound and its empirical formula, determine its molecular formula.

### ▶ OBJECTIVE FOR SECTION 6-4

Given the formula of a compound, determine the mole, mass, and percent composition of its elements.

## 6-4 THE COMPOSITION OF COMPOUNDS



**LOOKING AHEAD!** The formula of a compound relays a wealth of information about the component elements. We will now look deeper into how the component parts of a compound relate to its formula. ■

One plus two equals one? At first glance this seems like bad math. However, we do know that *one* frame plus *two* wheels equals *one* bicycle. So in the context of the relationship of parts to the whole, the math works. *Likewise*, one *carbon atom* plus two *oxygen atoms* equals one *molecule of carbon dioxide*. Now consider the compound sulfuric acid ( $\text{H}_2\text{SO}_4$ ). In Table 6-2, we have illustrated the relation of one mole of compound to all its component parts. All of these relationships can be used to construct conversion factors between the compound and its elements. We will use similar conversion factors in sample problems to separate compounds into their mole components, mass components, and, finally, percent composition.

**TABLE 6-2** The Composition of One Mole of  $\text{H}_2\text{SO}_4$ 

| One Mole of $\text{H}_2\text{SO}_4$     |                         |               |
|---|-------------------------|---------------|
| NUMBER OF ATOMS                         | MOLES OF ATOMS          | MASS OF ATOMS |
| $1.204 \times 10^{24}$ H atoms          | ← 2 mol H               | → 2.016 g H   |
| $6.022 \times 10^{23}$ S atoms          | ← 1 mol S               | → 32.07 g S   |
| $2.409 \times 10^{24}$ O atoms          | ← 4 mol O               | → 64.00 g O   |
| Totals: $4.215 \times 10^{24}$ atoms in | 7 mol atoms in          |               |
| $6.022 \times 10^{23}$ molecules        | ← one mole of molecules | → 98.09 g     |

### 6-4.1 The Mole Composition of a Compound

Our first task is simply to separate a quantity of a compound expressed in moles into the number of moles of each element that is part of the compound. To do this, we will establish a **mole ratio**, a conversion factor that shows *the relationship between the number of moles of a particular element, and a mole of the compound containing that element*. The formula of the compound provides this ratio. This calculation is illustrated in Example 6-10.

#### EXAMPLE 6-10

#### Converting Moles of a Compound into Moles of Its Component Elements

How many moles of each atom are present in 0.345 mol of  $\text{Al}_2(\text{CO}_3)_3$ ? What is the total number of moles of atoms present?

#### PROCEDURE

In this problem, note that there are two Al atoms, three C atoms, and nine O atoms in each formula unit of compound. Therefore, in 1 mol of compound, there are 2 mol of Al, 3 mol of C, and 9 mol of O atoms. These can all be expressed as mole ratios in factor form.

$$\frac{2 \text{ mol Al}}{\text{mol Al}_2(\text{CO}_3)_3} \quad \frac{3 \text{ mol C}}{\text{mol Al}_2(\text{CO}_3)_3} \quad \frac{9 \text{ mol O}}{\text{mol Al}_2(\text{CO}_3)_3}$$

#### SOLUTION

$$\text{Al: } 0.345 \text{ mol Al}_2(\text{CO}_3)_3 \times \frac{2 \text{ mol Al}}{\text{mol Al}_2(\text{CO}_3)_3} = \underline{\underline{0.690 \text{ mol Al}}}$$

$$\text{C: } 0.345 \text{ mol Al}_2(\text{CO}_3)_3 \times \frac{3 \text{ mol C}}{\text{mol Al}_2(\text{CO}_3)_3} = \underline{\underline{1.04 \text{ mol C}}}$$

$$\text{O: } 0.345 \text{ mol Al}_2(\text{CO}_3)_3 \times \frac{9 \text{ mol O}}{\text{mol Al}_2(\text{CO}_3)_3} = \underline{\underline{3.11 \text{ mol O}}}$$

Total moles of atoms present:

$$0.690 \text{ mol Al} + 1.04 \text{ mol C} + 3.11 \text{ mol O} = \underline{\underline{4.84 \text{ mol atoms}}}$$

#### ANALYSIS

A problem such as this works both ways, of course. We can hypothetically “build” molecules from the moles of its component elements. How many moles of aluminum carbonate could be built out of 8 moles of aluminum and sufficient amounts of carbon and oxygen? Use the mole ratio between aluminum and aluminum carbonate, but inverted so that you’re solving for the moles of aluminum carbonate.

$$8 \text{ moles Al} \times \frac{1 \text{ mol Al}_2(\text{CO}_3)_3}{2 \text{ mol Al}} = 4 \text{ mol Al}_2(\text{CO}_3)_3$$

#### SYNTHESIS

Mole ratios like those above will play an important role in *stoichiometry*, a topic explored in the next chapter. Notice that the total moles of elements present is 4.84, which is 14 times the number of moles of compound. This corresponds to 14 atoms of elements per molecule of compound.



### 6-4.2 The Mass Composition of a Compound

We can now extend this concept into the component masses of the elements. In the following example, we will calculate the mass of each element present in a specific mole quantity of limestone.

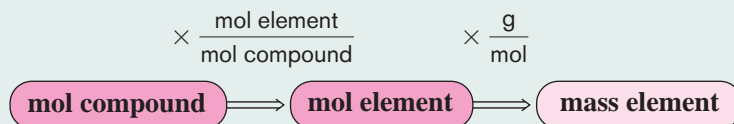
#### EXAMPLE 6-11

#### Converting Moles of a Compound into Masses of Its Component Elements

What masses of each element are present in 2.36 mole of limestone ( $\text{CaCO}_3$ )?

#### PROCEDURE

In this problem, convert the moles of each element present in the given quantity of the compound to the mass of that element. This is a two-step conversion as follows.



#### SOLUTION

$$\text{Ca: } 2.36 \text{ mol CaCO}_3 \times \frac{1 \text{ mol Ca}}{\text{mol CaCO}_3} \times \frac{40.08 \text{ g Ca}}{\text{mol Ca}} = \underline{\underline{94.6 \text{ g Ca}}}$$

$$\text{C: } 2.36 \text{ mol CaCO}_3 \times \frac{1 \text{ mol C}}{\text{mol CaCO}_3} \times \frac{12.01 \text{ g C}}{\text{mol C}} = \underline{\underline{28.3 \text{ g C}}}$$

$$\text{O: } 2.36 \text{ mol CaCO}_3 \times \frac{3 \text{ mol O}}{\text{mol CaCO}_3} \times \frac{16.00 \text{ g O}}{\text{mol O}} = \underline{\underline{113 \text{ g O}}}$$

#### ANALYSIS

The two-step nature of this problem comes from the desire to calculate mass (which requires the molar mass as a conversion factor) and the focus on a single element of a compound (mole ratio between the element and the compound) in each case.

#### SYNTHESIS

Could you go backward with this problem? Could you calculate the mass of limestone that could be made from 5.50 moles of calcium? What conversion factors are needed to solve this problem? Because you want the mass of limestone, you would need its molar mass. Because the problem asks you to relate limestone and calcium, you would also use the mole ratio between them.

$$5.50 \text{ mol Ca} \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol Ca}} \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 551 \text{ g CaCO}_3$$

### 6-4.3 The Percent Composition of a Compound

Perhaps the most common way of expressing the composition of elements in a compound is percent composition. **Percent composition** expresses the mass of each element per 100 mass units of compound. For example, if there is an 82-g quantity of nitrogen present in each 100 g of ammonia ( $\text{NH}_3$ ), the percent composition is expressed as 82% nitrogen.

The mass of one mole of carbon dioxide is 44.01 g, and it is composed of one mole of carbon atoms (12.01 g) and two moles of oxygen atoms ( $2 \times 16.00 = 32.00$  g). The percent composition is calculated by dividing the total mass of each component element by the total mass (molar mass) of the compound and then multiplying by 100%.

$$\frac{\text{total mass of component element}}{\text{total mass (molar mass)}} \times 100\% = \text{percent composition}$$

In  $\text{CO}_2$ , the percent composition of C is

$$\frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} \times 100\% = 27.29\% \text{ C}$$

and the percent composition of O is

$$\frac{32.00 \text{ g O}}{44.01 \text{ g CO}_2} \times 100\% = 72.71\%$$

### EXAMPLE 6-12

#### Calculating the Percent Composition of Limestone ( $\text{CaCO}_3$ )

What is the percent composition of all of the elements in limestone ( $\text{CaCO}_3$ )?

#### PROCEDURE

Find the molar mass and convert the *total* mass of each element to percent of molar mass.

#### SOLUTION

One mol of  $\text{CaCO}_3$  contains

1 mol of Ca (40.08 g)

1 mol of C (12.01 g)

3 mol of O  $\left( 3 \text{ mol O} \times \frac{16.00 \text{ g}}{\text{mol O}} = 48.00 \text{ g} \right)$

The molar mass =  $40.08 \text{ g} + 12.01 \text{ g} + 48.00 \text{ g} = 100.09 \text{ g} = 100.1 \text{ g}$ .

$$\% \text{ Ca: } \frac{40.08 \text{ g Ca}}{100.1 \text{ g CaCO}_3} \times 100\% = \underline{\underline{40.04\%}}$$

$$\% \text{ C: } \frac{12.01 \text{ g C}}{100.1 \text{ g CaCO}_3} \times 100\% = \underline{\underline{12.00\%}}$$

$$\% \text{ O: } \frac{48.00 \text{ g O}}{100.1 \text{ g CaCO}_3} \times 100\% = \underline{\underline{47.95\%}}$$

#### ANALYSIS

It is easier to find the percent composition of oxygen by subtracting the first two from 100%. That is,  $100.00\% - 40.04\% - 12.00\% = 47.96\%$ . The difference is due to rounding off. However, it is still best to calculate all three values individually and then check to see that they add to 100%. Notice that the percentages add to 99.99%, rather than 100%. This, again, is just a function of rounding with significant figures.

#### SYNTHESIS

Can you think of some applications for information like this? Why would it be important to know the percentage of an element in a particular compound? How would diverse areas such as mining, agriculture, drug companies, and petroleum producers benefit from knowing the percentage of a given element in a particular compound? Check out Making It Real, "Calcium in Our Diets—How Much Are You Getting?", for one specific example.



Marble is a form of limestone.

### EXAMPLE 6-13

#### Calculating the Percent Composition of Borazine

What is the percent composition of all the elements in borazine ( $\text{B}_3\text{N}_3\text{H}_6$ )?

#### PROCEDURE

Find the molar mass and convert the *total* mass of each element to percent of molar mass.

#### SOLUTION

One mole of  $\text{B}_3\text{N}_3\text{H}_6$  contains

$$3 \text{ mol of B} \left( 3 \text{ mol B} \times \frac{10.81 \text{ g}}{\text{mol B}} = 32.43 \text{ g} \right)$$

$$3 \text{ mol of N} \left( 3 \text{ mol N} \times \frac{14.01 \text{ g}}{\text{mol N}} = 42.03 \text{ g} \right)$$

$$6 \text{ mol of H} \left( 6 \text{ mol H} \times \frac{1.008 \text{ g}}{\text{mol H}} = 6.048 \text{ g} \right)$$

The molar mass = 32.43 g + 42.03 g + 6.048 g = 80.51 g

$$\% \text{ B: } \frac{32.43 \text{ g B}}{80.51 \text{ g B}_3\text{N}_3\text{H}_6} \times 100\% = \underline{\underline{40.28\%}}$$

$$\% \text{ N: } \frac{42.03 \text{ g N}}{80.51 \text{ g B}_3\text{N}_3\text{H}_6} \times 100\% = \underline{\underline{52.20\%}}$$

$$\% \text{ H: } \frac{6.048 \text{ g H}}{80.51 \text{ g B}_3\text{N}_3\text{H}_6} \times 100\% = \underline{\underline{7.51\%}}$$

### ANALYSIS

The general procedure presented here works for both molecular and ionic compounds. It works whether there are two elements present or eight elements present. Science is all about learning a few general principles and being able to adjust to a variety of related situations. What if just the name, not the formula, was provided? Use the skills you developed in Chapter 4 to determine the correct formula, and then use the above procedure to get the percentages. Being able to combine multiple skills is also a hallmark of science.

### SYNTHESIS

Relative amounts of a substance are most conveniently expressed as percentages. *Percent* literally means “parts per hundred”. When the amounts of substances are smaller, other relative measures are used. Parts per thousand, million, or billion can be used for relative amounts much smaller than percentages. Pollutants in water are often measured in ppm (parts per million), as are many trace elements in Earth’s crust. When converting a percent to a decimal, you’ve been conditioned to move the decimal point two places (e.g., 20% = 0.20). To convert ppm, you just move it six places (e.g., 20 ppm = 0.000020). So, if the barium concentration limit in drinking water is 6.5 ppm, this would correspond to only 0.00065%. We will consider ppm and ppb (parts per billion) in more detail in Chapter 12.



## Calcium in Our Diets—How Much Are You Getting?



Calcium is a major component of bones. Our bones are continuously undergoing change. Certain hormones cause bone to be

destroyed, while others cause it to be rebuilt. When the process gets out of balance and bone loss exceeds bone formation, a condition called *osteoporosis* may result. Bones can become brittle and subject to fracture or compression, a condition common in elderly people. Women are especially prone to this potentially debilitating disease, which is treated in two ways.

One popular drug interferes with the bone-destruction process, resulting in increased bone density. More commonly (and economically), osteoporosis is treated with calcium supplements. Three compounds that are used are calcium carbonate, calcium citrate, and calcium gluconate. These three compounds are all ionic, which means they are solids and can be taken in the form of a tablet. But which actually contains the most calcium in a 500-mg pill?

In Example 6-12, we calculated that calcium carbonate is 40.04% calcium. Similar calculations indicate that

calcium citrate is 24.1% calcium and calcium gluconate is 9.31% calcium. The accompanying table summarizes the calculations indicating the amount of calcium in one 500-mg tablet.

CALCIUM SUPPLEMENTS

| COMPOUND          | FORMULA  | %CALCIUM | Mg Ca/<br>500-Mg PILL |
|-------------------|--|----------|-----------------------|
| Calcium carbonate | $\text{CaCO}_3$                                  | 40.0     | 205 mg                |
| Calcium citrate   | $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$  | 24.1     | 121 mg                |
| Calcium gluconate | $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ | 9.31     | 46.6 mg               |

It would seem that calcium carbonate is the best. (It is also the cheapest.) However, calcium carbonate is also used as an antacid, so it decreases the acidity in the stomach. Since it needs excess stomach acid to dissolve, nutritionists recommend that it be taken with meals. (Meals cause stomach acid to be produced for digestion.) The total amount of calcium available is not the only important factor in choosing a supplement. How much calcium is actually absorbed during digestion is also a factor. The other two compounds have less amounts of calcium in one pill, but that calcium is actually better absorbed in the small intestine. Also, they do not have to be taken with meals. The decision of which supplement one takes depends on convenience, side effects, and the advice of a physician.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 6-4

**EXERCISE 6-4(a) KNOWLEDGE:** What are the mole ratios of elements present in  $\text{K}_2\text{CrO}_4$ ?

**EXERCISE 6-4(b) ANALYSIS:** How many moles of H atoms will react with 2.5 moles of N to make  $\text{NH}_3$ ?

**EXERCISE 6-4(c) ANALYSIS:** Fill in the blanks.

Vitamin C (ascorbic acid) is a compound with the formula  $\text{C}_6\text{H}_8\text{O}_6$ . The formula weight of the compound is \_\_\_\_\_ amu. In a 0.650-mol quantity of ascorbic acid, there is \_\_\_\_\_ mol of carbon, which equals \_\_\_\_\_ g of carbon. The compound is \_\_\_\_\_ % carbon.

**EXERCISE 6-4(d) ANALYSIS:** What is the percent composition by mass of all the elements in  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ?

**EXERCISE 6-4(e) SYNTHESIS:** How many moles of chlorine (Cl) are found in 45.0 g of aluminum chloride?

For additional practice, work chapter problems 6-36, 6-38, 6-40, 6-44, and 6-46.

## 6-5 EMPIRICAL AND MOLECULAR FORMULAS



**LOOKING AHEAD!** From the formula of a compound, we can calculate either the mass composition of the elements or their percent composition. In this section we will do just the opposite—that is, from the mass composition or the percent composition, we will obtain the ratio of the atoms of the elements in a compound. ■

▶ OBJECTIVES FOR  
SECTION 6-5

(a) Use percent or mass composition to determine the empirical formula of a compound. (b) Given the molar mass of a compound and its empirical formula, determine its molecular formula.

## 6-5.1 Empirical Formulas

Two common hydrocarbons (carbon–hydrogen compounds) are known as acetylene ( $\text{C}_2\text{H}_2$ ) and benzene ( $\text{C}_6\text{H}_6$ ). Actually, except for their classification as hydrocarbons, these two compounds have very few properties in common. Acetylene is a gas used in welding, and benzene is a liquid solvent. What they do have in common, however, is that they have the same percent composition. This is because they have the same empirical formula. *The empirical formula is the simplest whole-number ratio of atoms in a compound.* Most ionic compounds are represented by empirical formulas by virtue of the way that we write their formula units. The formula of a molecular compound, however, represents the actual number of atoms present in one molecule. One benzene molecule is composed of six carbon and six hydrogen atoms, but the empirical formula (the ratio of atoms present) is obtained by dividing the subscripts by 6. The same empirical formula (CH) is obtained for acetylene by dividing the subscripts by 2.

## 6-5.2 Calculating Empirical Formulas

The key to determining an empirical formula is to realize exactly what a formula tells us. When we picture individual molecules, then our interpretation of a chemical formula is an accounting of the atoms in that molecule. When we expand our concept to a mole of molecules, then we realize that the chemical formula is also the number of moles of each element in the chemical. So calculating the empirical formula is just calculating the relative number of moles of each element. To calculate the empirical formula of a compound from percent composition, we follow three steps.

1. Convert percent composition to an actual mass.
2. Convert mass to moles of each element.
3. Find the whole-number ratio of the moles of different elements.

This procedure is best illustrated by the following examples.

**EXAMPLE 6-14****Calculating the Empirical Formula from Percent Composition**

What is the empirical formula of laughing gas, which is composed of 63.6% nitrogen and 36.4% oxygen by mass?

**PROCEDURE**

Remember that *percent* means “parts per 100”. Therefore, if we simply assume that we have a 100-g quantity of compound, the percents convert to specific masses as follows.

$$63.6\% \text{ N} = \frac{63.6 \text{ g N}}{100 \text{ g compound}} \quad 36.4\% \text{ O} = \frac{36.4 \text{ g O}}{100 \text{ g compound}}$$

We now convert the masses to moles of each element.

$$63.6 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 4.54 \text{ mol N in 100-g compound}$$

$$36.4 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.28 \text{ mol O in 100-g compound}$$

The ratio of N to O atoms will be the same as the ratio of N to O moles. The formula cannot remain fractional, since only whole numbers of atoms are present in a compound. To find the whole-number ratio of moles, the mathematically simplest thing to do is to divide through by the smaller number of moles, which in this case is 2.28 mol of O.

**SOLUTION**

$$\text{N: } \frac{4.54}{2.28} = 1.99 \approx 2.00 \quad \text{O: } \frac{2.28}{2.28} = 1.00$$

The empirical formula of the compound is

**ANALYSIS**

Remember that what we are calculating here is the empirical formula. The actual formula could be  $\text{N}_4\text{O}_2$ ,  $\text{N}_6\text{O}_3$ , or any other where the ratio is 2:1. More information is needed to determine the exact molecular formula.

**SYNTHESIS**

This is a very common type of calculation for a chemist. Once a new compound is formed in the lab, an analysis is the next step. This is usually done by a commercial laboratory that specializes in elemental analysis. Knowing what elements to test for is key, but the list is typically evident based on the starting materials used. The analysis is reported in the percentages of each element that was tested for. It is then up to the chemist to establish the empirical formula from this data.

**EXAMPLE 6-15**

Magnetite is a mineral composed of iron and oxygen.

**Calculating the Empirical Formula from Mass Composition**

Pure magnetite is a mineral composed of an iron–oxygen binary compound. A 3.85-g sample of magnetite is composed of 2.79 g of iron. What is the empirical formula of magnetite?

**PROCEDURE**

- Find the mass of oxygen by subtracting the mass of the iron from the total mass.
- Convert the masses of iron and oxygen to moles.
- Find the whole-number ratio of moles of iron and oxygen. Divide by the smaller number of moles.

**SOLUTION**

- $3.85 \text{ g} - 2.79 \text{ g (Fe)} = 1.06 \text{ g (O)}$
- $2.79 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 0.0500 \text{ mole Fe}$   
 $1.06 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0663 \text{ mol O}$



$$(c) \text{ Fe: } \frac{0.0500}{0.0500} = 1.00 \quad \text{O: } \frac{0.0663}{0.0500} = 1.33$$

This time we're not quite finished, since  $\text{FeO}_{1.33}$  still has a fractional number that must be cleared. (You should keep at least two decimal places in these numbers; do not round off a number like 1.33 to 1.3 or 1.) This fractional number can be cleared by multiplying both subscripts by an integer that produces whole numbers. In this case, 1.33 is equivalent to  $1\frac{1}{3}$  or  $\frac{4}{3}$ , so both subscripts (the 1 implied for Fe and the 1.33 for O) can be multiplied by 3 to clear the fraction.



### ANALYSIS

A decimal value of 0.50 can be multiplied by 2; values of 0.33 and 0.67 can be multiplied by 3; values of 0.25 and 0.75 can be multiplied by 4; and values of 0.20, 0.40, 0.60, and 0.80 can be multiplied by 5. There are few examples that are more complex than these. Since the last decimal place is estimated, values such as 0.49 should be rounded off to 0.50.

### SYNTHESIS

So what would you do if, upon analysis of a compound containing C, H, and O, the moles calculated for each element were C = 1.33 mol, H = 2.50 mol, and O = 1 mol? Since the carbon is multiplied by 3 and the hydrogen is multiplied by 2, the common multiplier is 6. Therefore, everything should be multiplied by 6. The formula is  $\text{C}_8\text{H}_{15}\text{O}_6$ . Notice that something like this happens whenever the smallest subscript in the empirical formula is greater than 1.

## 6-5.3 The Molecular Formula of a Compound

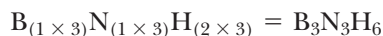
To determine the **molecular formula** of molecular compounds, we need to know how many empirical units are present in each molecular unit. Thus, it is necessary to know both the molar mass of the compound (g/mol) and the mass of one empirical unit (g/emp. unit). The ratio of these two quantities must be a whole number (represented as  $a$  below) and represents the number of empirical units in one mole of compound.

$$a = \frac{\text{molar mass}}{\text{emp. mass}} = \frac{X \text{ g/mol}}{Y \text{ g/emp. unit}} = 1, 2, 3, \text{ etc., emp. unit/mol}$$

The molecular formula is obtained by multiplying the subscripts of the empirical formula by  $a$ . For example, the empirical formula of borazine (from Example 6-13) is  $\text{BNH}_2$ . The mass of one empirical unit is  $[10.81 + 14.01 + (2 \times 1.008)] = 26.84$  g/emp. unit. Its molar mass is 80.5 g/mol.

$$a = \frac{80.5 \text{ g/mol}}{26.84 \text{ g/emp. unit}} = 3 \text{ emp. units/mol}$$

The molecular formula is 3 times the subscripts of the empirical formula.



### EXAMPLE 6-16

#### Determining the Molecular Formula from the Empirical Formula and Molar Mass

A phosphorus–oxygen compound has an empirical formula of  $\text{P}_2\text{O}_5$ . Its molar mass is 283.9 g/mol. What is its molecular formula?

### PROCEDURE

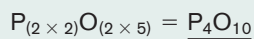
Find the number of empirical units in each mole of compound  $a$ . The empirical mass of the compound is found by adding two moles of phosphorus (30.97 g/mol) and five moles of oxygen (16.00 g/mol). Compare this to the given molar mass to determine the whole number multiplier.

$$(2 \times 30.97 \text{ g}) + (5 \times 16.00 \text{ g}) = 141.9 \text{ g/emp. unit}$$

### SOLUTION

$$a = \frac{283.9 \text{ g/mol}}{141.9 \text{ g/emp. unit}} = 2 \text{ emp. units/mol}$$

The molecular formula is



### ANALYSIS

When an empirical formula is calculated, particularly in a laboratory setting, masses are sometimes not determined exactly due to experimental errors. Therefore, subscripts that are calculated rarely come out to a whole number. A modest amount of rounding is required. On the other hand, once an empirical formula is determined, there are techniques that can determine molar mass with very little error at all. The ratio of empirical unit masses and molar masses will be exactly whole numbers. Anything off by even a small amount of that should be a red flag that there's an error in the calculation or formula.

### SYNTHESIS

Now the challenge is to calculate an empirical formula and then to compare that formula with a known molar mass, to determine the actual molecular formula. To determine if you can do this, check out Exercise 6-5(d) in Assessing the Objectives for Section 6-5.

The types of calculations performed in this section are of fundamental importance to the advancement of science. Over 20 million unique compounds have been reported and registered by the American Chemical Society, which serves as the world registry of compounds. To establish that a new discovery is a unique compound, several steps must be followed. *First*, it must be shown that the compound is indeed a pure substance. This is established by a study of its physical properties. For example, pure substances have definite and unchanging melting and boiling points, as was discussed in Chapter 3. *Second*, the formula of the new compound must be determined by elemental analysis. *Third*, the molecular formula of the new compound is calculated from the molar mass and the empirical formula. The molar mass may also be obtained commercially or measured experimentally by methods that will be discussed in Chapter 12. *Finally*, the structural formula, which is the order and arrangement of the atoms in the molecule, is determined. Various instruments available in most laboratories can provide information of this nature. The procedure may take anywhere from a few minutes for simple molecules to a few months for very complex molecules such as those associated with life processes.

In many cases, new compounds that are identified by these procedures are tested for anticancer or anti-AIDS activity. Or maybe the new compound has an application as a herbicide, an insecticide, a perfume, a food preservative, or any number of other possibilities. In any case, many of the new compounds that are reported each year have some practical application that improves the quality of our lives.

## ASSESSING THE OBJECTIVES FOR SECTION 6-5

**EXERCISE 6-5(a) KNOWLEDGE:** Which of these is not an empirical formula?

(a)  $N_2O_5$     (b)  $CCl_4$     (c)  $C_6H_{12}O_6$     (d)  $C_2H_6O$

**EXERCISE 6-5(b) ANALYSIS:** A compound contains 5.65 g iron and 4.85 g sulfur. What's its empirical formula?

**EXERCISE 6-5(c) ANALYSIS:** A compound with the empirical formula  $C_2H_4S$  has a measured molar mass of 180.2 g/mol. What is its molecular formula?

**EXERCISE 6-5(d) SYNTHESIS:** A molecular compound is composed of boron and hydrogen. It is 84.4% boron by mass and has a molar mass of 76.96 g/mol. What is its molecular formula?

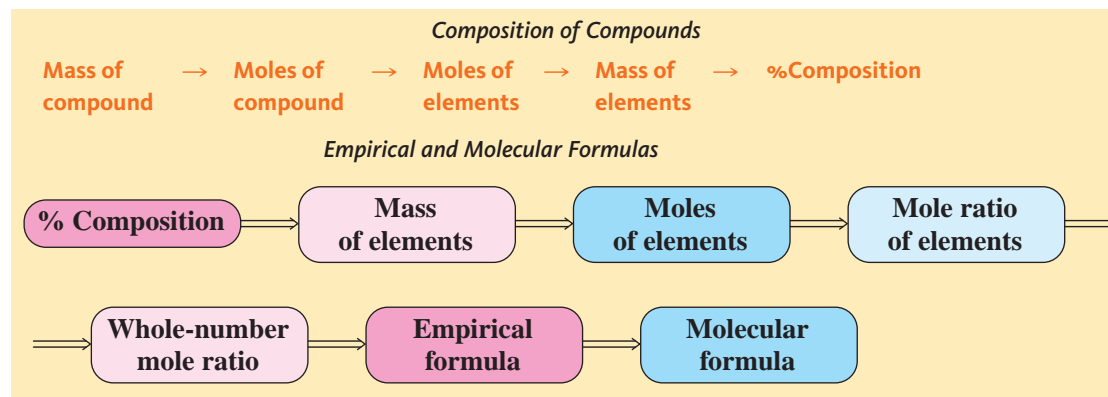
*For additional practice, work chapter problems 6-56, 6-58, 6-60, and 6-68.*

## PART B SUMMARY

### KEY TERMS

- 6-4.1** The **mole ratio** can be used to determine the moles of an element present in a given number of moles of compound. p. 183
- 6-4.3** The **percent composition** of a compound is a convenient way to represent the distribution of elements in a compound. p. 184
- 6-5.1** The **empirical formula** of a compound can be calculated from the percent composition. p. 187
- 6-5.3** The **molecular formula** of a compound is the actual formula of a compound. p. 189

## SUMMARY CHART



## CHAPTER SUMMARY

The atomic masses of the elements can be put to greater use than just comparing the masses of individual atoms. By using atomic masses as ratios, we can measure equivalent numbers of atoms without knowing the actual value of the number. The most useful measure of a number of atoms is obtained by expressing the atomic mass of an element in grams. This is referred to as the **molar mass of the element**, and it is the mass of a specific number of atoms. This number is known as the **mole (mol)**. The mole represents  $6.022 \times 10^{23}$  atoms or other individual particles, a quantity known as **Avogadro's number**.

The concept of the mole is then extended to compounds. The **molar mass of a compound** is the **formula weight** of the compound expressed in grams and is the mass of Avogadro's number of molecules or ionic formula units.

One important purpose of this chapter is for you to become comfortable with the interconversions among moles, mass, and numbers of atoms or molecules. The two conversion factors that are used for this are the molar mass and Avogadro's number.

The formula of a compound implies a **mole ratio**. It can be used to determine the number of moles, the masses, and the **percent composition** of each element in a compound.

In the reverse calculation, the **empirical formula** of a compound can be determined from its mass composition or percent composition. One needs to know the molar mass of a compound to determine the **molecular formula** from the empirical formula. The molecular formula is determined from the percent composition and the molar mass.

## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES               | EXERCISES          | CHAPTER PROBLEMS               |
|---------|---|------------------------|--------------------|--------------------------------|
| 6-1     | Calculate the masses of equivalent numbers of atoms of different elements.                            | 6-1                    | 1a, 1b, 1c, 1d, 1e | 5, 6, 8, 10                    |
| 6-2     | Define the mole and relate this unit to numbers of atoms and to the atomic masses of the elements.    | 6-2, 6-3, 6-4, 6-5     | 2a, 2b, 2c         | 14, 16, 18, 22, 23             |
| 6-3     | Perform calculations involving masses, moles, and number of molecules or formula units for compounds. | 6-6, 6-7, 6-8, 6-9     | 3a, 3b, 3c, 3d     | 25, 29, 31, 33                 |
| 6-4     | Given the formula of a compound, determine the mole, mass, and percent composition of its elements.   | 6-10, 6-11, 6-12, 6-13 | 4a, 4b, 4c, 4d, 4e | 35, 36, 39, 41, 42, 46, 48, 53 |
| 6-5     | Use percent or mass composition to determine the empirical formula of a compound.                     | 6-14, 6-15             | 5a, 5b             | 56, 59, 60, 62, 64, 67         |
|         | Given the molar mass of a compound and its empirical formula, determine its molecular formula.        | 6-16                   | 5c, 5d             | 69, 71, 73, 74                 |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

- 6-1(a)** (a) 35.453 g (b) 22.99 g (c) 207.2 g  
**6-1(b)** (a) 14:12, or 7:6 (b) 1:19 (c) 32:32, or 1:1  
**6-1(c)** 28.6 g of oxygen  
**6-1(d)** 23.0 g of fluorine  
**6-1(e)** No, you wouldn't use them all. The ratio of S to Fe shows that 8.00 g of S would react with only 13.9 g of Fe. There would be 1.1 g of Fe left over.  
**6-2(a)** Molar mass converts grams to moles. Avogadro's number converts molecules to moles.  
**6-2(b)** 8.00 moles. (Note: This answer is the same, regardless of what element you use.) The mass would be 408 g. (This result is specific to vanadium.)  
**6-2(c)**  $7.14 \times 10^{22}$  atoms of Zn (d)  $< 8.50$  g of C (b)  $< 0.280$  moles of Ca (c)  $< 4.55 \times 10^{22}$  atoms of Pb (a)  
**6-3(a)** 78.08 g and  $6.022 \times 10^{23}$  molecules  
**6-3(b)** (a) 101.0 amu (b) 146.1 g/mol  
**6-3(c)** 5.04 moles and  $3.04 \times 10^{24}$  molecules  
**6-3(d)** The number represents 1.66 moles; 269 g represents 1.66 moles of FeCl<sub>3</sub> (molar mass = 162 g/mol)

## PART B

## EXERCISES

- 6-4(a)** 2 mol K/1 mol K<sub>2</sub>CrO<sub>4</sub>, 1 mol Cr/1 mol K<sub>2</sub>CrO<sub>4</sub>, 4 mol O/1 mol K<sub>2</sub>CrO<sub>4</sub>  
**6-4(b)** 7.5 moles of H  
**6-4(c)** Vitamin C (ascorbic acid) is a compound with the formula C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>. The formula weight of the compound is 176.1 amu. In a 0.650-mol quantity of ascorbic acid, there is 3.90 mol of carbon, which equals 46.8 g of carbon. The compound is 40.9% carbon.  
**6-4(d)** In order of abundance, 44.4% O, 41.3% Cr, 11.1% N, and 3.2% H.  
**6-4(e)** The molar mass is 133.3 g/mol. The number of moles of AlCl<sub>3</sub> is 0.338 mol. The number of moles of Cl is 1.01 mol.  
**6-5(a)** (c) C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> simplifies to CH<sub>2</sub>O  
**6-5(b)** Fe<sub>2</sub>S<sub>3</sub>  
**6-5(c)** C<sub>6</sub>H<sub>12</sub>S<sub>3</sub>  
**6-5(d)** The empirical formula is BH<sub>2</sub>. The molecular formula is B<sub>6</sub>H<sub>12</sub>

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## Relative Masses of Particles (SECTION 6-1)

- 6-1.** One penny weighs 2.47 g and one nickel weighs 5.03 g. What mass of pennies has the same number of coins as there are in 1.24 lb of nickels?  
**6-2.** A small glass bead weighs 310 mg and a small marble weighs 8.55 g. A quantity of small glass beads weighs 5.05 kg. What does the same number of marbles weigh?  
**6-3.** A piece of pure gold has a mass of 145 g. What is the mass of the same number of silver atoms?  
**6-4.** A large chunk of pure aluminum has a mass of 212 lb. What is the mass of the same number of carbon atoms?  
**6-5.** A piece of copper wire has a mass of 16.0 g; the same number of atoms of a precious metal has a mass of 49.1 g. What is the metal?  
**6-6.** In the compound CuO, what mass of copper is present for each 18.0 g of oxygen?  
**6-7.** In the compound NaCl, what mass of sodium is present for each 425 g of chlorine?  
**6-8.** In a compound containing one atom of carbon and one atom of another element, it is found that 25.0 g of carbon is combined with 33.3 g of the other element. What is the element? What is the formula of the compound?  
**\*6-9.** In the compound MgBr<sub>2</sub>, what mass of bromine is present for each 46.0 g of magnesium? (Remember, there are two bromines per magnesium.)

- \*6-10.** In the compound SO<sub>3</sub>, what mass of sulfur is present for each 60.0 lb of oxygen?

## The Magnitude of the Mole (SECTION 6-2)

- 6-11.** If you could count two numbers per second, how many years would it take you to count Avogadro's number? If you were helped by the whole human race of 6.0 billion people, how long would it take?  
**6-12.** A small can of soda contains 350 mL. Planet Earth contains 326 million cubic miles ( $3.5 \times 10^{20}$  gal) of water. How many cans of soda would it take to equal all the water on Earth? How many moles of cans is this?  
**6-13.** What would the number in one mole be if the atomic mass were expressed in kilograms rather than grams? In milligrams?

## Moles of Atoms of Elements (SECTION 6-2)

- 6-14.** Fill in the blanks. Use the factor-label method to determine the answers.

| Element   | Mass in Grams | Moles of Atoms | Number of Atoms       |
|-----------|---------------|----------------|-----------------------|
| S         | 8.00          | 0.250          | $1.50 \times 10^{23}$ |
| (a) P     | 14.5          | _____          | _____                 |
| (b) Rb    | _____         | 1.75           | _____                 |
| (c) Al    | _____         | _____          | $6.02 \times 10^{23}$ |
| (d) _____ | 363           | _____          | $3.01 \times 10^{24}$ |
| (e) Ti    | _____         | _____          | 1                     |

**6-15.** Fill in the blanks. Use the factor-label method to determine the answers.

| Element   | Mass in Grams         | Moles of Atoms     | Number of Atoms       |
|-----------|-----------------------|--------------------|-----------------------|
| (a) Na    | 0.390                 | _____              | _____                 |
| (b) Cr    | _____                 | $3.01 \times 10^4$ | _____                 |
| (c) _____ | 43.2                  | _____              | $2.41 \times 10^{24}$ |
| (d) K     | $4.25 \times 10^{-6}$ | _____              | _____                 |
| (e) Ne    | _____                 | _____              | $3.66 \times 10^{21}$ |

**6-16.** What is the mass in grams of each of the following?

- (a) 1.00 mol of Cu                      (c)  $6.02 \times 10^{23}$  atoms of Ca  
 (b) 0.50 mol of S

**6-17.** What is the mass in grams of each of the following?

- (a) 4.55 mol of Be                      (c)  $3.40 \times 10^5$  mol of B  
 (b)  $6.02 \times 10^{24}$  atoms of Ca

**6-18.** How many individual atoms are in each of the following?

- (a) 32.1 mol of sulfur                  (c) 32.0 g of oxygen  
 (b) 32.1 g of sulfur

**6-19.** How many moles of atoms are in each of the following?

- (a) 281 g of Si                              (c) 19.0 atoms of fluorine  
 (b)  $7.34 \times 10^{25}$  atoms of phosphorus

**6-20.** Which has more atoms, 50.0 g of Al or 50.0 g of Fe?

**6-21.** Which contains the most Ni: 20.0 g,  $2.85 \times 10^{23}$  atoms, or 0.450 mol?

**6-22.** Which contains the most Cr: 0.025 mol,  $6.0 \times 10^{21}$  atoms, or 1.5 g of Cr?

**6-23.** A 0.251-g sample of a certain element is the mass of  $1.40 \times 10^{21}$  atoms. What is the element?

**6-24.** A 0.250-mol sample of a certain element has a mass of 49.3 g. What is the element?

### Formula Weight (SECTION 6-3)

**6-25.** What is the formula weight of each of the following? Express your answer to four significant figures.

- (a) KClO<sub>2</sub>                                  (d) H<sub>2</sub>SO<sub>4</sub>                                  (g) Fe<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>  
 (b) SO<sub>3</sub>                                      (e) Na<sub>2</sub>CO<sub>3</sub>  
 (c) N<sub>2</sub>O<sub>5</sub>                                  (f) CH<sub>3</sub>COOH

**6-26.** What is the formula weight of each of the following?

- (a) CuSO<sub>4</sub> · 6H<sub>2</sub>O (Include H<sub>2</sub>O's; they are included in one formula unit.)  
 (b) Cl<sub>2</sub>O<sub>3</sub>                                      (d) Na<sub>2</sub>BH<sub>3</sub>CO<sub>2</sub>  
 (c) Al<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>                              (e) P<sub>4</sub>O<sub>6</sub>

**6-27.** A compound is composed of three sulfate ions and two chromium ions. What is the formula weight of the compound?

**6-28.** What is the formula weight of strontium perchlorate?

### Moles of Compounds (SECTION 6-3)

**6-29.** Fill in the blanks. Use the factor-label method to determine the answers.

| Molecules                            | Mass in Grams | Number of Moles       | Number of Molecules or Formula Units |
|--------------------------------------|---------------|-----------------------|--------------------------------------|
| N <sub>2</sub> O                     | 23.8          | 0.542                 | $3.26 \times 10^{23}$                |
| (a) H <sub>2</sub> O                 | _____         | 10.5                  | _____                                |
| (b) BF <sub>3</sub>                  | _____         | _____                 | $3.01 \times 10^{21}$                |
| (c) SO <sub>2</sub>                  | 14.0          | _____                 | _____                                |
| (d) K <sub>2</sub> SO <sub>4</sub>   | _____         | $1.20 \times 10^{-4}$ | _____                                |
| (e) SO <sub>3</sub>                  | _____         | _____                 | $4.50 \times 10^{24}$                |
| (f) N(CH <sub>3</sub> ) <sub>3</sub> | 0.450         | _____                 | _____                                |

**6-30.** Fill in the blanks. Use the factor-label method to determine answers.

| Molecules                          | Mass in Grams | Number of Moles       | Number of Molecules or Formula Units |
|------------------------------------|---------------|-----------------------|--------------------------------------|
| (a) O <sub>3</sub>                 | 176           | _____                 | _____                                |
| (b) NO <sub>2</sub>                | _____         | $3.75 \times 10^{-3}$ | _____                                |
| (c) Cl <sub>2</sub> O <sub>3</sub> | _____         | _____                 | 150                                  |
| (d) UF <sub>6</sub>                | _____         | _____                 | $8.50 \times 10^{22}$                |

**6-31.** Tetrahydrocannabinol (THC) is the active ingredient in marijuana. A 0.0684-mol quantity of THC has a mass of 21.5 g. What is the molar mass of THC?

**6-32.** A 0.156-mol quantity of a compound has a mass of 7.28 g. What is the molar mass of the compound?

**6-33.** A 287-g quantity of a compound is the mass of  $1.07 \times 10^{24}$  molecules. What is the molar mass of the compound?

**6-34.** A 0.0681-g quantity of ethylene glycol (antifreeze) represents the mass of  $7.88 \times 10^{20}$  molecules. What is the molar mass of the compound?

### The Composition of Compounds (SECTION 6-4)

**6-35.** How many moles of each type of atom are in 2.55 mol of grain alcohol, C<sub>2</sub>H<sub>6</sub>O? What is the total number of moles of atoms? What is the mass of each element? What is the total mass?

**6-36.** How many moles are in 28.0 g of Ca(ClO<sub>3</sub>)<sub>2</sub>? How many moles of each element are present? How many total moles of atoms are present?

**6-37.** How many moles are in 84.0 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>? How many moles of each element are present? How many total moles of atoms are present?

**6-38.** What mass of each element is in 1.50 mol of H<sub>2</sub>SO<sub>3</sub>?

**6-39.** What mass of each element is in 2.45 mol of boric acid (H<sub>3</sub>BO<sub>3</sub>)?

**6-40.** How many moles of O<sub>2</sub> are in  $1.20 \times 10^{22}$  O<sub>2</sub> molecules? How many moles of oxygen atoms? What is the mass of oxygen molecules? What is the mass of oxygen atoms?

**6-41.** How many moles of Cl<sub>2</sub> molecules are in 985 g of Cl<sub>2</sub>? How many moles of Cl atoms are present? What is the mass of Cl atoms present?

**6-42.** What is the percent composition of a compound composed of 1.375 g of N and 3.935 g of O?

**6-43.** A sample of a compound has a mass of 4.86 g and is composed of silicon and oxygen. What is the percent composition if 2.27 g of the mass is silicon?



**6-44.** The mass of a sample of a compound is 7.44 g. Of that mass, 2.88 g is potassium, 1.03 g is nitrogen, and the remainder is oxygen. What is the percent composition of the elements?

**6-45.** What is the percent composition of all the elements in the following compounds?

- (a)  $C_2H_6O$                       (c)  $C_9H_{18}$                       (e)  $(NH_4)_2CO_3$   
 (b)  $C_3H_6$                         (d)  $Na_2SO_4$

**6-46.** What is the percent composition of all the elements in the following compounds?

- (a)  $H_2CO_3$                       (c)  $Al(NO_3)_3$   
 (b)  $Cl_2O_7$                         (d)  $NH_4H_2PO_4$

**6-47.** What is the percent composition of all the elements in borax ( $Na_2B_4O_7 \cdot 10H_2O$ )?

**6-48.** What is the percent composition of all the elements in acetaminophen ( $C_8H_9O_2N$ )? (Acetaminophen is an aspirin substitute.)

**6-49.** What is the percent composition of all the elements in saccharin ( $C_7H_5SNO_3$ )?

**6-50.** What is the percent composition of all the elements in amphetamine ( $C_9H_{13}N$ )? (Amphetamine is a stimulant.)

**\*6-51.** What mass of carbon is in a 125-g quantity of sodium oxalate?

**\*6-52.** What is the mass of phosphorus in a 25.0-lb quantity of sodium phosphate?

**\*6-53.** What mass of chromium is in a 275-kg quantity of chromium(III) carbonate?

**\*6-54.** Iron is recovered from iron ore,  $Fe_2O_3$ . How many pounds of iron can be recovered from each ton of iron ore? (1 ton = 2000 lb)

### Empirical Formulas (SECTION 6-5)

**6-55.** Which of the following are not empirical formulas?

- (a)  $N_2O_4$                       (c)  $H_2S_2O_3$                       (e)  $Mn_2O_7$   
 (b)  $Cr_2O_3$                       (d)  $H_2C_2O_4$

**6-56.** Convert the following mole ratios of elements to empirical formulas.

- (a) 0.25 mol of Fe and 0.25 mol of S  
 (b) 1.88 mol of Sr and 3.76 mol of I  
 (c) 0.32 mol of K, 0.32 mol of Cl, and 0.96 mol of O  
 (d) 1.0 mol of I and 2.5 mol of O  
 (e) 2.0 mol of Fe and 2.66 mol of O  
 (f) 4.22 mol of C, 7.03 mol of H, and 4.22 mol of Cl

**6-57.** Convert the following mole ratios of elements to empirical formulas.

- (a) 1.20 mol of Si and 2.40 mol of O  
 (b) 0.045 mol of C and 0.022 mol of S  
 (c) 1.00 mol of X and 1.20 mol of Y  
 (d) 3.11 mol of Fe, 4.66 mol of C, and 14.0 mol of O

**6-58.** What is the empirical formula of a compound that has the composition 63.2% oxygen and 36.8% nitrogen?

**6-59.** What is the empirical formula of a compound that has the composition 41.0% K, 33.7% S, and 25.3% O?

**6-60.** In an experiment it was found that 8.25 g of potassium combines with 6.75 g of  $O_2$ . What is the empirical formula of the compound?

**6-61.** Orlon is composed of very long molecules with a composition of 26.4% N, 5.66% H, and 67.9% C. What is the empirical formula of Orlon?

**6-62.** A compound is 21.6% Mg, 21.4% C, and 57.0% O. What is the empirical formula of the compound?

**6-63.** A compound is composed of 9.90 g of carbon, 1.65 g of hydrogen, and 29.3 g of chlorine. What is the empirical formula of the compound?

**6-64.** A compound is composed of 0.46 g of Na, 0.52 g of Cr, and 0.64 g of O. What is the empirical formula of the compound?

**\*6-65.** A compound is composed of 24.1% nitrogen, 6.90% hydrogen, 27.6% sulfur, and the remainder oxygen. What is the empirical formula of the compound?

**\*6-66.** Methyl salicylate is also known as oil of wintergreen. It is composed of 63.2% carbon, 31.6% oxygen, and 5.26% hydrogen. What is its empirical formula?

**\*6-67.** Nitroglycerin is used as an explosive and a heart medicine. It is composed of 15.9% carbon, 18.5% nitrogen, 63.4% oxygen, and 2.20% hydrogen. What is its empirical formula?

### Molecular Formulas (SECTION 6-5)

**6-68.** A compound has the following composition: 20.0% C, 2.2% H, and 77.8% Cl. The molar mass of the compound is 545 g/mol. What is the molecular formula of the compound?

**6-69.** A compound is composed of 1.65 g of nitrogen and 3.78 g of sulfur. If its molar mass is 184 g/mol, what is its molecular formula?

**6-70.** A compound has a composition of 18.7% B, 20.7% C, 5.15% H, and 55.4% O. Its molar mass is about 115 g/mol. What is the molecular formula of the compound?

**6-71.** A compound reported in 1970 has a composition of 34.9% K, 21.4% C, 12.5% N, 2.68% H, and 28.6% O. It has a molar mass of about 224 g/mol. What is the molecular formula of the compound?

**6-72.** Fructose is also known as fruit sugar. It has a molar mass of 180 g/mol and is composed of 40.0% carbon, 53.3% oxygen, and 6.7% hydrogen. What is the molecular formula of the compound?

**6-73.** A compound reported in 1982 has a molar mass of 834 g/mol. A 20.0-g sample of the compound contains 18.3 g of iodine and the remainder carbon. What is the molecular formula of the compound?

**6-74.** Quinine is a compound discovered in the bark of certain trees. It is an effective drug in the treatment of malaria. Its molar mass is 162 g/mol. It is 22.2% carbon, 22.2% hydrogen, 25.9% nitrogen, and 29.6% oxygen. What is the molecular formula of quinine?

### General Problems

**6-75.** The U.S. national debt was about \$4.5 trillion in 1994. How many moles of pennies would it take to pay it off?

**6-76.** A compound has the formula MN, where M represents a certain unknown metal. A sample of the compound

weighs 1.862 g; of that, 0.443 g is nitrogen. What is the identity of the metal, M?

**6-77.** What would be the number of particles in one mole if the atomic mass were expressed in ounces rather than grams? ( $28.375 \text{ g} = 1 \text{ oz}$ )

**6-78.** A certain alloy of copper has a density of  $3.75 \text{ g/mL}$  and is  $65.0\%$  by mass copper. How many copper atoms are in  $16.8 \text{ cm}^3$  of this alloy?

**6-79.** The element phosphorus exists as  $\text{P}_4$ . How many moles of molecules are in  $0.344 \text{ g}$  of phosphorus? How many phosphorus atoms are present in that amount of phosphorus?

**6-80.** Rank the following in order of increasing mass.

- 100 hydrogen atoms
- 100 moles of hydrogen molecules
- 100 grams of hydrogen
- 100 hydrogen molecules

**6-81.** Rank the following in order of increasing number of atoms.

- 100 lead atoms
- 100 moles of helium
- 100 grams of lead
- 100 grams of helium

**6-82.** Pyrite, a mineral containing iron, has the formula  $\text{FeS}_x$ . A quantity of  $2.84 \times 10^{23}$  formula units of pyrite has a mass of  $56.6 \text{ g}$ . What is the value of  $x$ ?

**6-83.** A compound has the formula  $\text{Na}_2\text{S}_4\text{O}_6$ .

- What ions are present in the compound? (The anion is all one species.)
- How many grams of sulfur are present in the compound for each  $10.0 \text{ g}$  of Na?
- What is the empirical formula of the compound?
- What is the formula weight of the compound?
- How many moles and formula units are present in  $25.0 \text{ g}$  of the compound?
- What is the percent composition of oxygen in the compound?

**6-84.** Glucose (blood sugar) has the formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . Calculate how many moles of carbon, individual hydrogen atoms, and grams of oxygen are in a  $10.0\text{-g}$  sample of glucose.

**6-85.** A compound has the formula  $\text{N}_2\text{O}_x$ . It is  $36.8\%$  nitrogen. What is the name of the compound?

**6-86.** A compound has the formula  $\text{SF}_x$ . One sample of the compound contains  $0.356 \text{ mol}$  of sulfur and  $8.57 \times 10^{23}$  atoms of fluorine. What is the name of the compound?

**6-87.** Dioxin is a compound that is known to cause cancer in certain laboratory animals.  $4.55 \times 10^{22}$  molecules of this compound have a mass of  $24.3 \text{ g}$ . Analysis of a sample of dioxin indicated the sample contained  $0.456 \text{ mol}$  of carbon,  $0.152 \text{ mol}$  of hydrogen,  $0.152 \text{ mol}$  of chlorine, and  $0.076 \text{ mol}$  of oxygen. What is the molecular formula of dioxin?

**6-88.** A certain compound has a molar mass of  $166 \text{ g/mol}$ . It is composed of  $47.1\%$  potassium,  $14.4\%$  carbon, and the remainder oxygen. What is the name of the compound?

**6-89.** A compound has the general formula  $\text{Cr}(\text{ClO}_x)_y$  and is  $14.9\%$  Cr,  $30.4\%$  chlorine, and the remainder oxygen. What is the name of the compound?

**6-90.** Epsom salts has the formula  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ . Calculate the value of  $x$  if the compound is  $51.1\%$  by mass water.

**6-91.** Potassium carbonate forms a hydrate,  $\text{K}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ . What is the value of  $x$  if the compound is  $20.7\%$  by mass water?

**6-92.** Nicotine is a compound containing carbon, hydrogen, and nitrogen. Its molar mass is  $162 \text{ g/mol}$ . A  $1.50\text{-g}$  sample of nicotine is found to contain  $1.11 \text{ g}$  of carbon. Analysis of another sample indicates that nicotine is  $8.70\%$  by mass hydrogen. What is the molecular formula of nicotine?

**6-93.** A hydrocarbon (a compound that contains only carbon and hydrogen) was burned, and the products of the combustion reaction were collected and weighed. All the carbon in the original compound is now present in  $1.20 \text{ g}$  of  $\text{CO}_2$ . All the hydrogen is present in  $0.489 \text{ g}$  of  $\text{H}_2\text{O}$ . What is the empirical formula of the compound? (*Hint:* Remember that all the moles of C atoms in  $\text{CO}_2$  and H atoms in  $\text{H}_2\text{O}$  came from the original compound.)

**6-94.** A  $0.500\text{-g}$  sample of a compound containing C, H, and O was burned, and the products were collected. The combustion reaction produced  $0.733 \text{ g}$  of  $\text{CO}_2$  and  $0.302 \text{ g}$  of  $\text{H}_2\text{O}$ . The molar mass of the compound is  $60.0 \text{ g/mol}$ . What is the molecular formula of the compound? (*Hint:* Find the mass of C and H in the original compound; the remainder of the  $0.500 \text{ g}$  is oxygen.)

## STUDENT WORKSHOP

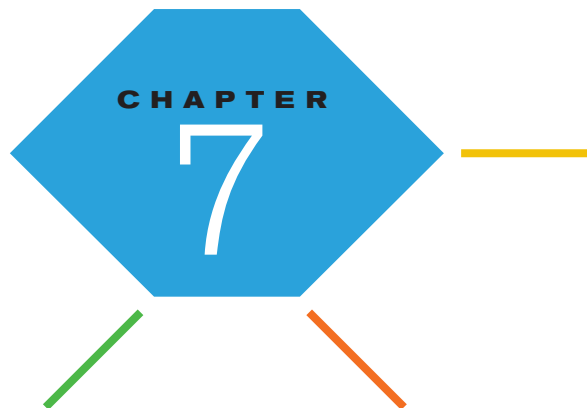
### Empirical Formulas

**Purpose:** To calculate empirical formulas and percent composition for hypothetical compounds. (Work in groups of three or four. Estimated time: 15 min.)

The following activity is a great way for a study group to practice calculations involving percent composition and empirical formulas.

- Each person in the group makes up the formula of an imaginary chemical compound.
  - Choose three arbitrary elements from the periodic table
  - Assign subscripts to each. (You should limit yourself to values of 1–5)

- Calculate the percent composition of each element in your compound.
- On a slip of paper, write out the elements present and their percent compositions, and trade this with another person in your group.
- From the data provided you, calculate the empirical formula of your classmate's compound.
- Confirm with your classmate the compound's formula based on his or her original work.



# Quantitative Relationships in Chemical Reactions



**T**he burning of charcoal releases the heat energy that grills our food. But the combustion of charcoal and fossil fuels releases carbon dioxide which affects our environment. The amount of carbon dioxide and heat energy released are contents discussed in this chapter.

**PART A**  
**MASS RELATIONSHIPS IN**  
**CHEMICAL REACTIONS**

**7-1** Stoichiometry

**7-2** Limiting Reactant



**MAKING IT REAL**

*Alcohol—The Limiting Reactant in Breathalyzers*

**7-3** Percent Yield

**PART B**  
**ENERGY RELATIONSHIPS IN**  
**CHEMICAL REACTIONS**

**7-4** Heat Energy in Chemical Reactions



**MAKING IT REAL**

*Hydrogen—The Perfect Fuel*

**SETTING THE STAGE** In the introduction to Chapter 5, we discussed the greenhouse effect and the result of global warming. The presence of increasing amounts of carbon dioxide, as well as other specific gases, is what seems to be causing the problem. However, carbon dioxide is a reactant in photosynthesis, so an increase in carbon dioxide may cause an increase in the amount and rate of production of vegetation (the product). Some early experiments indicate that some vegetation is affected noticeably but others less so. Increasing just one reactant may not lead to more growth unless all other reactants are also increased. It's like building an automobile. We need one engine and four tires per car. Having eight tires does not mean two cars unless we also have two engines as well as other necessary parts. In chemical reactions such as photosynthesis, the mass ratios of reacting compounds as well as the masses of the products that are formed are extremely important.

A chemical reaction involves not only product compounds but also energy. For example, when we barbecue over a charcoal fire, we are putting to use the large amount of heat energy that is liberated by the combustion reaction. In this case, the chemical energy in the charcoal (which is mostly carbon) is being converted into the heat energy of the fire. As mentioned in Chapter 2, this is an *exothermic* reaction. A reaction that absorbs heat energy is an *endothermic* reaction.

We will examine the mass relationships in Part A of this chapter. In Part B we will include energy as part of the quantitative relationships in chemical reactions.

**PART A**  
**MASS RELATIONSHIPS IN**  
**CHEMICAL REACTIONS**

**SETTING A GOAL**

- You will gain command over the aspects of stoichiometric calculations involving masses, moles, and molecules under both ideal and realistic conditions.

**OBJECTIVES**

- 7-1** Perform stoichiometry calculations using mole ratios from balanced equations.
- 7-2** Given the masses of two different reactants, determine the limiting reactant and calculate the yield of product.
- 7-3** Calculate the percent yield of a reaction from the measured actual yield and the calculated theoretical yield.

▶ **OBJECTIVE FOR**  
**SECTION 7-1**

Perform stoichiometry calculations using mole ratios from balanced equations.

## 7-1 STOICHIOMETRY



**LOOKING AHEAD!** The balanced chemical equation was introduced in Chapter 5 in terms of individual molecules and formula units. With the help of the mole, we are ready to scale-up our measurements into the macroscopic world of the laboratory. We will make important calculations in this section concerning the mass relationships between and among reactants and products. ■

### 7-1.1 Overview of Stoichiometry

Any decent cook knows that a good recipe calls for ingredients to be mixed in precise amounts. Likewise, any decent chemical company producing a weed killer or a fertilizer will not waste expensive chemicals by using more than the recipe requires. For the chemical company, the recipe is the balanced chemical equation. *The quantitative relationships among reactants and products are known as stoichiometry.*

The most important industrial process concerns the production of ammonia ( $\text{NH}_3$ ) from its elements, hydrogen and nitrogen. We will use the balanced equation representing this reaction as our example. (See Table 7-1.) The most basic relationship of the balanced equation refers to the ratio of molecules and is shown in line 1. But it is important to note that the equation also implies any multiple of the basic molecular ratios, as shown in lines 2, 3, and 4. In lines 5 and 6, the numbers have been changed to mole units and the corresponding masses to grams. We will focus on the mole relationships shown in line 5, as this successfully scales-up the stoichiometry of the equation to laboratory situations. The relationships of moles to number (line 4) and to mass (line 6) were discussed in the previous chapter.

**TABLE 7-1** Production of Ammonia

| $\text{N}_2(\text{g})$              | + | $3\text{H}_2(\text{g})$         | → | $2\text{NH}_3(\text{g})$        |
|-------------------------------------|---|---------------------------------|---|---------------------------------|
| 1. 1 molecule                       | + | 3 molecules                     | → | 2 molecules                     |
| 2. 12 molecules                     | + | 36 molecules                    | → | 24 molecules                    |
| 3. 1 dozen molecules                | + | 3 dozen molecules               | → | 2 dozen molecules               |
| 4. $6.022 \times 10^{23}$ molecules | + | $18.1 \times 10^{23}$ molecules | → | $12.0 \times 10^{23}$ molecules |
| 5. 1 mol                            | + | 3 mol                           | → | 2 mol                           |
| 6. 28 g                             | + | 6 g                             | → | 34 g                            |



### 7-1.2 The Mole Ratio

The key relationship that we will focus on in this chapter is the mole relationships between reactants and products given in line 5 in Table 7-1. The relationships and their expressions can be expressed in ratio forms as follows.

*1 mol of N<sub>2</sub> produces 2 mol of NH<sub>3</sub>*

This can be expressed in ratio form as (1)  $\frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3}$  or (2)  $\frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2}$ .

*1 mol of N<sub>2</sub> reacts with 3 mol of H<sub>2</sub>*

This can be expressed in ratio form as (3)  $\frac{1 \text{ mol N}_2}{3 \text{ mol H}_2}$  or (4)  $\frac{3 \text{ mol H}_2}{1 \text{ mol N}_2}$ .

*3 mol of H<sub>2</sub> produces 2 mol of NH<sub>3</sub>*

This can be expressed in ratio form as (5)  $\frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3}$  or (6)  $\frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$ .

The mole relation factors generated by the balanced equation will be referred to as the **mole ratios** in this text. Note that the coefficients in the balanced equation must be included in the mole ratios. The six mole ratios generated by the sample balanced equation will be used in the stoichiometry problems that follow. In these examples, the central conversion is from moles of one reactant or product to moles of another reactant or product. In Examples 7-2, 7-3, and 7-4, additional conversions are necessary.

### 7-1.3 Stoichiometry Problems

The examples below illustrate the following conversions.

mole → mole (Example 7-1)

mass → mole (Example 7-2)

mass → mass (Example 7-3)

mass → number (Example 7-4)

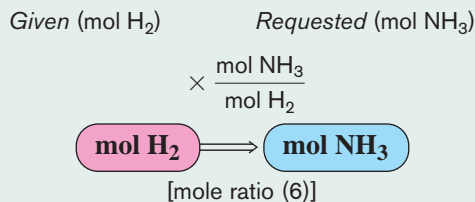
#### EXAMPLE 7-1

#### Converting Moles to Moles

How many moles of NH<sub>3</sub> can be produced from 5.00 mol of H<sub>2</sub>?

#### PROCEDURE

Convert moles of what's given (mol of H<sub>2</sub>) to moles of what's requested (mol NH<sub>3</sub>). This requires mole ratio (6) above, which has *mol H<sub>2</sub>* in the denominator and *mol NH<sub>3</sub>* in the numerator. The unit map for this problem is illustrated below.



#### SOLUTION

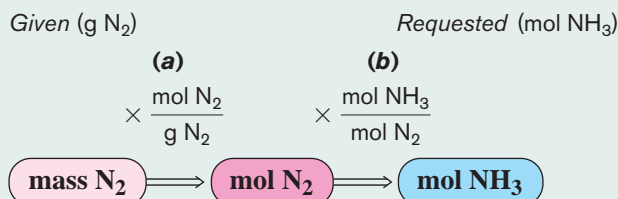
$$5.00 \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = \underline{\underline{3.33 \text{ mol NH}_3}}$$

**EXAMPLE 7-2****Converting Mass to Moles**

How many moles of  $\text{NH}_3$  can be produced from 33.6 g of  $\text{N}_2$ ?

**PROCEDURE**

Before we can convert moles of  $\text{N}_2$  to moles of  $\text{NH}_3$ , we must first convert the mass of  $\text{N}_2$  to moles of  $\text{N}_2$ . This means a two-step conversion. In the first step, the mass of  $\text{N}_2$  is converted to moles using the molar mass of  $\text{N}_2$  as the conversion factor **(a)**. In the second step, moles of  $\text{N}_2$  are converted to moles of  $\text{NH}_3$  using mole ratio (2) **(b)**. The complete unit map for this problem is illustrated below.

**SOLUTION**

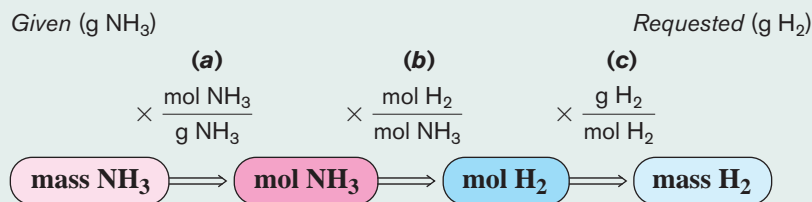
$$33.6 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.02 \text{ g N}_2} \times \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} = \underline{\underline{2.40 \text{ mol NH}_3}}$$

**EXAMPLE 7-3****Converting Mass to Mass**

What mass of  $\text{H}_2$  is needed to produce 119 g of  $\text{NH}_3$ ?

**PROCEDURE**

As in the last example, we must first convert the mass of what's given (119 g  $\text{NH}_3$ ) into moles using the molar mass of  $\text{NH}_3$  [step **(a)** below]. We then convert moles of  $\text{NH}_3$  to moles of  $\text{H}_2$  using mole ratio (5) [step **(b)** below]. Finally, since the mass of  $\text{H}_2$  is requested, we must convert moles of  $\text{H}_2$  to mass using the molar mass of  $\text{H}_2$  as a conversion factor [step **(c)** below]. The complete unit map for this problem is illustrated below.

**SOLUTION**

$$119 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3} \times \frac{2.016 \text{ g H}_2}{\text{mol H}_2} = \underline{\underline{21.1 \text{ g H}_2}}$$

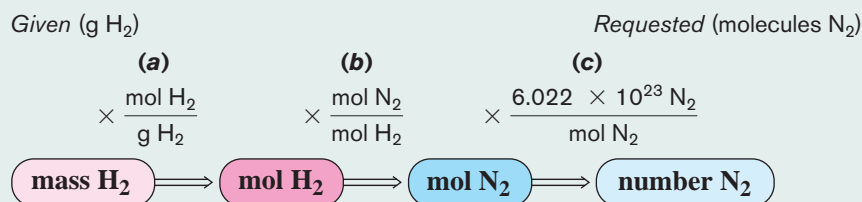
**EXAMPLE 7-4****Converting Mass to Number**

How many molecules of  $\text{N}_2$  are needed to react with 17.0 g of  $\text{H}_2$ ?

**PROCEDURE**

This problem reminds us that the mole relates to a number as well as a mass. In fact, this type of problem is generally not encountered because the actual numbers of molecules involved are not as important as their relative masses. In any case,

this problem is much like the previous example except that in the final step moles of  $N_2$  are converted to number of molecules [step (c) below]. The complete unit map for this problem is illustrated below.



### SOLUTION

$$17.0 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{1 \text{ mol } N_2}{3 \text{ mol } H_2} \times \frac{6.022 \times 10^{23} \text{ molecules } N_2}{\text{mol } N_2} = \underline{1.69 \times 10^{24} \text{ molecules } N_2}$$

### ANALYSIS

Each of these examples is very similar, but together they illustrate the wide range of possibilities that stoichiometry problems can adopt. The concept of the mole remains central to all quantitative chemistry. We can convert nearly any measured quantity (mass, volume, numbers of molecules) into moles and now, with the use of the mole ratio, into any other compound for which we have a balanced chemical reaction. It is now within our abilities to start with any measure of starting material and calculate any measure of product we wish.

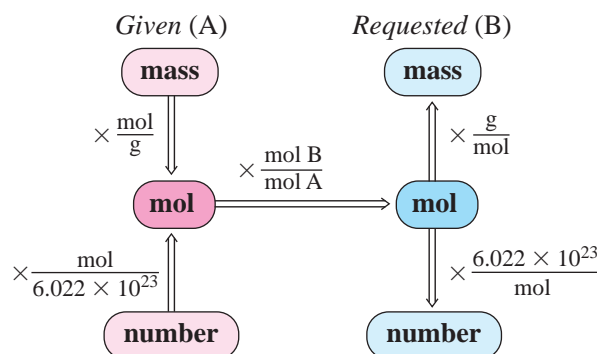
### SYNTHESIS

The most important aspect of stoichiometry is that by using the mole ratio, you can interconvert moles of any substance with any other substance within a reaction, given a *balanced* chemical equation. So if you had a reaction with four reactants and six products, you could calculate the amount of each reactant needed for the reaction and the amount of each product produced, while knowing initially the amount of only one of the 10 chemicals. How useful would this be to a chemical engineer, for instance? More than likely, an industrial process is required to make a certain amount of a specific chemical. It certainly would be useful to know how much of each reactant is required. It would be equally important to know how much other (usually waste) products will be produced. Stoichiometry now provides us the tools for these calculations.

Before we work through another example of a stoichiometry problem, let's summarize the procedure relating moles, mass, and number of molecules.

1. Write down (A) what is given and (B) what is requested.
2. a. If a mass is given, use the molar mass to convert mass to moles of what is given.  
b. If a number of molecules is given, use Avogadro's number to convert to moles of what is given.
3. Using the correct mole ratio from the balanced equation, convert moles of what is given to moles of what is requested.
4. a. If a mass is requested, convert moles of what is requested to the equivalent mass.  
b. If a number of molecules is requested, use Avogadro's number to convert to number of molecules of what is requested.

We represent this information in the general scheme shown in Figure 7-1.

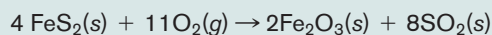


**FIGURE 7-1** General Procedure for Stoichiometry Problems Any three-step conversion is possible following the proper pathway.

### EXAMPLE 7-5

#### Converting the Mass of $FeS_2$ to Mass of $SO_2$

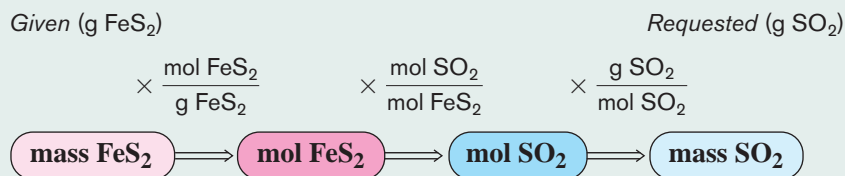
Some sulfur is present in coal in the form of pyrite ( $FeS_2$ ; also known as fool's gold). When it burns, it pollutes the air with the combustion product  $SO_2$ , as shown by the following chemical equation.



What mass of  $SO_2$  is produced by the combustion of 38.8 g of  $FeS_2$ ?

**PROCEDURE**

Given: 38.8 g of FeS<sub>2</sub>. Requested: ? g of SO<sub>2</sub>. Convert grams of FeS<sub>2</sub> to moles of FeS<sub>2</sub>, moles of FeS<sub>2</sub> to moles of SO<sub>2</sub>, and, finally, moles of SO<sub>2</sub> to grams of SO<sub>2</sub>. The complete unit map for this problem is illustrated below.



The mole ratio that relates moles of given to moles of requested (in the numerator) is

$$\frac{8 \text{ mol SO}_2}{4 \text{ mol FeS}_2}$$

**SOLUTION**

$$38.8 \text{ g FeS}_2 \times \frac{1 \text{ mol FeS}_2}{120.0 \text{ g FeS}_2} \times \frac{8 \text{ mol SO}_2}{4 \text{ mol FeS}_2} \times \frac{64.07 \text{ g SO}_2}{\text{mol SO}_2} = \underline{\underline{41.4 \text{ g SO}_2}}$$

**ANALYSIS**

This represents the most common type of stoichiometry problem, called a mass-to-mass calculation. Two more quick mass-to-mass calculations can be used to make an important point. What mass of O<sub>2</sub> is needed to react completely with the FeS<sub>2</sub>? Follow the same format as above and confirm that the answer is 28.5 g O<sub>2</sub>. Lastly, what mass of the second product, Fe<sub>2</sub>O<sub>3</sub>, should be produced? Again, your calculations should confirm that it is 25.8 g Fe<sub>2</sub>O<sub>3</sub>. This then gives us 38.8 g + 28.5 g = 67.3 g of total reactant and 41.4 g + 25.8 g = 67.2 g of total product. The law of conservation of mass is upheld. The small difference is due to rounding off.

**SYNTHESIS**

Any amount of chemical reactant or product calculated via a stoichiometric set-up is strictly theoretical; it represents the maximum amount of product (or the minimum amount of reactant) that can be produced (or is needed). Various real-life situations—such as loss due to transfer or purification, less-than-efficient reaction conditions, and operator error—will lead to actual amounts that are less than what was calculated. Still, these problems can be taken into account, and stoichiometry can give us accurate expectations of what will be produced. In the next two sections, we'll investigate in more detail these variations from our theoretical maximums.

**ASSESSING THE OBJECTIVE FOR SECTION 7-1**

**EXERCISE 7-1(a) KNOWLEDGE:** For the reaction  $\text{B}_2\text{O}_3 + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{BO}_3 + 3\text{H}_2\text{O}$ , write the corresponding mole ratios for B<sub>2</sub>O<sub>3</sub> with the other reactant and with each of the products.

**EXERCISE 7-1(b) ANALYSIS:** For the reaction  $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$ , what mass of NH<sub>3</sub> is needed to produce 75.0 g of H<sub>2</sub>O?

**EXERCISE 7-1(c) ANALYSIS:** Consider the combustion of methylamine (CH<sub>3</sub>NH<sub>2</sub>),  $4\text{CH}_3\text{NH}_2(l) + 9\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 2\text{N}_2(g) + 10\text{H}_2\text{O}(l)$ .

- How many moles of O<sub>2</sub> would react with 6.40 moles of methylamine?
- How many moles of N<sub>2</sub> are produced from 322 g of methylamine?
- What mass of H<sub>2</sub>O is produced along with 6.45 g of CO<sub>2</sub>?
- How many molecules of O<sub>2</sub> are required to produce 0.568 g of N<sub>2</sub>?

**EXERCISE 7-1(d) SYNTHESIS:** Using the unbalanced reaction  $\text{NaN}_3 \rightarrow \text{Na} + \text{N}_2$ , calculate the mass of each product formed from 100.0 g of reactant. Demonstrate that mass is conserved.

*For additional practice, work chapter problems 7-1, 7-4, 7-8, and 7-10.*

## 7-2 LIMITING REACTANT



**LOOKING AHEAD!** A common stoichiometry problem involves the conversion of a given mass of reactant to an equivalent mass of product. So far, for a specific amount of one reactant, we have assumed that the needed amounts of all other reactants are present. But how do we determine the amount of product formed if there are specific amounts of each reactant present? This is the subject of this section. ■

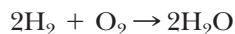
### ▶ OBJECTIVE FOR SECTION 7-2

Given the masses of two different reactants, determine the limiting reactant and calculate the yield of product.

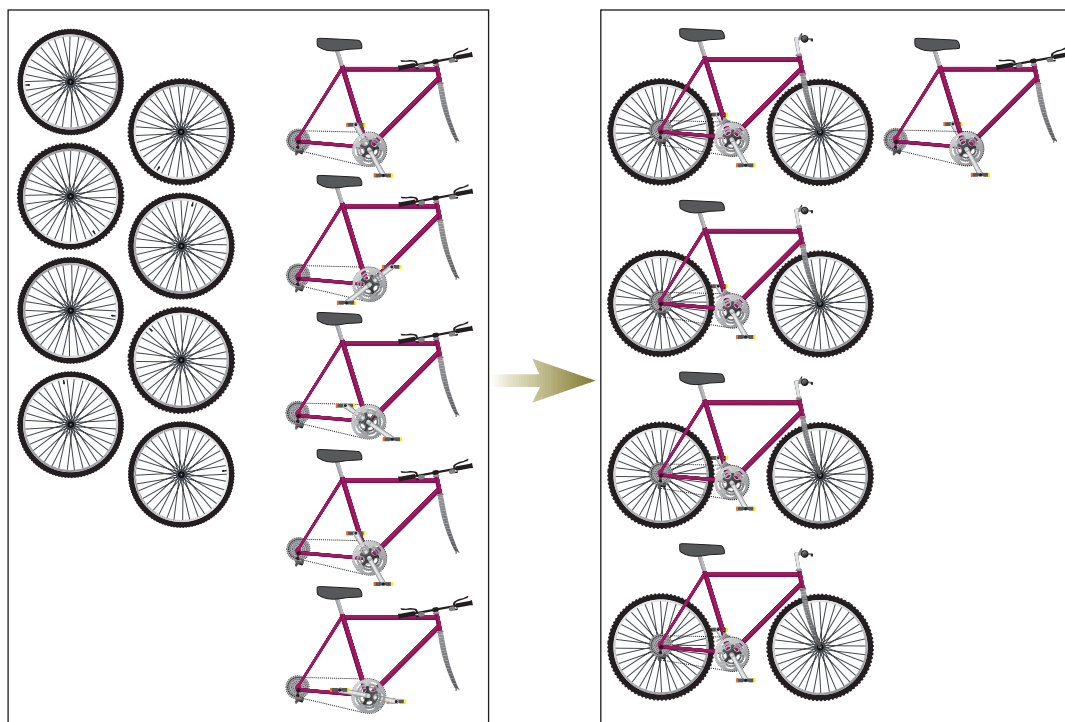
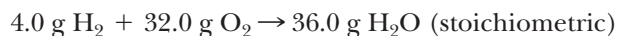
### 7-2.1 The Definition of Limiting Reactant

Assume that you are assembling bicycles from eight wheels and five frames. You can only produce four bicycles, since the number of wheels limits the final number of complete units. You would have one frame in excess. (See Figure 7-2.)

In the case of a chemical reaction, *if specific amounts of each reactant are mixed, the reactant that produces the least amount of product is called the limiting reactant.* In other words, the amount of product formed is limited by the reactant that is completely consumed. We can illustrate this with the simple example of the production of water from its elements, hydrogen and oxygen.



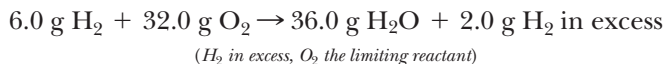
The stoichiometry of the reaction tells us that two moles (4.0 g) of hydrogen react with one mole (32.0 g) of oxygen to produce two moles (36.0 g) of water. Thus any time hydrogen and oxygen react in a 4:32 mass ratio, all reactants are consumed and only product appears. *When reactants are mixed in exactly the mass ratio determined from the balanced equation, the mixture is said to be stoichiometric.*



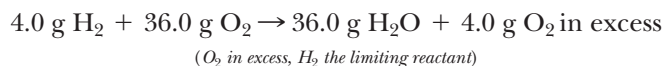
**FIGURE 7-2 Building Bicycles** The number of wheels limits the number of bicycles that can be produced.



What if we mix a 6.0-g quantity of  $\text{H}_2$  with a 32.0-g quantity of  $\text{O}_2$ ? Do we produce 38.0 g water? No, we still produce only 36.0 g of  $\text{H}_2\text{O}$  using only 4.0 g of the  $\text{H}_2$ . Thus,  $\text{H}_2$  is present in excess, and the amount of product is limited by the amount of  $\text{O}_2$  present. In this case,  $\text{O}_2$  becomes the limiting reactant.



If we mix a 4.0-g quantity of  $\text{H}_2$  with a 36.0-g quantity of  $\text{O}_2$ , 36.0 g of  $\text{H}_2\text{O}$  is again produced. In this case, the  $\text{H}_2$  is completely consumed and limits the amount of water formed. Thus,  $\text{H}_2$  is now the limiting reactant and  $\text{O}_2$  is present in excess.



## 7-2.2 Solving Limiting Reactant Problems

When quantities of more than one reactant are given, it is necessary to determine which is the limiting reactant. This is accomplished as follows.

1. Convert the amount of *each reactant* to the number of moles (or mass) of product using the general procedure shown in Figure 7-1.
2. The limiting reactant produces the smallest amount of product.

Notice that each *reactant* must be converted into *product* to solve the problem in the manner outlined. So if the reaction contains three different reactants, three individual calculations will need to be performed, and the answers compared. We will illustrate the calculation of limiting reactant with two examples.

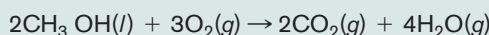
### EXAMPLE 7-6

#### Determining the Limiting Reactant



Race cars at the Indianapolis 500 burn methanol as a fuel.

Methanol ( $\text{CH}_3\text{OH}$ ) is used as a fuel for racing cars. It burns in the engine according to the equation

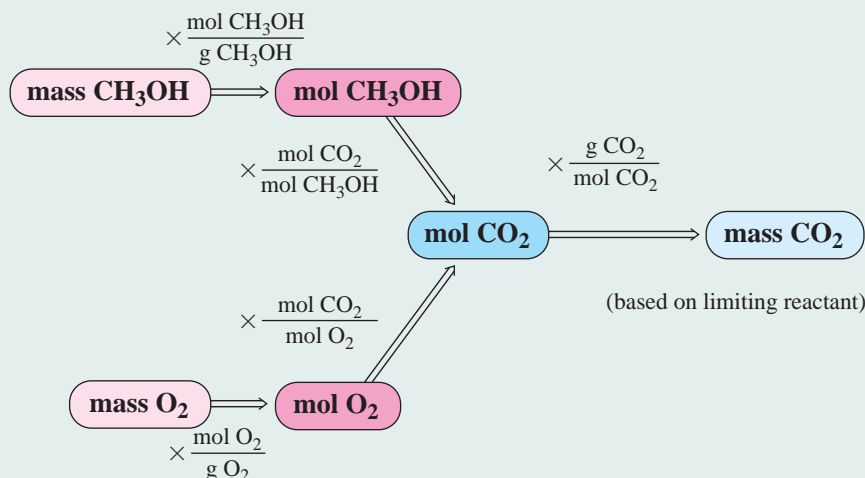


If 40.0 g of methanol is mixed with 46.0 g of  $\text{O}_2$ , what is the mass of  $\text{CO}_2$  produced?

#### PROCEDURE

1. Convert mass of  $\text{CH}_3\text{OH}$  to moles of  $\text{CH}_3\text{OH}$  and then to moles of  $\text{CO}_2$ , and convert mass of  $\text{O}_2$  to moles of  $\text{O}_2$  and then to moles of  $\text{CO}_2$ .
2. Convert the smaller number of moles of  $\text{CO}_2$  to mass of  $\text{CO}_2$ .

The complete unit map for this problem is illustrated below.



**SOLUTION**

$$1. \text{CH}_3\text{OH}: 40.0 \text{ g-CH}_3\text{OH} \times \frac{1 \text{ mol-CH}_3\text{OH}}{32.04 \text{ g-CH}_3\text{OH}} \times \frac{2 \text{ mol CO}_2}{2 \text{ mol-CH}_3\text{OH}} = 1.25 \text{ mol CO}_2$$

$$\text{O}_2: 46.0 \text{ g-O}_2 \times \frac{1 \text{ mol-O}_2}{32.00 \text{ g-O}_2} \times \frac{2 \text{ mol CO}_2}{3 \text{ mol-O}_2} = 0.958 \text{ mol CO}_2$$

Therefore,  $\text{O}_2$  is the limiting reactant.

2. The yield is determined from the amount of product formed from the limiting reactant. Thus, we simply convert the 0.958 mol of  $\text{CO}_2$  produced by the  $\text{O}_2$  to grams of  $\text{CO}_2$ .

$$0.958 \text{ mol CO}_2 \times \frac{44.01 \text{ g CO}_2}{\text{mol CO}_2} = \underline{\underline{42.2 \text{ g CO}_2}}$$

**ANALYSIS**

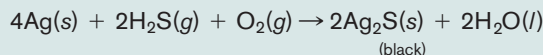
As a rule, whenever the mass of a single reactant is mentioned in the problem, it is assumed that all other reactants are present in excess. On the other hand, anytime amounts of two (or more) different compounds are specifically mentioned, it is generally impossible to tell which is in excess without performing the limiting reactant calculation. So anytime there are two given starting masses, expect that the problem requires the calculation of the limiting reactant.

**SYNTHESIS**

How does this type of problem apply to the everyday world? Again, picture a chemical engineer designing an industrial process. When several reactants are necessary for a multistep process, it makes financial and production sense to design the process so that the most expensive and/or scarcest reactant is the limiting one and all other reactants are present in excess. For instance, it makes no sense to neglect to add enough water to completely react with a more expensive reactant when water is plentiful and cheap. The engineer needs to calculate the amount of product each reactant will produce and ensure that there is plenty of the cheaper reactants to fully complete the process.

**EXAMPLE 7-7****Determining the Limiting Reactant**

Silver tarnishes (turns black) in homes because of the presence of small amounts of  $\text{H}_2\text{S}$  (a gas that originates from the decay of food and smells like rotten eggs). The reaction is

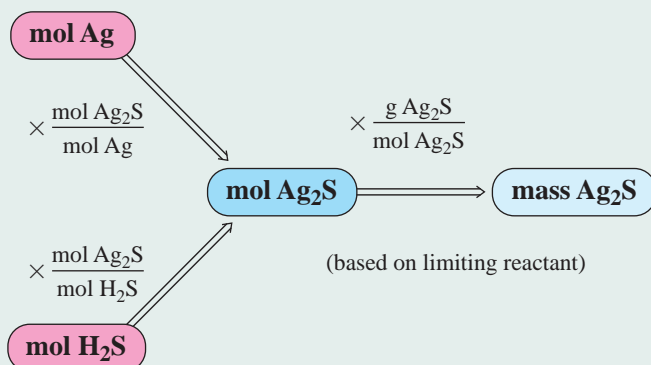


If 0.145 mol of Ag is present with 0.0872 mol of  $\text{H}_2\text{S}$  and excess  $\text{O}_2$ ,

- (a) What mass of  $\text{Ag}_2\text{S}$  is produced?  
 (b) What mass of the other reactant remains in excess?

**PROCEDURE (a)**

Convert moles of Ag and moles of  $\text{H}_2\text{S}$  to moles of  $\text{Ag}_2\text{S}$  produced. Then convert the number of moles of  $\text{Ag}_2\text{S}$  to mass of  $\text{Ag}_2\text{S}$  based on the limiting reactant. The complete unit map for procedure (a) is illustrated below.



Silver tarnishes from the presence of  $\text{H}_2\text{S}$  in the atmosphere.

**SOLUTION (a)**

$$\text{Ag: } 0.145 \text{ mol Ag} \times \frac{2 \text{ mol Ag}_2\text{S}}{4 \text{ mol Ag}} = 0.0725 \text{ mol Ag}_2\text{S}$$

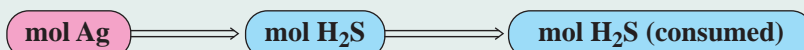
$$\text{H}_2\text{S: } 0.0872 \text{ mol H}_2\text{S} \times \frac{2 \text{ mol Ag}_2\text{S}}{2 \text{ mol H}_2\text{S}} = 0.0872 \text{ mol Ag}_2\text{S}$$

Since Ag produces the smaller yield of  $\text{Ag}_2\text{S}$ , Ag is the limiting reactant. To find the mass of  $\text{Ag}_2\text{S}$  formed, convert moles of  $\text{Ag}_2\text{S}$  produced by the Ag to mass of  $\text{Ag}_2\text{S}$ .

$$0.0725 \text{ mol Ag}_2\text{S} \times \frac{247.9 \text{ g Ag}_2\text{S}}{\text{mol Ag}_2\text{S}} = \underline{\underline{18.0 \text{ g Ag}_2\text{S}}}$$

**PROCEDURE (b)**

To find the mass of  $\text{H}_2\text{S}$  in excess, we first find the mass of  $\text{H}_2\text{S}$  that was consumed in the reaction along with the Ag. Use the mole ratio relating moles of  $\text{H}_2\text{S}$  to moles of Ag. The complete unit map for procedure (b) is illustrated below.



Next, find the moles of  $\text{H}_2\text{S}$  remaining or unreacted by subtracting the moles consumed from the original amount present.

$$\text{mol H}_2\text{S (original)} - \text{mol H}_2\text{S (consumed)} = \text{mol H}_2\text{S (in excess)}$$

Finally, convert moles of unreacted  $\text{H}_2\text{S}$  to mass.

**SOLUTION (b)**

$$0.145 \text{ mol Ag} \times \frac{2 \text{ mol H}_2\text{S}}{4 \text{ mol Ag}} = 0.0725 \text{ mol H}_2\text{S consumed}$$

$$0.0872 \text{ mol} - 0.0725 \text{ mol} = 0.0147 \text{ mol H}_2\text{S in excess}$$

$$0.0147 \text{ mol H}_2\text{S} \times \frac{34.09 \text{ g H}_2\text{S}}{\text{mol H}_2\text{S}} = \underline{\underline{0.501 \text{ g H}_2\text{S in excess}}}$$

**ANALYSIS**

The law of conservation of mass continues to be upheld here as well. All chemical species in the problem converted into masses gives

$$15.6 \text{ g Ag} + 3.0 \text{ g H}_2\text{S} + 1.2 \text{ g O}_2 (19.8 \text{ g total})$$

$$\text{produces } 18.0 \text{ g Ag}_2\text{S} + 1.3 \text{ g H}_2\text{O} (19.3 \text{ g total})$$

Why don't the two totals match up this time? The difference is the calculated excess of  $\text{H}_2\text{S}$ , which must be included in the product total. An extra 0.5 g (roughly) mass-balances both sides and keeps conservation of mass alive and well.

**SYNTHESIS**

These types of problems represent what is potentially the most difficult type of calculation found in an introductory class. In particular, when asked to calculate the amount of excess reactant, it helps to consider another analogy to the limiting reactant. Assume that one is assembling a three-page exam from 85 copies of pages 1 and 2 but only 80 copies of page 3. How many extra sheets of page 1 and page 2 will be left over? We can very quickly answer: 5 pages each. But think more analytically about how you arrived at that conclusion. You first converted the amount of limiting reactant into each of page 1 and page 2, realizing that it would require 80 of each page to complete the test. You then *subtracted* the amount you used from the amount you started with to arrive at the 5 extra pages apiece. Essentially, this problem does the same types of calculations with the added complication of mole ratios. Can you make the analogy fit step by step?

**ASSESSING THE OBJECTIVE FOR SECTION 7-2**

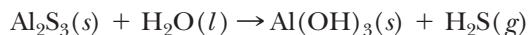
**EXERCISE 7-2(a) KNOWLEDGE:** The recipe for a batch of sugar cookies is

2 cups flour    3 eggs    1 cup sugar    1 stick butter    1 tsp vanilla

In the cupboard are 12 cups of flour, a dozen eggs, 10 cups of sugar, 5 sticks of butter, and a 40 tsp of vanilla. What is the limiting reactant, and how many batches of cookies will you make?

**EXERCISE 7-2(b) ANALYSIS:**  $\text{PF}_3(g) + \text{F}_2(g) \rightarrow \text{PF}_5(g)$ 

If 100.0 g of  $\text{PF}_3$  reacts with 50.0 g of  $\text{F}_2$ , what mass of  $\text{PF}_5$  will be produced?

**EXERCISE 7-2(c) ANALYSIS:** Unbalanced equation:

If 48.0 g  $\text{Al}_2\text{S}_3$  reacts with 32.0 g  $\text{H}_2\text{O}$ ,

- What is the limiting reactant?
- How much  $\text{Al}(\text{OH})_3$  will be produced?
- How much of the excess reactant remains after the reaction is complete?

**EXERCISE 7-2(d) SYNTHESIS:** An engineer is overseeing the production of  $\text{C}_2\text{H}_5\text{Cl}$  by mixing equal masses of  $\text{C}_2\text{H}_4$  and  $\text{HCl}$ . If she could only add one chemical to increase production, which one should she choose?

For additional practice, work chapter problems 7-21, 7-28, and 7-29.



### Alcohol—The Limiting Reactant in Breathalyzers



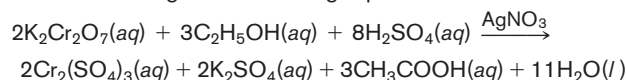
Drunk driving takes as many as 20,000 lives each year in the United States alone. To combat this problem, communities have adopted strict standards by which a driver may be labeled as intoxicated. By 1964, 39 states had adopted a limit of 0.10%

blood alcohol concentration as the legal limit. Since then, many states have lowered this to 0.08%. Other countries are stricter. The limit in Ireland and Japan is 0.05%, and in Sweden it is 0.02%. That could be as little as one drink. How do police measure the blood alcohol?

The best method is to take a blood sample. The blood is analyzed by a device that measures the amount of volatile compounds (those that vaporize) in the blood. The device, called a gas chromatograph, is highly accurate. However, it could take an hour or more to get blood drawn by a trained professional and have the concentration of alcohol measured. A lot of alcohol can be metabolized in one hour. So it is important to get a reading when the driver is stopped if such a test is suggested. Usually, a suspect is asked to perform some physical tasks such as walking a straight line or standing on one foot. Also, the officer may observe the movement of the eyes. In the latter test, if the driver is under the influence, the eye tends to jerk involuntarily when following a penlight. If the officer suspects intoxication, he or she may subject the suspect to a portable *breathalyzer* test.

When one has been drinking, water and alcohol vapor are expelled from the lungs with each breath. By measuring a specific volume of breath, the amount of alcohol in the breath can be determined. This is directly proportional to the amount

of alcohol in the blood. There are several modern devices, including fuel cells, that measure alcohol in the breath, but the original test involved a chemical reaction. The breath is forced through an aqueous solution where alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) reacts according to the following equation.



In words, ethyl alcohol reacts with a potassium dichromate solution containing excess sulfuric acid. Also present is silver nitrate ( $\text{AgNO}_3$ , shown above the reaction arrow), which acts as a catalyst to speed up the reaction. Acetic acid ( $\text{CH}_3\text{COOH}$ ) is formed from the alcohol. Potassium dichromate solutions have a pronounced yellow color. As will be discussed in more detail in the next chapter, the solution reflects yellow light because its complement (blue light) is absorbed. (See Making It Real pg. 223.) So the absorbance of blue light is a measure of the intensity of the yellow reflected light. The absorbance is measured with a device called a spectrometer. The limiting reactant in this reaction is the alcohol. Potassium dichromate and sulfuric acid are present in excess. However, the more alcohol present in a sample of breath, the more potassium dichromate that reacts and the less the amount of the light beam absorbed. If all the potassium dichromate is used up (i.e., it becomes the limiting reactant), all the yellow light disappears in the solution and no blue light is absorbed. Additional alcohol will not change anything at this point. By measuring the change in the yellow light in the sample, the amount of alcohol can be determined.

Still, the best evidence of intoxication is from a sample of blood. This is usually done if the suspect fails the breathalyzer test. The best way to beat the rap for drunk driving is to let somebody else drive if you've been drinking.

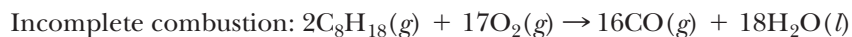
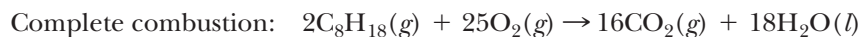
**OBJECTIVE FOR SECTION 7-3**

Calculate the percent yield of a reaction from the measured actual yield and the calculated theoretical yield.

**7-3 PERCENT YIELD**

**LOOKING AHEAD!** There is something else that we have been taking for granted in the problems worked so far. We have assumed that at least one reactant has been completely converted into products and that the reactants form only the products shown. This is not always the case, however. In this section, we will look into incomplete reactions. ■

An efficient automobile engine burns gasoline (mainly a hydrocarbon,  $C_8H_{18}$ ) to form carbon dioxide and water. Untuned engines, however, do not burn gasoline efficiently. They produce carbon monoxide and may even exhaust unburned fuel. The two relevant combustion reactions are shown below.



Note that if we were asked to calculate the mass of  $CO_2$  produced from a given amount of  $C_8H_{18}$ , our answer would not be correct if all the hydrocarbon were not converted to  $CO_2$ . *The measured amount of product obtained in any reaction is known as the **actual yield**. The **theoretical yield** is the calculated amount of product that would be obtained if all the reactant were converted to a given product. The **percent yield** is the ratio of the two, with the actual yield in grams or moles divided by the theoretical yield in grams or moles times 100%.*

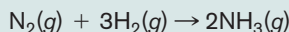
$$\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \text{percent yield}$$

In other reactions, there is another reason for the incomplete conversion of reactants to products. In these cases, a reverse reaction occurs whereby reactants are reformed from products. This limits, to some extent, the percent of reactants that are converted to products. These are known as *reversible* reactions. An example is the reaction illustrated previously in which nitrogen and hydrogen react to produce ammonia. Hydrogen and nitrogen are not completely converted to ammonia because some of the ammonia decomposes back to its two elements. Reversible reactions will be discussed in more detail in Chapters 13 and 15.

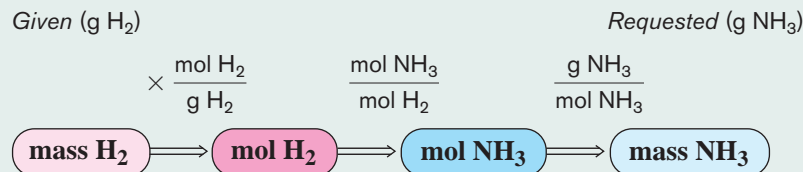
To determine the percent yield, it is necessary to determine the theoretical yield (which is what we've been doing all along) and compare this with the actual yield.

**EXAMPLE 7-8****Determining the Percent Yield**

In a given experiment, a 4.70-g quantity of  $H_2$  is allowed to react with  $N_2$ ; a 12.5-g quantity of  $NH_3$  is formed. What is the percent yield based on the  $H_2$ ? The equation for the reaction is

**PROCEDURE**

Find the mass of  $NH_3$  that would form if the entire 4.70 g of  $H_2$  was converted to  $NH_3$  (the theoretical yield). Using the actual yield (12.5 g), find the percent yield. The complete unit map for this problem is illustrated below.





The mole ratio needed is

$$\frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$$

### SOLUTION

$$4.70 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} \times \frac{17.03 \text{ g NH}_3}{\text{mol NH}_3} = 26.5 \text{ g NH}_3 \text{ (theoretical yield)}$$

$$\frac{12.5 \text{ g}}{26.5 \text{ g}} \times 100\% = \underline{\underline{47.2\% \text{ yield}}}$$

### ANALYSIS

One of the keys to success in working percent yield problems is to be able to identify an amount of compound as being an actual or a theoretical amount. Essentially the terms *actual* and *experimental* are interchangeable, as are the terms *theoretical* and *calculated*. Any value determined by a stoichiometry calculation is theoretical in nature. Once you've positively identified the actual and theoretical amounts, these problems become just a regular mass-to-mass stoichiometry calculation with one extra formula (the calculation of percent yield) thrown in.

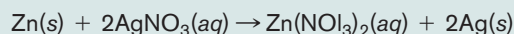
### SYNTHESIS

Typically, chemists would like to try to increase the percent yield of a reaction as much as possible. What types of things might they do to this end, other than use improved experimental technique? Changing reaction conditions is always a good place to start. Varying things like temperature, pressure, solvent, and reaction time can alter percent yield, for better or worse. Experimentation is called for. If the reaction is of the reversible type, increasing the *excess* reactant can actually increase the experimental yield. This, of course, doesn't affect the theoretical yield, which is determined from the limiting reactant. An increase in actual yield while theoretical yield stays the same will increase the percent yield. How reactions are affected by conditions is a subject of Chapter 15.

## EXAMPLE 7-9

### Determining the Actual Yield from Percent Yield

Zinc and silver undergo a single-replacement reaction according to the equation



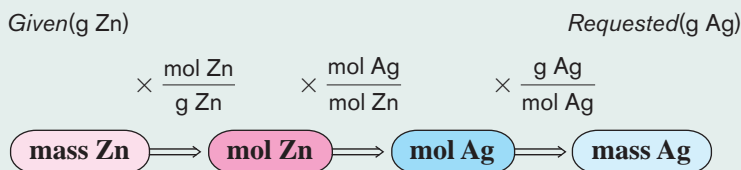
When 25.0 g of zinc is added to the silver nitrate solution, the percent yield of silver is 72.3%. What mass of silver is formed?

### PROCEDURE

Find the theoretical yield of silver by converting the mass of zinc to the equivalent mass of silver. Use the percent yield to calculate the actual yield. This can be accomplished algebraically by rearranging the equation to solve for actual yield as follows:

$$\text{actual yield} = \frac{\text{percent yield}}{100\%} \times \text{theoretical yield}$$

The complete unit map for this example is shown below.



### SOLUTION

$$25.0 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{2 \text{ mol Ag}}{1 \text{ mol Zn}} \times \frac{107.9 \text{ g Ag}}{\text{mol Ag}} = 82.5 \text{ g Ag (theoretical yield)}$$

$$\frac{72.3\%}{100\%} \times 82.5 \text{ g Ag} = \underline{\underline{59.6 \text{ g Ag (actual yield)}}$$

**ANALYSIS**

When we designate something the theoretical yield, we are stating that it is the theoretical *maximum*. It makes sense, then, that the actual yield would be less than that.

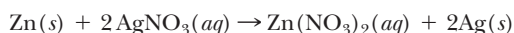
**SYNTHESIS**

A third type of problem involving percent yield is to inquire how much reactant is necessary to produce a given amount of product, assuming a percent yield less than 100%. The trick here is to perform the percent yield calculation first, to calculate theoretical yield, and then use that amount in the mass-to-mass stoichiometry calculation to determine the amount of starting material. For example, if a reaction had a 50% yield, this means that you'd have to use *double* the amount of starting material you'd have calculated for a straightforward stoichiometry problem with 100% yield. For an example, see Exercise 7-3(c) in Assessing the Objective for Section 7-3.

**ASSESSING THE OBJECTIVE FOR SECTION 7-3**

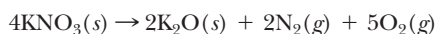
**EXERCISE 7-3(a) KNOWLEDGE:** If a chemical reaction theoretically should produce 32.0 g of product, but the actual amount is 24.0 g, what is the percent yield for the reaction?

**EXERCISE 7-3(b) ANALYSIS:** For the reaction



If 10.0 g of Zn produces 25.0 g of Ag, what's the percent yield of the reaction?

**EXERCISE 7-3(c) ANALYSIS:** For the reaction



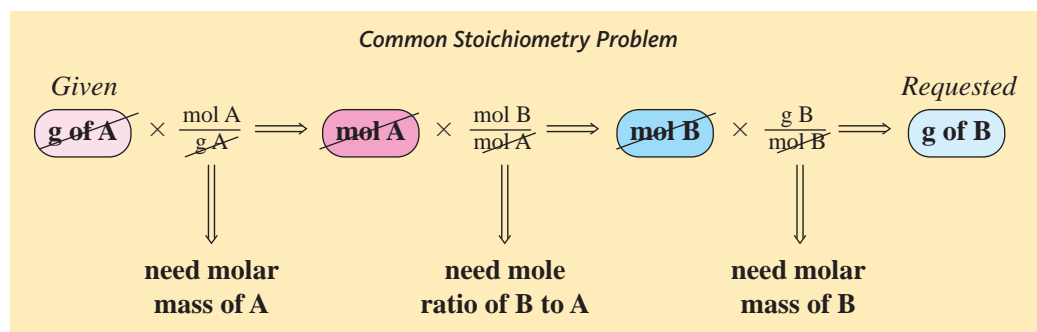
What mass of  $\text{KNO}_3$  is needed to produce 20.0 g  $\text{K}_2\text{O}$ , assuming the reaction produces an 84.0% yield?

**EXERCISE 7-3(d) SYNTHESIS:** Anyone with experience in a teaching lab knows that students frequently report percent yields in excess of 100%. Could this be accurate? What are some potential explanations for yields this high?

*For additional practice, work chapter problems 7-32, 7-35, and 7-37.*

**PART A SUMMARY****KEY TERMS**

- 7-1.1** **Stoichiometry** calculations involve conversions among amounts of reactants and products. p. 198
- 7-1.2** **Mole ratios** from balanced equations are the keys to solving stoichiometry problems. p. 199
- 7-2.1** The **limiting reactant** is completely consumed in a reaction. p. 203
- 7-3** The **percent yield** is calculated from the **theoretical yield** and **actual yield**. p. 208

**SUMMARY CHART**

**PART B**  
ENERGY RELATIONSHIPS IN  
CHEMICAL REACTIONS

**SETTING A GOAL**

- You will extend your knowledge of stoichiometry to include amounts of heat involved in chemical reactions.

**OBJECTIVE**

- 7-4** Given the change in enthalpy for a reaction, calculate the amount of heat gained or released by a given mass of reactant.

## 7-4 HEAT ENERGY IN CHEMICAL REACTIONS



**LOOKING AHEAD!** Matter is not all that is involved in chemical reactions. The other component of the universe, energy, is also an intimate part of chemical reactions. A definite and measurable amount of energy is involved in any chemical change. ■

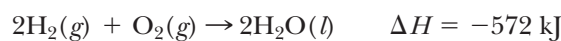
**OBJECTIVE FOR SECTION 7-4**

Given the change in enthalpy for a reaction, calculate the amount of heat gained or released by a given mass of reactant.

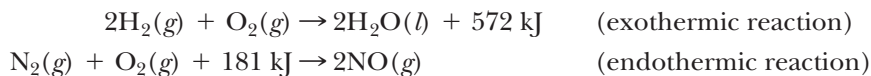
The amount of heat energy (measured in kilocalories or kilojoules) involved in a reaction is a constant amount that depends on the amount of reactants consumed. For example, if one mole of hydrogen undergoes combustion to form liquid water, 286 kJ of heat is evolved.

### 7-4.1 Thermochemical Equations

A balanced equation that includes heat energy is referred to as a **thermochemical equation**. A thermochemical equation can be represented in either of two ways. In the first, the heat is shown separately from the balanced equation using the symbol  $\Delta H$ . This is referred to as heat of the reaction. The symbol is known technically as the *change in enthalpy*. By convention, a negative sign for  $\Delta H$  corresponds to an exothermic reaction, and a positive sign corresponds to an endothermic reaction. From the perspective of the reaction, this convention makes sense. Loss of heat energy by the reaction is exothermic and thus negative. Gain of heat energy is endothermic and thus positive. Written in this manner, the thermochemical equation for the combustion of two moles of hydrogen is



Notice in the preceding equation that the heat evolved is per *two* moles of  $\text{H}_2$  consumed or per *two* moles of  $\text{H}_2\text{O}$  formed. This result is general for any reaction. The enthalpy reported for a reaction is for the amount in moles of compounds represented by the balancing coefficients. The second way a thermochemical equation can be represented shows the heat energy as if it were a reactant or product. In exothermic reactions heat energy is a product, and in endothermic reactions heat energy is a reactant. A positive sign is used in either case.



### 7-4.2 Calculation of Heat Energy in a Reaction

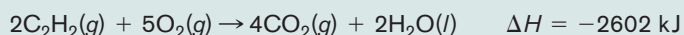
The heat energy involved in a chemical reaction may be treated quantitatively in a manner similar to the amount of a reactant or product. The enthalpy of the reaction, with units of kJ/mol, is analogous to molar mass and its units of g/mol. Where molar mass allows us to convert between grams and moles, reaction enthalpies allow us to convert between energy and moles. The following examples illustrate the calculations implied by a thermochemical equation.

**EXAMPLE 7-10****Converting Heat to Mass**

The combustion of acetylene produces a flame hot enough to melt iron.

$C_2H_2$ ,  $-520.4 \text{ kJ/mol } O_2$ , and  $-1301 \text{ kJ/mol } H_2O$ . You could then use these values to calculate the amount of water produced or the amounts of  $C_2H_2$  or oxygen needed for the specified amount of heat.

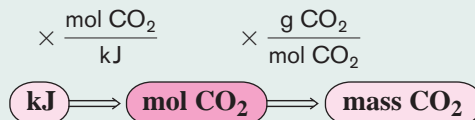
Acetylene, which is used in welding torches, undergoes combustion according to the following thermochemical equation:



If 550 kJ of heat is evolved in the combustion of a sample of  $C_2H_2$ , what is the mass of  $CO_2$  formed?

**PROCEDURE**

Two steps are required, as illustrated below.

**SOLUTION**

$$550 \text{ kJ} \times \frac{4 \text{ mol } CO_2}{2602 \text{ kJ}} \times \frac{44.01 \text{ g } CO_2}{\text{mol } CO_2} = \underline{\underline{37.2 \text{ g } CO_2}}$$

**ANALYSIS**

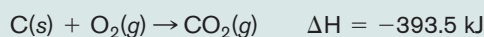
Notice that the enthalpy of the reaction is  $-2602 \text{ kJ}/4 \text{ mol } CO_2$ , or  $-650.5 \text{ kJ/mol } CO_2$ . What is the enthalpy expressed relative to the three other species in the reaction?  $-1301 \text{ kJ/mol}$

**SYNTHESIS**

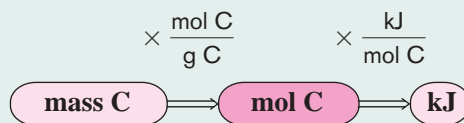
The combustion of all hydrocarbons produces heat, but which burns best with the greatest amount of heat? The answer differs depending on whether you want your answer in units of kJ/mol or kJ/g. When evaluating heats of reaction on a per mole basis, the bigger, the better. One mole of a large molecule will have many more carbons and therefore can produce much more heat. A better comparison is on a per gram basis. And when we do it that way, we find that the smallest hydrocarbon, methane, has the largest heat of combustion at  $-55.6 \text{ kJ/g}$ . The heats of combustion per gram are also important for the health conscious. One gram of fat produces about nine Calories (about 36 kJ), whereas one gram of protein or carbohydrate produces about four Calories (about 16 kJ). As you can see, fat contains more than twice as many Calories on a mass basis than proteins or carbohydrates.

**EXAMPLE 7-11****Converting Mass to Heat**

Carbon dioxide forms from its elements, as illustrated by the following thermochemical equation:



How much heat will be generated from 50.0 g of C?

**PROCEDURE****SOLUTION**

$$50.0 \text{ g } C \times \frac{1 \text{ mol } C}{12.01 \text{ g } C} \times \frac{-393.5 \text{ kJ}}{\text{mol } C} = \underline{\underline{-1640 \text{ kJ}}}$$

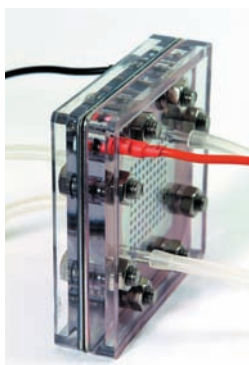
The negative sign indicates that heat is being released by this reaction.

**ANALYSIS**

Don't confuse the  $-393.5$  kJ reported in conjunction with the reaction with the  $1640$  kJ reported as the heat released by the reaction. Officially the  $-393.5$  kJ is the enthalpy of the reaction and has units of kJ/mol, though those are often not reported, as it can be per mole of any of the reactants. The values are analogous to molar mass and mass, respectively.

**SYNTHESIS**

Let's continue to examine where calculations like these might be useful. How might someone in an industrial setting benefit from this sort of information? It's clearly important when designing equipment for processes to know whether the reaction being run is endothermic or exothermic. Will you need to supply heat? Or will heat be produced and need to be drawn away with cooling equipment? Exactly how much heat will there be? Is the equipment sturdy enough to withstand the generated heat? Is the cooling system efficient enough to avoid damage, meltdowns, or explosions? These are some fairly important considerations, and they are determined by examining heats of reactions.

**Hydrogen—The Perfect Fuel**

Fuel cells make efficient use of hydrogen.

The 6.5 billion citizens of this planet all need something to burn. We need fuel to cook our food, to keep our homes warm, and to harvest our crops. Of course, many of us drive cars and other vehicles, which takes even more fuel. Throughout most of history, the main fuel was wood. Now, we mainly use fossil fuels such as coal, natural gas, and oil. Many of the planet's forests have already been lost, and there is a limit to the amount of fossil fuels stored in the earth.

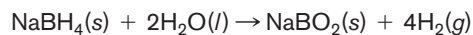
Nuclear energy can help, but more is needed. Enter the simplest and lightest of the elements—hydrogen.

Why is hydrogen such a good fuel? There are many reasons. First, when it burns it forms only water, which does not accumulate in the atmosphere and cause global warming. Also, it is very light, producing  $143$  kJ/g compared to  $55.6$  kJ/g for natural gas and  $48.1$  kJ/g for gasoline. Hydrogen is already the workhorse fuel of the space program. It is used in the rockets and in the fuel cells that produce electricity in the space shuttles. A fuel cell uses the reaction of hydrogen with oxygen to form water to

produce electrical energy rather than heat energy (see Section 13-6). Fuel cells are thought to be the wave of the future, for both utilities and automobiles.

So why not use hydrogen more? First, pure hydrogen is expensive. The cheapest way to produce hydrogen is to extract it from fossil fuels such as methane ( $\text{CH}_4$ ). That is still comparatively expensive, and it produces carbon dioxide, a greenhouse gas. The best hope is in the electrolysis of water. Electrolysis uses energy (i.e.,  $286$  kJ/mol) to break water down into its elements (hydrogen and oxygen). Since it takes so much energy, this process is also expensive. However, there is intensive research to find an inexpensive way to do this. There is hope that solar energy can be harnessed for this task, but it needs to be made more efficient and less expensive.

Another problem is the storage of hydrogen. Its boiling point is  $-253^\circ\text{C}$ , which means that the liquid state cannot exist at room temperature. Thus, it has to be stored as a gas under high pressure, which is inherently dangerous. One possibility that is being explored is to store the hydrogen in a solid compound. For example, if water is added to sodium borohydride ( $\text{NaBH}_4$ ), the reaction generates hydrogen gas, as illustrated by the following equation.



The storage of hydrogen is a problem that will be solved, however.

**EXERCISE 7-4(a) KNOWLEDGE:** The combustion of  $\text{C}_2\text{H}_4$  releases  $556$  kJ/mol  $\text{CO}_2$ . Write two thermodynamic equations for that reaction that express that heat in two different ways.

**ASSESSING THE OBJECTIVE FOR SECTION 7-4**



**EXERCISE 7-4(b) ANALYSIS:** For the reaction in the previous exercise, what mass of  $C_2H_4$  is required to produce 250 kJ of heat, assuming 100% yield?

**EXERCISE 7-4(c) SYNTHESIS:** Consider the reaction  $2H_2 + O_2 \rightarrow 2H_2O$ . This is the combination reaction to form water; it is exothermic, with an enthalpy of  $-572$  kJ. Does it follow that the decomposition of water,  $2H_2O \rightarrow 2H_2 + O_2$ , must be endothermic, with an enthalpy of  $+572$  kJ?

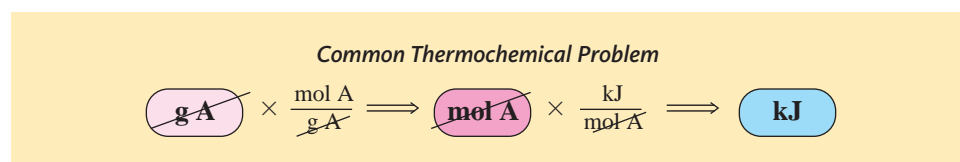
For additional practice, work chapter problems 7-40, 7-43, and 7-45.

## PART B SUMMARY

### KEY TERMS

**7-4.1 Thermochemical equations** include the changes in **enthalpy** ( $\Delta H$ ) as well as the compounds involved. p. 211

### SUMMARY CHART



## CHAPTER SUMMARY

In this chapter, we examined how chemical equations tell us about the relationships between masses of reactants and masses of products. These are calculations of **stoichiometry**. In these problems, the balanced equation provides the **mole ratios** for conversion from moles of one compound in the reaction to moles of another. All of these conversions are summarized in Figure 7-1.

When reactants are mixed in other than stoichiometric amounts, it is necessary to determine the **limiting reactant**. The limiting reactant is completely consumed; thus, it determines the amount of product formed.

Some reactions lead to more than one set of products, and others reach a state of equilibrium before all reactants are converted to products. In either case, the **actual yield** of a product may be less than the **theoretical yield**. The actual yield can be expressed as a percent of the theoretical yield. This is called the **percent yield**.

Finally, we studied the relation of heat energy to chemical reactions. In a **thermochemical equation**, the heat evolved or absorbed is represented as either a reactant or product, or as the heat of the reaction, which is referred to as the change in **enthalpy** and is symbolized as  $\Delta H$ .

### OBJECTIVES

| SECTION    | YOU SHOULD BE ABLE TO...  | EXAMPLES                | EXERCISES      | CHAPTER PROBLEMS        |
|------------|---|-------------------------|----------------|-------------------------|
| <b>7-1</b> | Perform stoichiometry calculations using mole ratios from balanced equations.   | 7-1, 7-2, 7-3, 7-4, 7-5 | 1a, 1b, 1c, 1d | 3, 5, 7, 10, 13, 15, 19 |
| <b>7-2</b> | Given the masses of two different reactants, determine the limiting reactant and calculate the yield of product.          | 7-6, 7-7                | 2a, 2b, 2c, 2d | 23, 24, 27, 30, 31      |
| <b>7-3</b> | Calculate the percent yield of a reaction from the measured actual yield and the calculated theoretical yield.            | 7-8, 7-9                | 3a, 3b, 3c, 3d | 32, 33, 34, 37          |
| <b>7-4</b> | Given the change in enthalpy for a reaction, calculate the amount of heat gained or released by a given mass of reactant. | 7-10, 7-11              | 4a, 4b, 4c     | 43, 44, 45, 47          |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

- 7-1(a)**  $\frac{1 \text{ mol B}_2\text{O}_3}{6 \text{ mol NaOH}}, \frac{1 \text{ mol B}_2\text{O}_3}{2 \text{ mol Na}_3\text{BO}_3}, \frac{1 \text{ mol B}_2\text{O}_3}{3 \text{ mol H}_2\text{O}}$
- 7-1(b)** 47.3 g NH<sub>3</sub>
- 7-1(c)** (a) 14.4 mol O<sub>2</sub> (b) 5.18 mol N<sub>2</sub> (c) 6.60 g H<sub>2</sub>O  
(d)  $5.49 \times 10^{22}$  molecules of O<sub>2</sub>
- 7-1(d)** 35.4 g Na + 64.6 g N<sub>2</sub> = 100 g total product
- 7-2(a)** Eggs are the limiting reactant. You can make four batches of cookies.
- 7-2(b)** 144 g PF<sub>5</sub>
- 7-2(c)** (a) H<sub>2</sub>O (b) 46.2 g Al(OH)<sub>3</sub> (c) 3.6 g Al<sub>2</sub>S<sub>3</sub>
- 7-2(d)** The chemicals add in a 1:1 mole ratio. Therefore, the lighter chemical has the most moles. The compound with the greater molar mass, the HCl, is the limiting reactant. Add HCl.
- 7-3(a)** 24.0 g/32.0 g = 75.0 % yield

**7-3(b)** The theoretical yield of Ag is 33.0 g. The percent yield is 75.8%.

**7-3(c)** 51.1 g KNO<sub>3</sub>

**7-3(d)** No, it couldn't be. The sample may be contaminated (unevaporated water is very common). Alternately the student may have made an experimental or mathematical error in calculating their yield.

## PART B

## EXERCISES

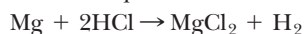
- 7-4(a)** (1)  $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 1112 \text{ kJ}$ ;  
(2)  $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H = -1112 \text{ kJ}$
- 7-4(b)** 6.31 g C<sub>2</sub>H<sub>4</sub>
- 7-4(c)** Yes! It does. Reverse processes differ only by the sign of their enthalpies. It's analogous to saying that if you had to climb 100 ft to get to the top of a hill, then you must descend 100 ft (-100 ft) in order to get back down.

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## Stoichiometry (SECTION 7-1)

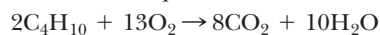
**7-1.** Given the balanced equation



provide the proper mole ratio for each of the following mole conversions.

- (a) Mg to H<sub>2</sub> (c) HCl to H<sub>2</sub>  
(b) Mg to HCl (d) MgCl<sub>2</sub> to HCl

**7-2.** Given the balanced equation



provide the proper mole ratio for each of the following mole conversions.

- (a) CO<sub>2</sub> to C<sub>4</sub>H<sub>10</sub> (c) CO<sub>2</sub> to O<sub>2</sub>  
(b) O<sub>2</sub> to C<sub>4</sub>H<sub>10</sub> (d) O<sub>2</sub> to H<sub>2</sub>O

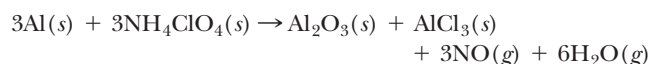
**7-3.** Given the balanced equation



provide the proper mole ratio for each of the following mole conversions.

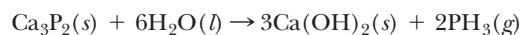
- (a) Cu to NO<sub>2</sub> (d) Cu(NO<sub>3</sub>)<sub>2</sub> to HNO<sub>3</sub>  
(b) HNO<sub>3</sub> to Cu (e) NO<sub>2</sub> to Cu  
(c) H<sub>2</sub>O to NO<sub>2</sub> (f) Cu to H<sub>2</sub>O

**7-4.** The reaction that takes place in the reusable solid rocket booster for the space shuttle is shown by the following equation.



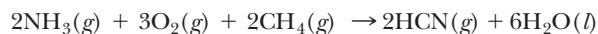
- (a) How many moles of each product are formed from 10.0 moles of Al?  
(b) How many moles of each product are formed from 3.00 moles of NH<sub>4</sub>ClO<sub>4</sub>?

**7-5.** Phosphine (PH<sub>3</sub>) is a poisonous gas once used as a fumigant for stored grain. It is prepared according to the following equation.



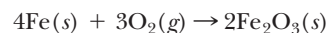
- (a) How many moles of phosphine are prepared from 5.00 moles of Ca<sub>3</sub>P<sub>2</sub>?  
(b) How many moles of phosphine are prepared from 5.00 moles of H<sub>2</sub>O?

**7-6.** Hydrogen cyanide is an important industrial chemical used to make a plastic, acrylonitrile. HCN is prepared according to the following equation.



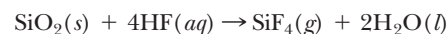
- (a) How many moles of O<sub>2</sub> and CH<sub>4</sub> react with 10.0 moles of NH<sub>3</sub>?  
(b) How many moles of HCN and H<sub>2</sub>O are produced from 10.0 moles of O<sub>2</sub>?

**7-7.** Iron rusts according to the equation



- (a) What mass of rust (Fe<sub>2</sub>O<sub>3</sub>) is formed from 0.275 mole of Fe?  
(b) What mass of rust is formed from 0.275 mole of O<sub>2</sub>?  
(c) What mass of O<sub>2</sub> reacts with 0.275 mole of Fe?

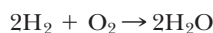
**7-8.** Glass (SiO<sub>2</sub>) is etched with hydrofluoric acid according to the equation



If 4.86 moles of HF reacts with SiO<sub>2</sub>,

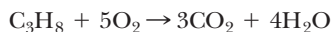
- (a) What mass of SiF<sub>4</sub> forms? (c) What mass of SiO<sub>2</sub> reacts?  
(b) What mass of H<sub>2</sub>O forms?

**7-9.** Consider the reaction



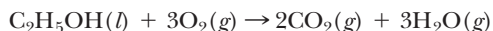
- How many moles of  $\text{H}_2$  are needed to produce 0.400 mole of  $\text{H}_2\text{O}$ ?
- How many moles of  $\text{H}_2\text{O}$  will be produced from 0.640 g of  $\text{O}_2$ ?
- How many moles of  $\text{H}_2$  are needed to react with 0.032 g of  $\text{O}_2$ ?
- What mass of  $\text{H}_2\text{O}$  would be produced from 0.400 g of  $\text{H}_2$ ?

**7-10.** Propane burns according to the equation



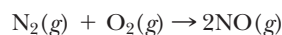
- How many moles of  $\text{CO}_2$  are produced from the combustion of 0.450 mole of  $\text{C}_3\text{H}_8$ ? How many moles of  $\text{H}_2\text{O}$ ? How many moles of  $\text{O}_2$  are needed?
- What mass of  $\text{H}_2\text{O}$  is produced if 0.200 mol of  $\text{CO}_2$  is also produced?
- What mass of  $\text{C}_3\text{H}_8$  is required to produce 1.80 g of  $\text{H}_2\text{O}$ ?
- What mass of  $\text{C}_3\text{H}_8$  is required to react with 160 g of  $\text{O}_2$ ?
- What mass of  $\text{CO}_2$  is produced by the reaction of  $1.20 \times 10^{23}$  molecules of  $\text{O}_2$ ?
- How many moles of  $\text{H}_2\text{O}$  are produced if  $4.50 \times 10^{22}$  molecules of  $\text{CO}_2$  are produced?

**7-11.** The alcohol component of gasohol burns according to the equation

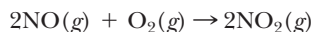


- What mass of alcohol is needed to produce 5.45 mol of  $\text{H}_2\text{O}$ ?
- How many moles of  $\text{CO}_2$  are produced along with 155 g of  $\text{H}_2\text{O}$ ?
- What mass of  $\text{CO}_2$  is produced from 146 g of  $\text{C}_2\text{H}_5\text{OH}$ ?
- What mass of  $\text{C}_2\text{H}_5\text{OH}$  reacts with 0.898 g of  $\text{O}_2$ ?
- What mass of  $\text{H}_2\text{O}$  is produced from  $5.85 \times 10^{24}$  molecules of  $\text{O}_2$ ?

**7-12.** In the atmosphere,  $\text{N}_2$  and  $\text{O}_2$  do not react with each other. In the high temperatures of an automobile engine, however, the following reaction occurs.

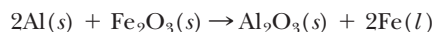


When the  $\text{NO}$  reaches the atmosphere through the engine exhaust, a second reaction takes place.



The  $\text{NO}_2$  is a brownish gas that contributes to the haze of smog and is irritating to the nasal passages and lungs. What mass of  $\text{N}_2$  is required to produce 155 g of  $\text{NO}_2$ ?

**7-13.** Elemental iron is produced in what is called the *thermite reaction* because it produces enough heat that the iron is initially in the molten state. The liquid iron can then be used to weld iron bars together.



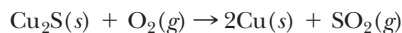
What mass of  $\text{Al}$  is needed to produce 750 g of  $\text{Fe}$ ? How many formula units of  $\text{Fe}_2\text{O}_3$  are used in the process?

**7-14.** Antacids, which contain calcium carbonate, react with stomach acid according to the equation



What mass of stomach acid reacts with 1.00 g of  $\text{CaCO}_3$ ?

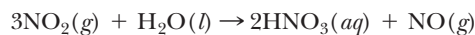
**7-15.** Elemental copper can be recovered from the mineral chalcocite,  $\text{Cu}_2\text{S}$ . From the following equation, determine what mass of  $\text{Cu}$  is formed from  $7.82 \times 10^{22}$  molecules of  $\text{O}_2$ .



**7-16.** Fool's gold (pyrite) is so named because it looks much like gold. When it is placed in aqueous  $\text{HCl}$ , however, it dissolves and gives off the pungent gas  $\text{H}_2\text{S}$ . Gold itself does not react with aqueous  $\text{HCl}$ . From the following equation, determine how many individual molecules of  $\text{H}_2\text{S}$  are formed from 0.520 mol of pyrite ( $\text{FeS}_2$ ).



**7-17.** Nitrogen dioxide may form so-called acid rain by reaction with water in the air according to the equation



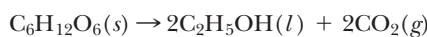
What mass of nitric acid is produced from 18.5 kg of  $\text{NO}_2$ ?

**7-18.** Elemental chlorine can be generated in the laboratory according to the equation



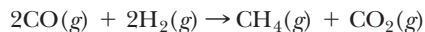
What mass of  $\text{Cl}_2$  is produced from the reaction of 665 g of  $\text{HCl}$ ?

**7-19.** The fermentation of sugar to produce ethyl alcohol is represented by the equation



What mass of alcohol is produced from 25.0 mol of sugar?

**7-20.** Methane gas can be made from carbon monoxide gas according to the equation



What mass of  $\text{CO}$  is required to produce  $8.75 \times 10^{25}$  molecules of  $\text{CH}_4$ ?

### Limiting Reactant (SECTION 7-2)

**7-21.** Nitrogen gas can be prepared by passing ammonia over hot copper(II) oxide according to the equation

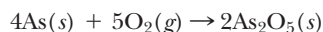


How many moles of  $\text{N}_2$  are prepared from the following mixtures?

- 3.00 mol of  $\text{CuO}$  and 3.00 mol of  $\text{NH}_3$
- 3.00 mol of  $\text{CuO}$  and 2.00 mol of  $\text{NH}_3$
- 3.00 mol of  $\text{CuO}$  and 1.00 mol of  $\text{NH}_3$
- 0.628 mol of  $\text{CuO}$  and 0.430 mol of  $\text{NH}_3$
- 5.44 mol of  $\text{CuO}$  and 3.50 mol of  $\text{NH}_3$

**7-22.** How many moles remain of the reactant in excess in problem 7-21(a) and (c)?

**7-23.** Consider the equation illustrating the combustion of arsenic.

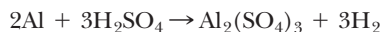


How many moles of  $\text{As}_2\text{O}_5$  are prepared from the following mixtures?

- (a) 4.00 mol of As and 4.00 mol of  $\text{O}_2$
- (b) 3.00 mol of As and 4.00 mol of  $\text{O}_2$
- (c) 5.62 mol of As and 7.50 mol of  $\text{O}_2$
- (d) 3.86 mol of As and 4.75 mol of  $\text{O}_2$

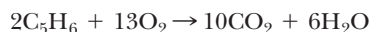
**7-24.** How many moles remain of the reactant in excess in problem 7-23(a) and (b)?

**7-25.** Consider the equation



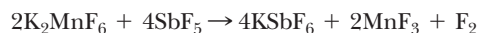
If 0.800 mol of Al is mixed with 1.00 mol of  $\text{H}_2\text{SO}_4$ , how many moles of  $\text{H}_2$  are produced? How many moles of one of the reactants remain?

**7-26.** Consider the equation



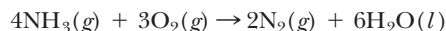
If 3.44 mol of  $\text{C}_5\text{H}_6$  is mixed with 20.6 mol of  $\text{O}_2$ , what mass of  $\text{CO}_2$  is formed?

**7-27.** Elemental fluorine is very difficult to prepare by ordinary chemical reactions. In 1986, however, a chemical reaction was reported that produces fluorine.



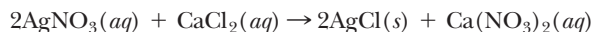
If a 525-g quantity of  $\text{K}_2\text{MnF}_6$  is mixed with a 900-g quantity of  $\text{SbF}_5$ , what mass of  $\text{F}_2$  is produced?

**7-28.** Consider the equation



If a 40.0-g sample of  $\text{O}_2$  is mixed with 1.50 mol of  $\text{NH}_3$ , which is the limiting reactant? How many moles of  $\text{N}_2$  form?

**7-29.** Consider the equation



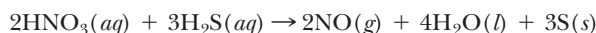
If a solution containing 20.0 g of  $\text{AgNO}_3$  is mixed with a solution containing 10.0 g of  $\text{CaCl}_2$ , which compound is the limiting reactant? What mass of  $\text{AgCl}$  forms? What mass of one of the reactants remains?

**7-30.** Limestone ( $\text{CaCO}_3$ ) dissolves in hydrochloric acid as shown by the equation



If 20.0 g of  $\text{CaCO}_3$  and 25.0 g of  $\text{HCl}$  are mixed, what mass of  $\text{CO}_2$  is produced? What mass of one of the reactants remains?

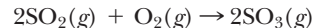
**7-31.** Consider the balanced equation



If a 10.0-g quantity of  $\text{HNO}_3$  is mixed with 5.00 g of  $\text{H}_2\text{S}$ , what are the masses of each product and of the reactant present in excess after reaction occurs?

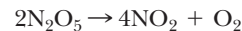
## Theoretical and Percent Yield (SECTION 7-3)

**7-32.** Sulfur trioxide is prepared from  $\text{SO}_2$  according to the equation



This is a reversible reaction in which not all  $\text{SO}_2$  is converted to  $\text{SO}_3$  even with excess  $\text{O}_2$  present. In a given experiment, 21.2 g of  $\text{SO}_3$  was produced from 24.0 g of  $\text{SO}_2$ . What is the theoretical yield of  $\text{SO}_3$ ? What is the percent yield?

**7-33.** The following is a reversible decomposition reaction.



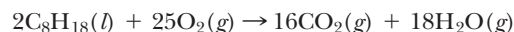
When 25.0 g of  $\text{N}_2\text{O}_5$  decomposes, it is found that 10.0 g of  $\text{NO}_2$  forms. What is the percent yield?

**7-34.** The following equation represents a reversible combination reaction.



If 25.0 g of  $\text{PCl}_5$  reacts, there is a 45.0% yield of  $\text{POCl}_3$ . What is the actual yield in grams?

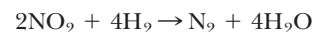
**7-35.** Octane in gasoline burns in an automobile engine according to the equation



If a 57.0-g sample of octane is burned, 152 g of  $\text{CO}_2$  is formed. What is the percent yield of  $\text{CO}_2$ ?

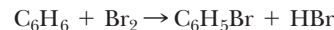
**\*7-36.** In problem 7-35, the  $\text{C}_8\text{H}_{18}$  that is *not* converted to  $\text{CO}_2$  forms CO. What is the mass of CO formed? (CO is a poisonous pollutant that is converted to  $\text{CO}_2$  in a car's catalytic converter.)

**\*7-37.** Given the reversible reaction



what mass of hydrogen is required to produce 250 g of  $\text{N}_2$  if the yield is 70.0%?

**\*7-38.** When benzene reacts with bromine, the principal reaction is



If the yield of bromobenzene ( $\text{C}_6\text{H}_5\text{Br}$ ) is 65.2%, what mass of bromobenzene is produced from 12.5 g of  $\text{C}_6\text{H}_6$ ?

**\*7-39.** A second reaction between  $\text{C}_6\text{H}_6$  and  $\text{Br}_2$  (see problem 7-38) produces dibromobenzene ( $\text{C}_6\text{H}_4\text{Br}_2$ ).

- (a) Write the balanced equation illustrating this reaction.
- (b) If the remainder of the benzene from problem 7-38 reacts to form dibromobenzene, what is the mass of  $\text{C}_6\text{H}_4\text{Br}_2$  produced?

## Heat in Chemical Reactions (SECTION 7-4)

**7-40.** When one mole of magnesium undergoes combustion to form magnesium oxide, 602 kJ of heat energy is evolved. Write the thermochemical equation in both forms.

**7-41.** In problem 7-12, the reaction between  $\text{N}_2$  and  $\text{O}_2$  was discussed. A 90.5-kJ quantity of heat energy must be supplied per mole of  $\text{NO}$  formed. Write the balanced

thermochemical equation in both forms. Is the reaction exothermic or endothermic?

**7-42.** To decompose one mole of  $\text{CaCO}_3$  to  $\text{CaO}$  and  $\text{CO}_2$ , 176 kJ must be supplied. Write the balanced thermochemical equation in both forms.

**7-43.** The complete combustion of one mole of octane ( $\text{C}_8\text{H}_{18}$ ) in gasoline evolves 5480 kJ of heat. The complete combustion of one mole of methane in natural gas ( $\text{CH}_4$ ) evolves 890 kJ. How much heat is evolved per 1.00 g by each of these fuels?

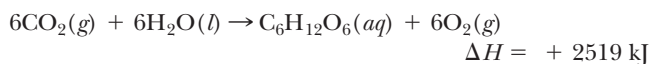
**7-44.** Methyl alcohol ( $\text{CH}_3\text{OH}$ ) is used as a fuel in racing cars. It burns according to the equation



What amount of heat is evolved per 1.00 g of alcohol? How does this compare with the amount of heat per gram of octane in gasoline? (See problem 7-43.)

**7-45.** The thermite reaction was discussed in problem 7-13. For the balanced equation,  $\Delta H = -850 \text{ kJ}$ . What mass of aluminum is needed to produce 35.8 kJ of heat energy?

**7-46.** Photosynthesis is an endothermic reaction that forms glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) from carbon dioxide, water, and energy from the sun. The balanced equation is



What mass of glucose is formed from 975 kJ of energy?

**7-47.** When butane ( $\text{C}_4\text{H}_{10}$ ) in a cigarette lighter undergoes combustion, it evolves 2880 kJ per mole of butane. What is the mass of water formed if 1250 kJ of heat evolves?

### General Problems

**\*7-48.** Liquid iron is made from iron ore ( $\text{Fe}_2\text{O}_3$ ) in a three-step process in a blast furnace as follows.

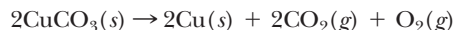
- $3\text{Fe}_2\text{O}_3(s) + \text{CO}(g) \rightarrow 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2(g)$
- $\text{Fe}_3\text{O}_4(s) + \text{CO}(g) \rightarrow 3\text{FeO}(s) + \text{CO}_2(g)$
- $\text{FeO}(s) + \text{CO}(g) \rightarrow \text{Fe}(l) + \text{CO}_2(g)$

What mass of iron would eventually be produced from 125 g of  $\text{Fe}_2\text{O}_3$ ?

**7-49.** A 50.0-g sample of *impure*  $\text{KClO}_3$  is decomposed to  $\text{KCl}$  and  $\text{O}_2$ . If a 12.0-g quantity of  $\text{O}_2$  is produced, what percent of the sample is  $\text{KClO}_3$ ? (Assume that all of the  $\text{KClO}_3$  present decomposes.)

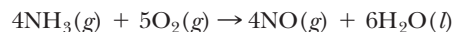
**7-50.** In Example 7-5,  $\text{SO}_2$  was formed from the burning of pyrite ( $\text{FeS}_2$ ) in coal. If a 312-g quantity of  $\text{SO}_2$  was collected from the burning of 6.50 kg of coal, what percent of the original sample was pyrite?

**\*7-51.** Copper metal can be recovered from an ore,  $\text{CuCO}_3$ , by the decomposition reaction



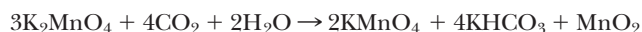
What is the mass of a sample of *impure* ore if it is 47.5%  $\text{CuCO}_3$  and produces 350 g of  $\text{Cu}$ ? (Assume complete decomposition of  $\text{CuCO}_3$ .)

**\*7-52.** Consider the equation



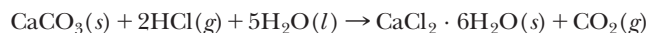
When an 80.0-g quantity of  $\text{NH}_3$  is mixed with 200 g of  $\text{O}_2$ , a 40.0-g quantity of  $\text{NO}$  is formed. Calculate the percent yield based on the limiting reactant.

**\*7-53.** Consider the equation



How many moles of  $\text{MnO}_2$  are produced if 9.50 mol of  $\text{K}_2\text{MnO}_4$ ,  $6.02 \times 10^{24}$  molecules of  $\text{CO}_2$ , and 90.0 g of  $\text{H}_2\text{O}$  are mixed?

**\*7-54.** Calcium chloride hydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) is a solid used to melt ice at low temperatures. It is prepared according to the equation



What mass of the hydrate is prepared from a mixture of 0.250 mole of  $\text{H}_2\text{O}$ ,  $9.50 \times 10^{22}$  molecules of  $\text{HCl}$ , and 15.0 g of  $\text{CaCO}_3$ ?

**\*7-55.** A 2.85-g quantity of gaseous methane is mixed with 15.0 g of chlorine to produce a liquid, compound X, and gaseous hydrogen chloride. Compound X is 14.1% C, 2.35% H, and 83.5% Cl. Its molecular formula is the same as its empirical formula.

- From the formula of X, write a balanced equation. (*Hint:* Balance hydrogens before chlorines.)
- What is the theoretical yield of compound X?

**\*7-56.** A 10.00-g sample of gaseous ethane ( $\text{C}_2\text{H}_6$ ) reacts with chlorine to form gaseous hydrogen chloride and a liquid compound (Y) that has a molar mass of 168 g/mol. Compound Y is 14.3% carbon, 84.5% chlorine, and the remainder hydrogen. The reaction produces 12.0 g of compound Y, which is 57.0% yield.

- Write the balanced equation illustrating the reaction.
- What mass of ethane was required?

**\*7-57.** The remainder of the ethane from problem 7-56 reacts to form a liquid compound (Z) that is 18.0% carbon, 79.8% chlorine, and 2.25% hydrogen. The empirical and molecular formulas of this compound are the same.

- Write the balanced equation illustrating the reaction.
- What mass of compound Z is formed?



## Limiting Reactants

**Purpose:** To manipulate a model to evaluate a reaction containing a limiting agent. (Work in groups of three or four. Estimated time: 30 min.)

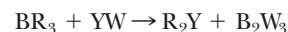
**Equipment:** 12 Lego blocks of each of these colors: white, red, blue, and yellow. These will be used to make “molecules” of different combinations of “atoms.”

- Construct the following molecules: one blue (B) and one white (W) to make a BW; two red (R) and one yellow (Y) to make an R<sub>2</sub>Y.
- Create as many of these molecules as you can, and discard the excess blocks.
  - What is the largest number of BW molecules you can make?
  - What is the largest number of R<sub>2</sub>Y's?
- Rearrange the given molecules into two new molecules, R<sub>4</sub>W and BY<sub>2</sub>.
  - Write out a balanced chemical reaction:
 
$$? BW + ? R_2Y \rightarrow ? R_4W + ? BY_2$$

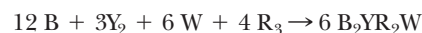
- Given the initial amounts of the two reactants:

- Which was the limiting reactant?
- How many molecules of product were you able to make?
- How many of the excess reactants were unreacted?
- How many of the original BW and R<sub>2</sub>Y molecules reacted?

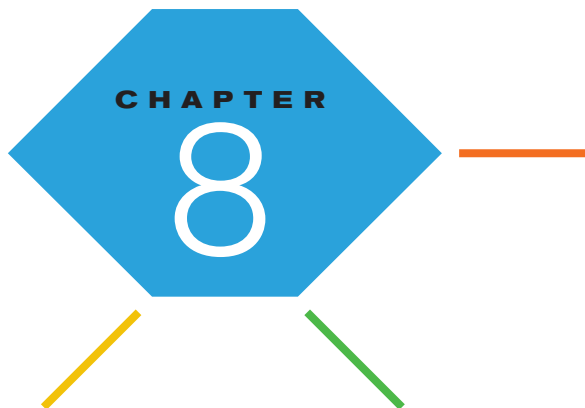
- Repeat this procedure for the following reaction:



- Now, make 12 B's, 6 Y<sub>2</sub>'s, 12 W's, and 4 R<sub>3</sub>'s. From the equation:



- Predict how many B<sub>2</sub>YR<sub>2</sub>W's you can make from each of the given colors.
- Predict which one(s) is/are the limiting reactant(s).
- Predict how many of the excess reactants are going to be left over.
- Perform the experiment and see if you were correct.



# Modern Atomic Theory



**F**ireworks produce spectacular colors.

Each color is caused by the presence of a specific element. The information that flows from the emission of color by the atoms of hot, gaseous elements is a topic of this chapter.

**PART A**  
**THE ENERGY OF THE  
ELECTRON IN THE ATOM**

**8-1** The Emission Spectra of the  
Elements and Bohr's Model



**MAKING IT REAL**

*Roses Are Red; Violets Are Blue—But Why?*



**MAKING IT REAL**

*Solving Crimes with Light*

**8-2** Modern Atomic Theory: A Closer  
Look at Energy Levels

**PART B**  
**THE PERIODIC TABLE AND  
ELECTRON CONFIGURATION**

**8-3** Electron Configurations of the  
Elements

**8-4** Orbital Diagrams of the Elements  
(Optional)

**8-5** Periodic Trends

**SETTING THE STAGE** Dazzling explosions with bursts of bright silver and streaks of green, yellow, red, and blue from spectacular displays of fireworks light up the sky. The Fourth of July and the Olympics would not be complete without displays of these exciting colors. It has been known for hundreds of years that when certain minerals are added to fireworks, specific colors are produced. We now know that it is the presence of specific elements in these minerals that are responsible for the colors. Strontium imparts a red color; barium, green; copper, blue; and sodium, yellow. In fact, the specific colors emitted by hot, gaseous atoms can be used to identify elements much like fingerprints are used to identify individuals. The study of the colors of these *emission spectra* is what opened the door to a deeper understanding of the chemistry of the elements.

Often in science, when a theory is developed to explain one phenomenon, other mysteries are explained as well. This happened with the theory that explained the emission spectra of the elements—most specifically, hydrogen. The theory, which emphasized the electrons in the atom, led to an understanding of the theoretical basis of the periodic table. As we explained in Chapter 4, this marvelous table displays elements that are chemically related in vertical columns called *groups*. Although the existence of chemically related elements has been known for over 200 years, only since the 1930s have scientists had a feeling for *why* elements are chemically related.

A theory of the atom that emphasized the electrons was first advanced in 1913 by a student of Lord Rutherford (see Section 2-2.3) named Niels Bohr. This had the immediate effect of explaining the emission spectrum of hydrogen, the simplest of the elements. More significant to our purposes, however, is that Bohr's theory eventually led to a new, improved theory that explained and predicted chemical similarities among certain elements.

In Part A in this chapter, we will see how the emission spectra provided the clue for an understanding of the basis of the periodic table. In Part B, we will apply this information to properties of the elements that relate to the periodic table.

**PART A**  
**THE ENERGY OF THE**  
**ELECTRON IN THE ATOM**

**SETTING A GOAL**

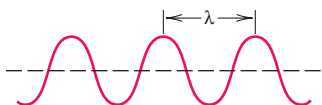
- You will understand historically how elemental emission spectra were used to determine the structure electrons adopt within an atom.

**OBJECTIVES**

- 8-1 (a)** Describe the relationships among the wavelengths of light, energy, and color. **(b)** Describe the relationship between emission spectra and the electronic structure of the hydrogen atom as explained by Bohr's model.
- 8-2 (a)** Differentiate among a shell, a subshell, and an orbital. **(b)** Identify an *s*, *p*, or *d* type orbital from its shape.

**OBJECTIVES FOR SECTION 8-1**

**(a)** Describe the relationships among the wavelengths of light, energy, and color. **(b)** Describe the relationship between emission spectra and the electronic structure of the hydrogen atom as explained by Bohr's model.



**8-1 THE EMISSION SPECTRA OF THE ELEMENTS AND BOHR'S MODEL**



**LOOKING AHEAD!** Hot, gaseous atoms in fireworks give off spectacular light, but any substance glows if it is heated to a high enough temperature. For example, the tungsten filament in an incandescent lightbulb emits a bright light as a result of heat generated by the flow of electricity. Understanding the nature of emitted light was the clue that led to an understanding of the periodic table. ■

**8-1.1 Electromagnetic Radiation and Wavelength**

Light, which is also known as **electromagnetic radiation**, is a form of energy like heat or electricity. Light travels through space in tiny packets of energy called photons in waves much like the waves moving across a pond or a lake. All light waves travel at the same velocity in a vacuum at the phenomenal rate of  $3.0 \times 10^{10}$  cm/s (186,000 mi/s). Light waves have properties called wavelength and amplitude. The amplitude of a wave refers to its height, which in turn relates to the intensity of light. The amplitude, or intensity, of light is not important to our discussion, so it will not be mentioned further. *The wavelength of light refers to the distance between two adjacent peaks in the wave.* Wavelength is very important for our purposes because it relates to the energy of light. Wavelength is represented by the Greek letter λ (lambda).

**8-1.2 The Continuous Spectrum**

Consider the white light emitted by a tungsten filament. We can analyze this light by passing it through a glass prism. Specific colors have different velocities when traveling through a medium such as glass. (See Figure 8-1.) As a result of the geometry of the prism, the white light is separated into its component colors, which appear as a continuous range of colors that we associate with a rainbow. *Since one color blends gradually into another, this is known as a continuous spectrum.* A rainbow after a rainstorm is a continuous spectrum caused by the separation of sunlight, which contains the complete spectrum of colors, into its component colors by raindrops in the air.

Each color of light in a rainbow has a specific wavelength. Violet light, on one end of the spectrum, has the shortest wavelength. Red, on the other end of the spectrum, has the longest. Important to our consideration of light, however, is that the energy of light is inversely proportional to its wavelength. That is,

$$E \propto \frac{1}{\lambda} \quad E = \frac{hc}{\lambda}$$



**FIGURE 8-1 The Spectrum of Incandescent Light** When a narrow beam of light from an ordinary lightbulb is passed through a glass prism, the white light is found to contain all the colors of the visible spectrum.



where  $\lambda$  (lambda) is the symbol of wavelength,  $h$  is a constant of proportionality known as Planck's constant, and  $c$  is the velocity of light in a vacuum, which is also a constant.

Because of the inverse relationship, the larger the value of  $\lambda$ , the lower the energy. Thus red light, with the longest wavelength, has the lowest energy in the visible spectrum. Violet, with the smallest wavelength, has the highest energy. The visible part of the spectrum has wavelengths between 400 nm ( $1 \text{ nm} = 10^{-9} \text{ m}$ ) and about 750 nm. The spectrum of electromagnetic radiation extends in both directions well beyond the wavelengths of visible light. Light that extends somewhat beyond violet is termed *ultraviolet light* (less than 400 nm). It is not visible but is highly energetic. Indeed, it is powerful enough to damage living organisms. For example, UVA (320–400 nm) and UVB (280–320 nm) light from the sun can cause various types of skin cancer. Light with extremely small wavelengths and thus extremely high energies includes X-rays and gamma rays. Only small amounts of this radiation can be tolerated by living systems. (See Figure 8-2.)

*Infrared light* has wavelengths somewhat longer than 750 nm and is also outside the visible range of the electromagnetic spectrum. Beyond infrared light are the longer wavelengths of radio and TV waves. Light with wavelengths longer than 750 nm is not known to cause damage to living tissue.



### Roses Are Red; Violets Are Blue—But Why?



The three primary colors.

From the beauty of flowers and sky to the brightness of rubies and emeralds, we marvel at the colors of light that lie in the visible part of the spectrum (wavelengths 400–750 nm).

It was mentioned

earlier in this chapter that the sun emits the complete spectrum of colors of the rainbow. Blended together, sunlight appears nearly white. Fireworks emit discrete colors depending on the element that is heated in the explosion. But most of what our eyes receive is a result of reflected light rather than emitted light.

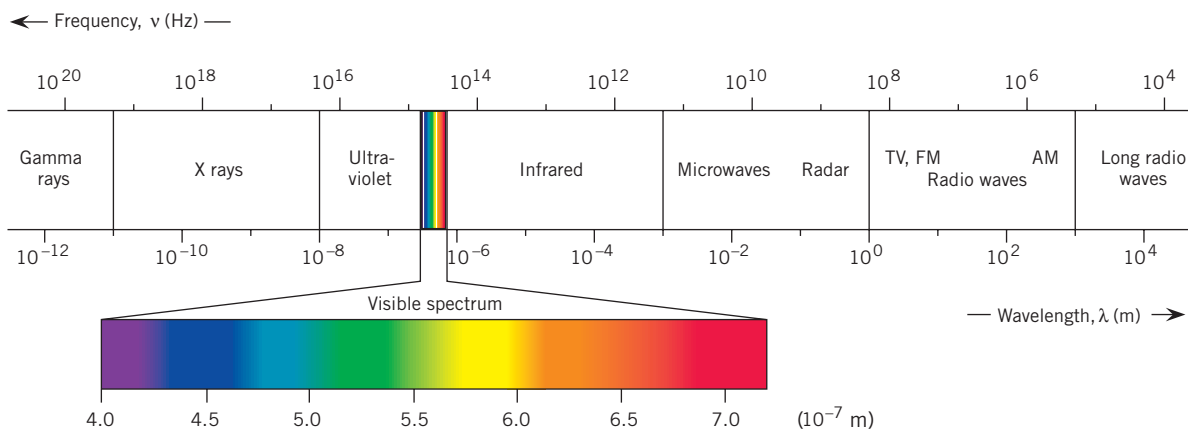
When white light is directed at a surface, the amount of reflection determines its shade. If all of the light is reflected, the surface appears white. If all of the light is absorbed, the surface appears black. (That is why light-colored clothing is preferred in the summer, since it reflects the light energy.) If part of the light is absorbed and part is reflected, the surface appears as a shade of gray.

Most of the wonderful colors of our world result from absorption of specific regions of the light spectrum. There are three primary colors of light, as shown in the photograph. Red light comprises the highest third of the wavelengths of visible light (the lowest energies). Green is the middle third of the wavelengths, and blue is the lower third. A blend of all three appears white. It is only when one region of the spectrum is absorbed that we perceive color. A rose appears red because it absorbs the blue–green part of the spectrum and reflects the complement to these colors, which is red. If only the blue part is absorbed and both red and green are reflected, we see a yellow rose. A violet absorbs the red–green part of the spectrum and reflects blue. Leaves appear green because they absorb the red–blue part of the spectrum. Some of that absorbed light energy is converted into chemical energy in the production of sugars by *photosynthesis*.

Color television works on the same principle. Three different signals are shot through different primary-color filters and then transmitted to the TV set. The three signals are then automatically blended back together to provide the proper color. Older sets had red, green, and blue drives that were manually adjusted.

We are lucky. Not all animals see color. Life for us would certainly be dull without the “wonderful world of color.”





**FIGURE 8-2** The Spectrum of Light Light energy ranges from gamma rays to radio waves.

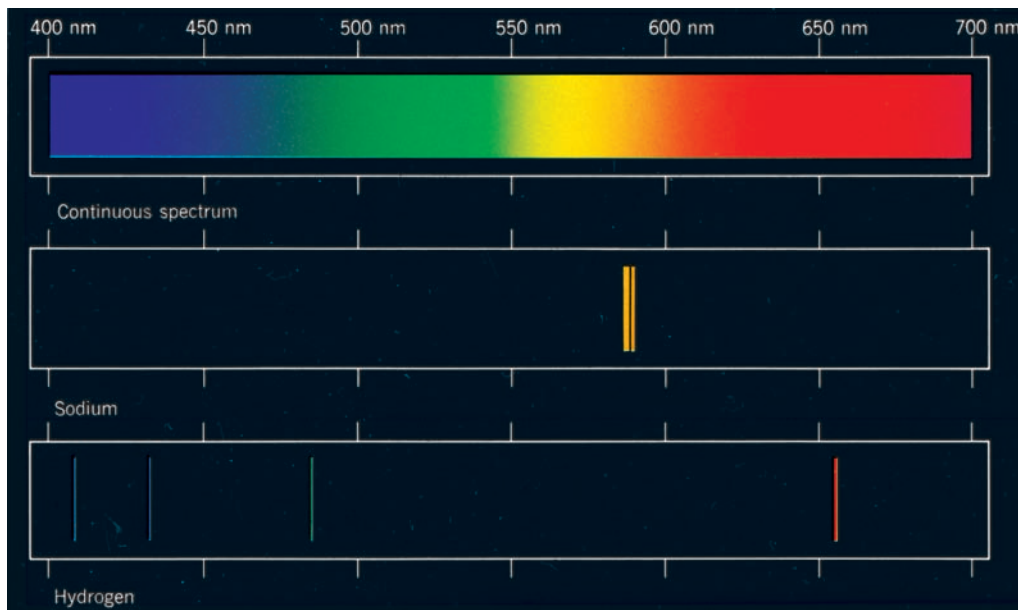
### 8-1.3 The Discrete Spectrum

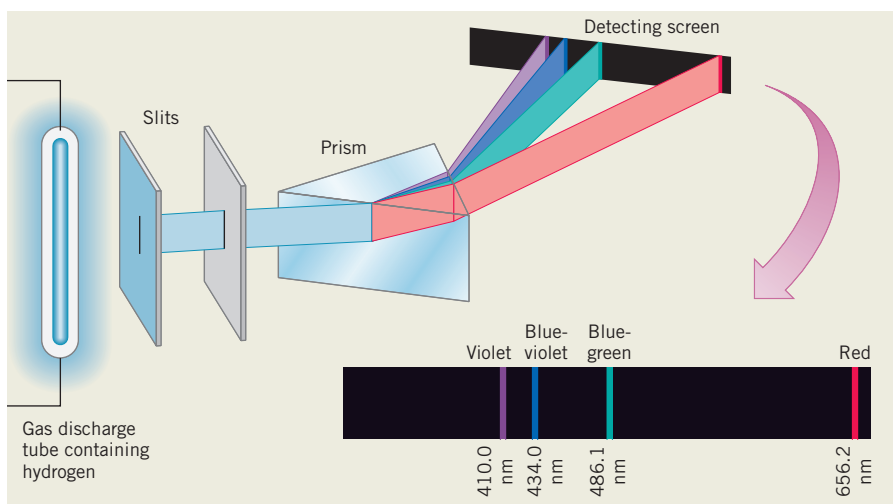
When an element is heated enough so that the hot, gaseous atoms emit light, the results are different from the continuous spectrum emitted by the sun or a lightbulb. Only specific, or discrete, colors are produced. Since the colors are discrete, the energies emitted from the atoms are discrete. The spectrum of each element (called its atomic emission spectrum) is unique to that element and is the reason specific elements are used in fireworks. (See Figure 8-3.) *The atomic emission spectra of elements are referred to as **discrete**, or **line**, spectra.* In Figure 8-4, the spectrum of hydrogen in the visible range is shown along with the wavelengths of light of the four lines that appear. Energy is supplied to the hydrogen gas by an electrical discharge similar to that in the familiar neon light.

### 8-1.4 Bohr's Model

By 1913, the nuclear theory of the atom proposed by Lord Rutherford was generally accepted by scientists. In that year, Neils Bohr set out to develop this theory further in order to explain the origin of the discrete spectrum of hydrogen. His main goal was to explain how the electron in the hydrogen atom was responsible for the energy

**FIGURE 8-3** The Continuous Spectrum and the Emission Spectra of Sodium and Hydrogen in the Visible Range The light from an incandescent light (top) is continuous, whereas the atomic spectra of sodium (middle) and hydrogen (bottom) are composed of discrete colors.





**FIGURE 8-4** Production of the Line Spectrum of Hydrogen The light from excited hydrogen atoms is passed through a glass prism. The prism divides the light into four discrete colors in the visible range.

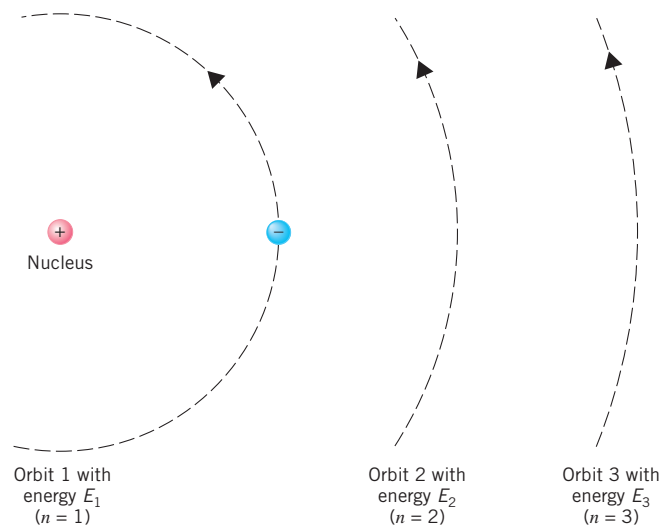
emitted in the form of light. Bohr did not realize that his theory would lay the foundation for the explanation of other phenomena such as the periodicity of elements and the way atoms bond to each other.

First, Bohr proposed that the electron in the hydrogen atom revolves around the nucleus in a stable, circular orbit. The electrostatic attraction of the negative electron for the positive proton is counterbalanced by the centrifugal force of the orbiting electron. These two forces offset each other and keep the electron in a stable orbit. His theory of the hydrogen atom is analogous to the orbiting of the planets around the sun and thus is often referred to as a model. *A model is a description or analogy used to help visualize a phenomenon.* Bohr's model does not seem so revolutionary at first glance, but classical physics prohibits such a model. Classical, or Newtonian, physics, which was all that was known at the time, stated that a charged particle (the electron) orbiting around another charged particle (the proton) would lose energy and spin into the nucleus. Bohr sidestepped this problem by postulating (suggesting without proof as a necessary condition) that classical physics does not apply in the small dimensions of the atom and that other laws are appropriate. Eventually, he would be proven correct.

### 8-1.5 Quantized Energy Levels

Second, Bohr suggested that there are several orbits that the electron may occupy. Furthermore, these orbits that are available to the electron are **quantized**, which means that they are at definite, or discrete, distances from the nucleus. Since the energy of a particular orbit depends on its distance from the nucleus, the energy of an electron in such an orbit is also quantized. *The discrete orbits available to an electron in a hydrogen atom are referred to as energy levels.* (See Figure 8-5.) Each energy level in the hydrogen atom is designated by an integral number known as the **principal quantum number** and given the symbol  $n$ . The first energy level is designated  $n = 1$ ; the second level,  $n = 2$ ; etc.

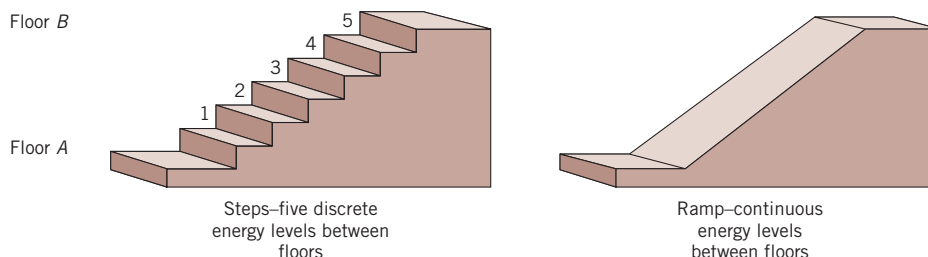
The quantized energy levels in the hydrogen atom can be compared with a stairway in your home. In Figure 8-6, you can see that between floor A and floor B there are five steps that are analogous to energy levels in an atom. Since you cannot stand (with both feet together) between steps, we can say that each step represents a discrete, or *quantized*, amount of energy. On the other hand, a ramp between the two floors represents a *continuous* change in energy. In this case, all energy levels would be possible between floors.



**FIGURE 8-5** Bohr's Model of the Hydrogen Atom In this model, the electron can exist only in definite, or discrete, energy states.

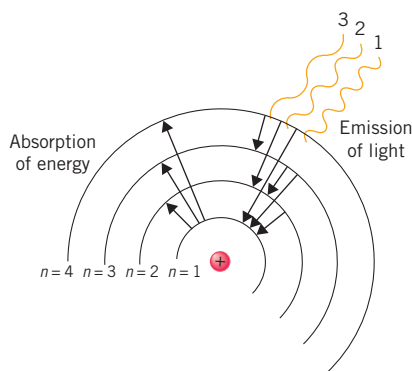
**FIGURE 8-6** Discrete versus Continuous Energy Levels

The steps represent discrete energy levels; the ramp, continuous energy levels.

**8-1.6** The Ground State and Excited States

Under normal conditions, *the single electron in a hydrogen atom occupies the lowest energy level, which is the orbit closest to the nucleus. This is called the **ground state**.* When energy is supplied to a hydrogen atom, such as when it is heated, the electron can absorb the appropriate amount of energy needed to “jump” from the ground state (i.e., the  $n = 1$  level) to a higher energy level (i.e.,  $n = 2, 3, 4$ , etc.). Because of its new position in a higher energy level, the electron now has potential energy, just like a weight suspended above the ground. *Energy levels higher than the ground state are called **excited states**.* What is most significant, according to Bohr, is what happens when the electron “falls” back down to lower excited states or all the way to the ground state. He suggested that the electron gives up this extra energy in the form of light when it falls back. Since energy levels are quantized, the difference in energy between any two levels is also quantized. When an electron falls back to a lower energy level, it must emit a discrete amount of energy. Since this energy is emitted as light, the light would have a discrete energy, a discrete wavelength, and a discrete color (if the light is in the visible region of the spectrum), thus explaining the line spectrum of hydrogen. (See Figure 8-7.)

This is the qualitative explanation of the discrete spectrum. The real significance of Bohr’s model is that he was able to calculate the expected wavelength of light in the hydrogen spectrum from the mathematical relationships. The experimental values listed in Figure 8-4 correspond well with those computed by Bohr. Bohr’s model worked specifically for the hydrogen atom. Calculations of the wavelengths of the lines in the discrete spectra of other elements had to await more sophisticated models.

**FIGURE 8-7** Light Emitted from a Hydrogen Atom

An electron in an excited state emits energy in the form of light when it drops to a lower energy level.

**ASSESSING THE OBJECTIVES FOR SECTION 8-1**

**EXERCISE 8-1(a) KNOWLEDGE:** Fill in the blanks.

Long wavelengths of light have \_\_\_\_\_ (high/low) frequencies and \_\_\_\_\_ (high/low) energies. The color of visible light with the highest energy is \_\_\_\_\_, and the color of visible light with the longest wavelength is \_\_\_\_\_. White light contains all colors of light, called a \_\_\_\_\_ spectrum. Light from heated gaseous element sources gives off only discrete energies to form a \_\_\_\_\_ spectrum. Niels Bohr suggested that the orbits of an electron were \_\_\_\_\_ or set to specific values. The lowest energy state is the \_\_\_\_\_ state, and the higher states are the \_\_\_\_\_ states.

**EXERCISE 8-1(b) KNOWLEDGE:** List the parts of the electromagnetic spectrum in order. Label the appropriate ends of the list as high energy/low energy and large wavelength/small wavelength.

**EXERCISE 8-1(c) ANALYSIS:** In a sentence or two, describe what causes the lines in the hydrogen spectrum.

**EXERCISE 8-1(d) SYNTHESIS:** Bohr’s model applied only to the results of the hydrogen spectrum. Is this of any significance when considering other elements?

**EXERCISE 8-1(e) SYNTHESIS:** Neon lights excite electrons in atoms of neon to produce a colored light. If the energy produced is quantized, why can we make lights of many different colors?

*For additional practice, work chapter problems 8-1, 8-2, and 8-3.*

MAKING

REAL

IT

## Solving Crimes with Light



Analysis of light can provide forensic scientists with an amazing amount of information about evidence found at a crime scene. Perhaps one of the more important objects found at a scene are glass particles. Maybe a window was broken or someone was killed by a hit-and-run driver. Did the tiny particles of glass found in the clothes of a suspect originate from the location of the crime or did they come from somewhere else? In

Chapter 3, we discussed how density is an intensive property that helps connect two fragments as originating from the same pane of glass. Two other measurements can also be important evidence. The elements and their relative abundances present in the glass as well as the refractive index of the glass are also significant clues. First, consider the elements present in a fragment of glass or a paint sample.

As we mentioned, every element has its characteristic line spectrum that is as specific to the element as a fingerprint is to an individual. A sample of glass or paint can be analyzed in a device called an *emission spectrograph*. The instrument contains a source of intense heat, on the order of 7000 to 10,000°C, into which the sample is introduced and vaporized. The emitted light is focused by a lens through a glass prism, which breaks the light into its component lines. (See Figure 8-4.) These are then recorded on a photographic plate. Since many elements are present, a large number of lines result. The process is used more to compare samples rather than to determine exactly what elements are present. If two glass or paint samples match, it is strong evidence that they originated from the same source.

An intensive physical property known as the *refractive index* is also used to compare glass samples. It is the ratio of the velocity of a specific wavelength of light in a vacuum divided by the velocity in the medium. For example, a refractive index of 1.25 means that the light travels 25% faster in a vacuum than through the medium in question. Perhaps you have noticed this effect when you viewed something at the bottom of a container of water. When you reach in for the object, it is not where your eyes tell you it is. This is because the light waves travel slower and have been bent as they pass through the water.

Forensic scientists also use refractive index to compare glass fragments from a crime scene. The actual refractive index of a piece of glass can be hard to measure directly, so it is done by placing the glass in a medium such as a silicone oil. When a transparent solid such as glass is immersed in a liquid, the boundaries of the glass are apparent because of the difference in refractive index of the glass and the liquid. If the oil is heated, its refractive index changes by a known amount, but the refractive index of the solid glass does not change. When the oil and the glass have the same refractive index, the boundaries of the glass are not visible and the glass seems to disappear. At this point, the refractive index of the glass can be determined by reference to a table listing the refractive indexes of the liquid as a function of temperature. This all used to be done visually but now it is carried out automatically with the help of a computer.

When the density and refractive index of two glass samples are very close together, it serves as admissible evidence in court. However, a conviction usually depends on additional evidence, such as hair, fibers, and fingerprints, that can help connect a suspect to a crime scene.

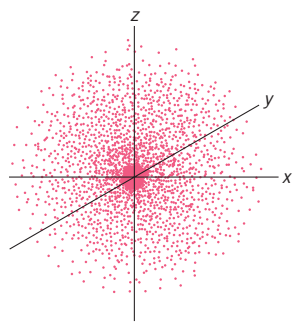
## 8-2 MODERN ATOMIC THEORY: A CLOSER LOOK AT ENERGY LEVELS

### OBJECTIVES FOR SECTION 8-2

(a) Differentiate among a shell, a subshell, and an orbital. (b) Identify an *s*, *p*, or *d* type orbital from its shape.



**LOOKING AHEAD!** Bohr's model is still used in the popular press as a convenient, simple way to represent the atom, with electrons as particles circling a nucleus. In the modern scientific view of the atom, however, the characteristics of the electron are much more complex. Therefore, a more sophisticated view of the electron has evolved. In this section, we will examine the results of the modern view of the electron in the hydrogen atom. ■



**FIGURE 8-8 Electron Density** The electron density of the ground state of hydrogen is spherical.

### 8-2.1 The Wave Mechanical Model

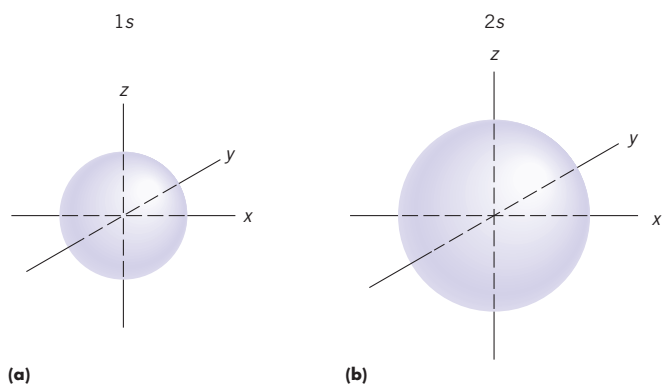
Soon after Bohr's model was presented, experiments confirmed that the electron has properties both of a particle (mass) *and* of light (wave nature). Because of its dual nature, the electron could not be viewed as a simple particle circling the nucleus at a definite distance. Also, if the electron moved with a high velocity, as Bohr had claimed, one could not know its location with much certainty. The faster a particle moves, the less we would know about its location. This is analogous to a fastball thrown by a professional baseball pitcher. The faster the ball is thrown, the less the batter knows about its location and the less likely that the ball will be hit. *The wave nature of the electron and the uncertainty of its location led to a complex mathematical approach to the electron in the hydrogen atom, known as wave mechanics.* Using the equations of the wave mechanical model, only the probability of finding the electron in a given region of space at a certain instant could be determined. Bohr calculated the exact radius of the ground-state energy level for the electron in hydrogen. In the wave mechanical model, this radius represents the highest *probability* of finding the electron. We no longer view the electron as orbiting in a specific path around the nucleus. In fact, the motion of an electron in an atom in this model is not understood.

Locating the electron in the vicinity of the nucleus is like trying to locate a fast-moving dancer on a stage with a strobe light. With each flash of the strobe, we find the dancer in a different location. However, if we marked the dancer's position at each flash, eventually we would probably see a pattern and notice that she has a higher probability of being in certain locations on the floor than others. For example, the exact center of the stage would have the highest probability and the wings would have a low probability. A similar situation would occur if we were to try to measure the position of the electron in a hydrogen atom. That is, each time we would locate the electron, it would most likely be in a different location than before. However, if we took enough measurements, a pattern would eventually develop. For example, in Figure 8-8 a typical pattern of electron probability is shown. The figure includes  $x$ ,  $y$ , and  $z$  coordinates to emphasize the three-dimensional nature of the points. Notice that this pattern suggests that the probability of finding the electron, known as the *electron density*, is in a spherical region of space around the nucleus for the ground state of hydrogen.

### 8-2.2 The First Shell and $s$ Orbitals

*The region of space where there is the significant probability of finding a particular electron is known as an orbital.* (Note that this is a different concept from Bohr's orbits.) An orbital is sometimes viewed as an "electron cloud," as if the electron were spread out in a volume of space like a cloud. In some places the cloud is thick and in others it is thin. It is difficult to represent an orbital either as a huge number of dots or as a cloud, so, for convenience, we illustrate the shape of this orbital as a solid sphere, as shown in Figure 8-9a. This sphere is understood to represent a volume of space containing about 90% of the electron density. (We do not envision the electron as moving around on the surface of this sphere.) *A spherical volume of probability (the electron cloud) is known as an  $s$  orbital.*

The energy levels, or orbits, that Bohr described do have meaning in our modern approach but are now known as **shells**. We will refer to the energy levels as shells, which may contain one or more orbitals. The first shell in hydrogen ( $n = 1$ ), which is known as the ground state of hydrogen because it has the lowest energy, contains only the one spherical  $s$  orbital. Normally, that's the state occupied by the hydrogen's single electron.



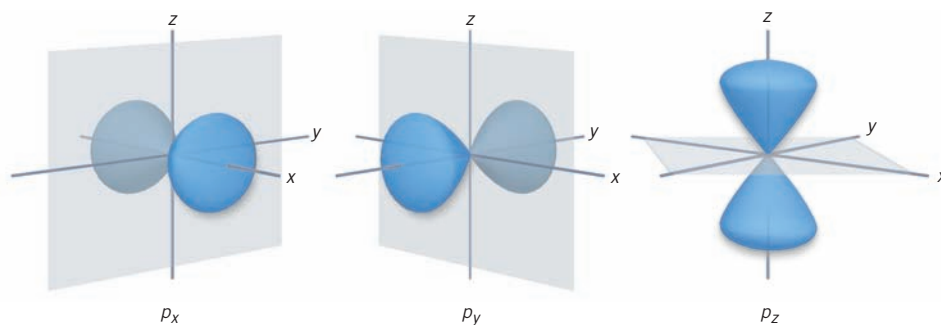
**FIGURE 8-9  $s$  Orbitals** The  $s$  orbitals are represented as spheres. The  $2s$  orbital (b) extends farther from the nucleus than the  $1s$  orbital (a).



### 8-2.3 The Second Shell and $p$ Orbitals

Now let's look at the first excited state of hydrogen, which is the second shell (i.e.,  $n = 2$ ). The second shell is normally unoccupied, just like vacant rooms on the second floor of a home. We find in this shell that there are two kinds of orbitals. First, there is a spherical orbital (an  $s$  orbital) much like the one in the first level except that its maximum electron density (probability) is farther from the nucleus than the  $s$  orbital in the first shell. In other words, it is a bigger shell. (See Figure 8-9b.)

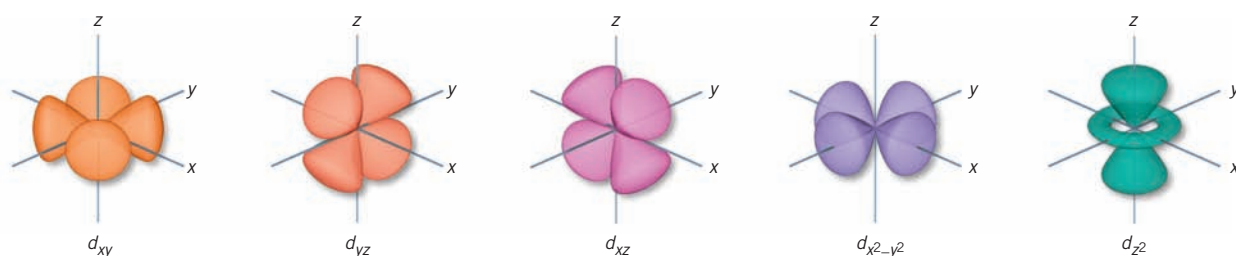
The second kind of orbital present in the second shell is known as a  **$p$  orbital** and has two regions of high probability, called lobes, on either side of the nucleus. The electron distribution in a  $p$  orbital is not spherical but is shaped much like a weird baseball bat with two fat ends. The difference between an  $s$  and a  $p$  orbital is analogous to dorm rooms that have different dimensions or shapes. The first-floor rooms may be perfectly square, but the second-floor rooms may be rectangular. In fact, there are three distinct  $p$  orbitals lying at  $90^\circ$  angles to each other. In a three-coordinate graph, if we define  $x$  as the axis along which the two lobes of a  $p$  orbital are directed, we can designate that  $p$  orbital as the  $p_x$  orbital. The other two  $p$  orbitals are each at  $90^\circ$  angles to the  $p_x$  orbital and each other. They are referred to as the  $p_y$  and the  $p_z$  orbitals. The surfaces that represent about 90% of the electron density of the  $p$  orbitals are shown in Figure 8-10. Again, we do not visualize the electron as a particle moving about the surface of this orbital representation. Instead, for this purpose, it is more useful to picture electrons as clouds occupying a region of space. The second shell has four regions of space that may contain electrons—one  $s$  orbital and three  $p$  orbitals. *The orbitals of the same type in each shell make up what is referred to as a subshell.* A subshell is labeled with a number corresponding to the shell (1, 2, 3, etc.) and the type of orbital that makes up that subshell ( $s$ ,  $p$ , etc.). Thus, the first shell has only a single  $s$  subshell, which is called the 1s. The second shell contains an  $s$  subshell (the 2s) and a  $p$  subshell (the 2p), which is made up of three individual  $p$  orbitals.



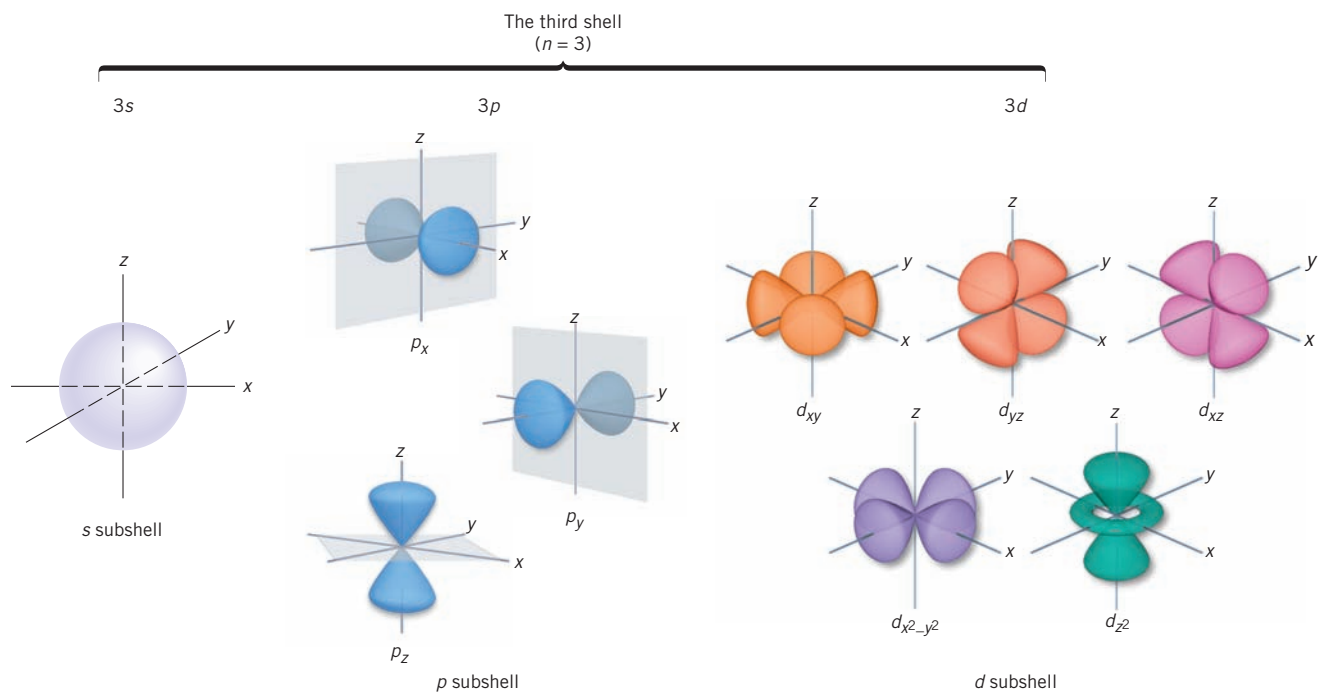
**FIGURE 8-10**  $p$  Orbitals Each  $p$  orbital has two lobes.

### 8-2.4 Outer Shells with $d$ and $f$ Orbitals

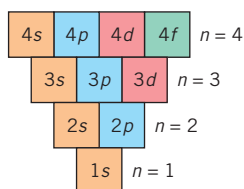
Now let's continue outward in the hydrogen atom and consider the third shell (i.e.,  $n = 3$ ). Each successive shell is larger and has one additional type of orbital. Thus, the third shell has three types of orbitals, or three subshells. Like the first two, it has a spherical 3s orbital and like the second level it has three different 3p orbitals. The third type of orbital found in the third shell is known as a  **$d$  orbital**. There are five  $d$  orbitals, and their shape is more complex. Most of them have four lobes, as illustrated in Figure 8-11. Three of these  $d$  orbitals have significant electron density between



**FIGURE 8-11**  $d$  Orbitals Except for the  $d_{z^2}$ , the  $d$  orbitals have four lobes.



**FIGURE 8-12 The Third Shell** There are three subshells containing a total of nine orbitals in the third shell.



**FIGURE 8-13 Subshells** Each successive shell has one additional subshell.

the axes ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ) and two have significant density along the axes ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ). The third shell with its three subshells and nine orbitals is summarized in Figure 8-12.

The fourth shell ( $n = 4$ ) has all of the same types of orbitals as the third shell (i.e., one 4s, three 4p, and five 4d orbitals) and one additional type known as an **f orbital**. The shapes of the seven 4f orbitals are even more complex than the d orbitals. They are of little consequence to us, since electrons occupying these orbitals are rarely involved in bonding, as we will see in the next chapter. The subshells present in the

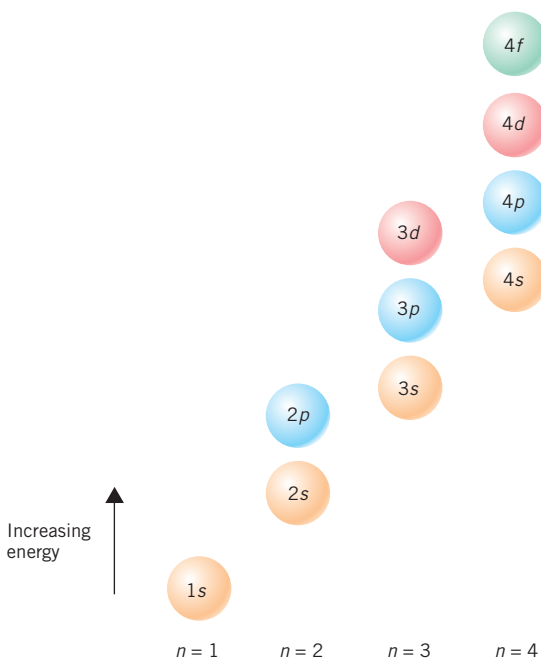
first four shells are shown in Figure 8-13. Just as successive shells have higher energy, successive subshells also have higher energy. (All the orbitals in a specific subshell have the same energy.) In atoms with more than one electron, the energy of the subshells *within a shell* is not the same and increases in the order

$$s < p < d < f$$

increasing energy

We can now adjust our representation of the shells and subshells to account for the difference in energy of the subshells within a shell. In Figure 8-14 we show the first four shells with their subshells in order of increasing energy. Notice that the 4s energy level appears to be lower in energy than the 3d. This is not a mistake, and we will refer back to this situation in the next section.

The capacity of electrons in a subshell is determined by the number of orbitals in that particular subshell. *Each orbital can hold two electrons.* Thus, the capacity of an s subshell is 2, a p subshell is 6 (two electrons in each of three orbitals), a d subshell is 10, and an f subshell is 14. This information is summarized in Table 8-1. The total electron capacity of a shell, including all the orbitals in all the subshells, works out to be conveniently equal to  $2n^2$ . Thus, the first shell ( $n = 1$ ) holds 2 electrons, the second shell ( $n = 2$ ) holds 8, the third shell holds 18, and so on.

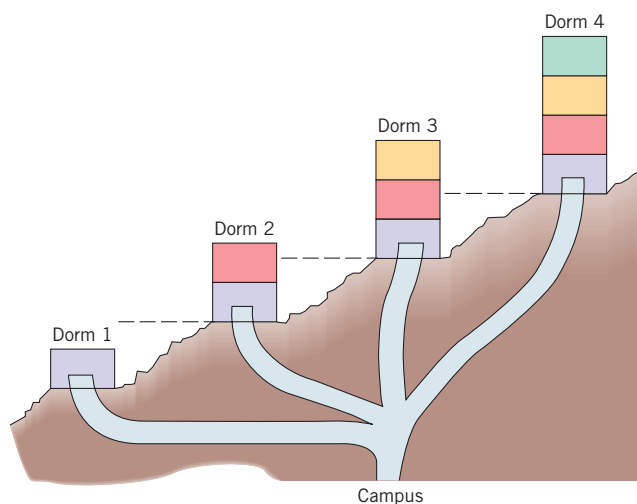


**FIGURE 8-14 Energy of the Subshells** The subshells within a shell have different energies.

**TABLE 8-1** Shells and Subshells

|                   |   |     |        |           |
|-------------------|---|-----|--------|-----------|
| Shell             | 1 | 2   | 3      | 4         |
| Subshell          | s | s p | s p d  | s p d f   |
| Subshell capacity | 2 | 2 6 | 2 6 10 | 2 6 10 14 |
| Shell capacity    | 2 | 8   | 18     | 32        |

Consider an analogy to shells and subshells. An orbital is analogous to a dorm room, which is a region of space with the highest probability of finding a particular student. That is, the student spends more time there than in any other single place. Assume that a dormitory is analogous to a shell and the floors within that dorm as analogous to subshells. We will assume that there are four dorms, with each dorm located farther and farther up a hill. The dorm lowest on the hill is the lowest in energy, since it is the easiest to reach. In Figure 8-15 the dorms are labeled 1 through 4. As we go to higher-energy dorms up the hill, they become larger, with each having one additional floor. (Recall that each successive shell has one additional subshell.) Just as the dorms are at different energy levels, so are the floors within a dorm. (In real-world dorms, students are quite aware of the difference in energy of the floors, since the elevator is often out of order or wedged open somewhere.) Obviously, the lower the floor in a specific dorm, the lower the energy. In summary, individual dorms are analogous to specific shells that represent different energy levels and distances from the nucleus in an atom. Floors within a dorm are analogous to subshells that represent different energy levels *within* the shell. Rooms on a floor are analogous to orbitals. All rooms on the same floor have the same energy, as do all orbitals in the same subshell in an atom. We'll continue with this analogy later when we include electrons in our model.



**FIGURE 8-15** Floors within a Dorm The floors represent different subdivisions of energy within each dorm, analogous to the subshells within each shell.

**EXERCISE 8-2(a) KNOWLEDGE:** Fill in the blanks.

Wave mechanics tell us that the electron exists in a region of space known as an \_\_\_\_\_. The four types of these regions are labeled \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_. The lowest in energy of these four has a \_\_\_\_\_ shape. A principal energy level, called a \_\_\_\_\_, can be subdivided into \_\_\_\_\_. Such a subdivision contains all of the same type of \_\_\_\_\_ in that particular energy level.

**EXERCISE 8-2(b) KNOWLEDGE:** Evaluate the  $n = 3$  shell.

- What is its capacity (how many electrons can be held)?
- What subshells are present?
- What are the capacities of each subshell?
- How many orbitals are present in each subshell?

**ASSESSING THE  
OBJECTIVES FOR  
SECTION 8-2**

**EXERCISE 8-2(c) SYNTHESIS:** Based on the descriptions of the other types of orbitals, how many lobes would you predict an *f* type orbital to have? How might you then symmetrically arrange that?

**EXERCISE 8-2(d) SYNTHESIS:** Use the patterns established in this section to answer these questions about the fifth shell of an atom.

- How many subshells should it have?
- How many orbitals are there in the *g* subshell (the one after *f*)?
- How many electrons should the *g* subshell hold?
- What is the total electron capacity of the fifth shell?

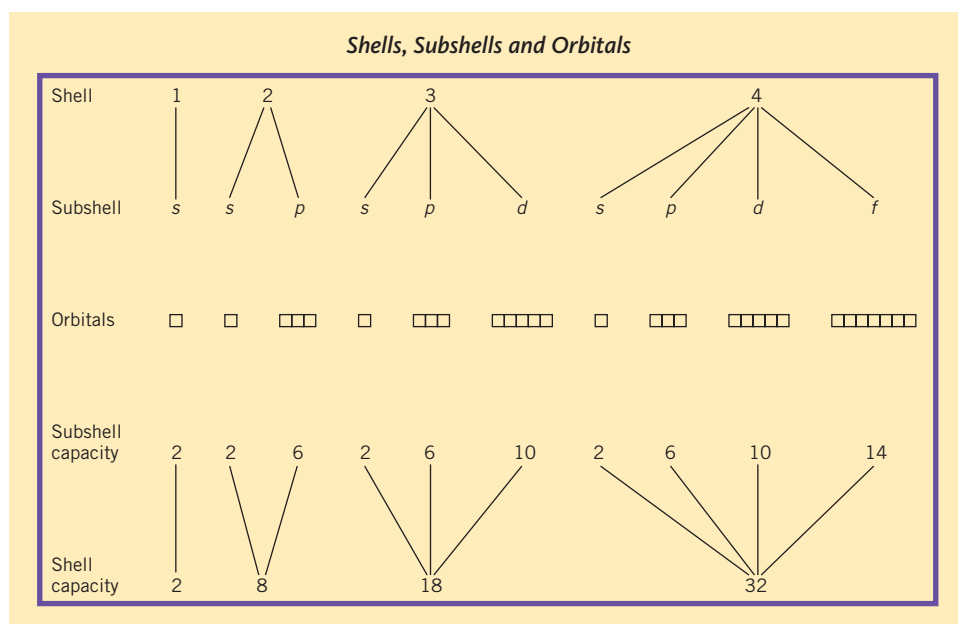
For additional practice, work chapter problems 8-6, 8-12, 8-13, and 8-15.

## PART A SUMMARY

### KEY TERMS

- 8-1.1** The energy of **electromagnetic radiation** is proportional to its **wavelength**. p. 222
- 8-1.2** The **continuous spectrum** in the visible region contains all colors of the rainbow. p. 222
- 8-1.3** Hot, gaseous elements give off a **discrete** or **line spectrum**. p. 224
- 8-1.4** The **Bohr model** of the hydrogen atom describes the location of the electron in discrete **energy levels**. p. 225
- 8-1.5** In the Bohr model, the energy of the electron is **quantized** and indicated by a **principal quantum number**. p. 225
- 8-1.6** The electron in the hydrogen atom is either in the **ground state** or higher **excited states**. p. 226
- 8-2.1** In **wave mechanics** the energy of the electron is described in terms of probability. p. 228
- 8-2.2** The electron in an atom exists in a region of space called an **orbital**. The first **shell** contains only a single **s orbital**. p. 228
- 8-2.3** The second shell also contains three **p orbitals**, which constitute a **subshell**. p. 229
- 8-2.4** The third shell also contains a **d orbital** and the fourth shell also contains an **f orbital**. pp. 229–230

### SUMMARY CHART



## PART B THE PERIODIC TABLE AND ELECTRON CONFIGURATION

### SETTING A GOAL

- You will have a detailed understanding of the structure of electrons in atoms and how this affects that element's properties.

### OBJECTIVES

- 8-3** Using the periodic table, write the outer electron configuration of the atoms of a specific element.
- 8-4** Using orbital diagrams, determine the distribution of electrons in an atom.
- 8-5** Using the periodic table, predict trends in atomic and ionic radii, ionization energy, and electron affinity.

## 8-3 ELECTRON CONFIGURATIONS OF THE ELEMENTS

### ▶ OBJECTIVE FOR SECTION 8-3

Using the periodic table, write the outer electron configuration of the atoms of a specific element.



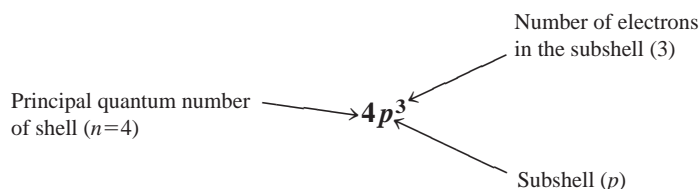
**LOOKING AHEAD!** Fortunately, all the elements have the same types of orbitals as the hydrogen atom. The assignment of electrons to specific shells and subshells makes the basis of the periodic table apparent. Once this is accepted, the periodic table is all that is needed to establish the electron configuration of any element. ■

### 8-3.1 The Aufbau Principle and Electron Configuration

In our analogy to the dorm, an orbital is analogous to a room on a floor. A floor may have only one room analogous to an  $s$  subshell or be composed of several rooms (analogous to  $p$ ,  $d$ , or  $f$  subshells). Assigning electrons to orbitals in an atom is much like assigning students to rooms in a dormitory. Students will occupy the available rooms on the floors that require the least energy to get to. *In the case of atoms, electrons occupy the available orbitals in the subshells of lowest energy.* This is known as the **Aufbau principle** (from the German for “building up”). *The assignment of all the electrons in an atom into specific shells and subshells is known as the element's electron configuration.* In this section, we will consider only the electron's shell and subshell designations. In the next section, we will also consider the orbital assignment. In the dorm analogy, it is like considering only the dorm and floor assignment but not the specific room on a floor.

### 8-3.2 Assignment of Electrons into Shells and Subshells

A shell is designated by the principal quantum number ( $n$ ) and the subshell by the appropriate letter. The number of electrons in that subshell can be displayed with an appropriate superscript number. For example, the existence of three electrons in the  $p$  subshell of the fourth shell ( $n = 4$ ) is shown as follows:



Applying the Aufbau principle, we begin with the ground state of the one electron in the simplest and first element, hydrogen. The electron is in the  $n = 1$  shell, which has an  $s$  subshell. The electron configuration for H is





The next element, helium, has two electrons. The  $1s$  subshell has a capacity of two electrons, so He has the configuration

$$1s^2$$

Next comes Li, with three electrons. The first two electrons fill the first shell, but the third must be in the second shell ( $n = 2$ ). The second shell has two subshells, the  $s$  and the  $p$ , but the  $s$  is lower in energy, so it fills first. The next element is Be. Its four electrons must also be in the  $1s$  and  $2s$  subshells. The electron configurations of Li and Be are

$$\text{Li: } 1s^2 2s^1 \quad \text{Be: } 1s^2 2s^2$$

The next element is B. Four of its five electrons have the same configuration as Be, but the fifth electron begins the filling of the next subshell, the  $2p$ . The next five elements, C through Ne, complete the filling of the  $2p$  subshell.

$$\begin{array}{lll} \text{B: } 1s^2 2s^2 2p^1 & \text{N: } 1s^2 2s^2 2p^3 & \text{F: } 1s^2 2s^2 2p^5 \\ \text{C: } 1s^2 2s^2 2p^2 & \text{O: } 1s^2 2s^2 2p^4 & \text{Ne: } 1s^2 2s^2 2p^6 \end{array}$$

With the element neon, all the orbitals in the second shell are full. We now continue with the element sodium, which has 11 electrons. The first 10 electrons fill the first and second shells as before, so the 11th electron is assigned to the third shell. The third shell has three subshells, the  $3s$ ,  $3p$ , and  $3d$ . The lowest in energy is the  $3s$  subshell, so the 11th electron is in the  $3s$  subshell. At this point, it becomes somewhat tedious to write all of the filled subshells. A shorthand method of writing configurations is to represent all the filled subshells of a noble gas by the symbol of that noble gas in brackets (e.g., [Ne]). Thus, in the following electron configurations, we will assume

$$[\text{Ne}] = 1s^2 2s^2 2p^6$$

We chose a noble gas to use in our shorthand notation for a good reason. As we will see in the next chapter, electrons in noble gas cores are particularly stable and not involved in bonding, so we can treat them as a group. It is like a closed club of 10 people where no one drops out and no new members are accepted. Using the [Ne] core symbolism, the electron configurations of the next eight elements after neon are shown as follows.

$$\begin{array}{ll} \text{Na: } [\text{Ne}]3s^1 & \text{P: } [\text{Ne}]3s^2 3p^3 \\ \text{Mg: } [\text{Ne}]3s^2 & \text{S: } [\text{Ne}]3s^2 3p^4 \\ \text{Al: } [\text{Ne}]3s^2 3p^1 & \text{Cl: } [\text{Ne}]3s^2 3p^5 \\ \text{Si: } [\text{Ne}]3s^2 3p^2 & \text{Ar: } [\text{Ne}]3s^2 3p^6 \end{array}$$

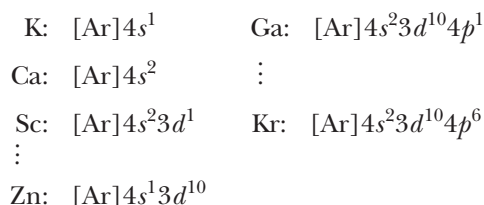
At this point, it helps to pay close attention to the location of elements in the periodic table. Notice that the electron configuration of Li is similar to that of Na (i.e.,  $[\text{He}]2s^1$  and  $[\text{Ne}]3s^1$ ), Be to Mg, B to Al, and so forth. Notice also that these pairs of elements are in the same groups in the periodic table. This is very significant. In fact, we can make a general statement for this observation. *The electron configuration of the elements is a periodic property.* Elements in the same group have the same outer subshell electron configurations but in different shells. As we will see in the next chapter, these similar electron configurations are a major reason that the elements in a group have similar chemical properties. The existence of subshells composed of orbitals is a result of our understanding of wave mechanics. By placing electrons in these subshells, we have actually developed the theoretical basis for the periodic table. Now, however, we will continue with the electron configurations of elements beyond argon. Again, we will use the noble gas core shorthand with [Ar] representing the 18 electrons in the orbitals of argon.

The next element after Ar presents a question. The third subshell in the third shell ( $3d$ ) is still empty and available, so at first we may be inclined to assign the 19th electron in K to the  $3d$  subshell. However, now refer to the periodic table on the

inside back cover. Notice that both Li and Na have an  $s^1$  configuration and K is right under Na. The location of K (under Na) indicates that it should have its outermost electron in the  $4s$  subshell. This is indeed the case. Using noble gas shorthand notation, the configuration of K is



To understand how the  $4s$  fills before the  $3d$ , let's return to the analogy of the dorms, as shown in Figure 8-15. Although dorm 4 as a whole is at a higher level than dorm 3, note that not all floors in dorm 3 are lower than those in dorm 4. In fact, it is easier to proceed farther up the hill to occupy the lowest floor in dorm 4 than to go all the way up to the third floor in dorm 3. In the case of the assignment of the electrons in atoms, a similar phenomenon is true. As shown in Figure 8-14, the  $4s$  subshell is lower in energy than the  $3d$  subshell; thus the  $4s$  fills first. After two electrons are assigned to the  $4s$ , the  $3d$  begins filling with the element Sc. The next nine elements after Sc also involve the filling of the  $3d$  subshell. After the  $3d$  is filled at Zn, the next higher energy subshell is the  $4p$ . This subshell is completely filled at the next noble gas, Kr.



### 8-3.3 Exceptions to the Normal Order of Filling

The electron configurations of many elements are not always exactly as we would predict by following the usual order of filling. For example, there are two notable exceptions among the transition elements when the  $d$  subshells are filling. The actual electron configurations of chromium (#24) and copper (#29) are



If the normal order had been followed, we would predict the configuration of Cr to be  $[\text{Ar}]4s^23d^4$  and Cu to be  $[\text{Ar}]4s^23d^9$ . These exceptions are explained on the basis of a particular stability for a half-filled and a completely filled subshell (the  $3d$ ).

There are many other exceptions, especially where  $d$  and  $f$  subshells are concerned. *We should be aware that such exceptions exist, but it is not important or necessary to know them all.*

### 8-3.4 Using the Periodic Table to Determine Electron Configuration

In Chapter 4, we first presented the periodic table as a valuable tool in locating periods and groups, gases and solids, nonmetals and metals. We have now developed the theoretical basis of the periodic table with the concept of electron configuration. It is appropriate, then, that we use the periodic table itself as a guide to the electron configuration of an element. If we superimpose electron configurations onto the periodic table, the periodic relationship becomes apparent. In Figure 8-16, we show the periodic table with the subshell configuration common to a group at the top of each vertical column. The specific subshell representation is shown within each period. The electron configurations of the subshell that is in the process of filling are shown in more detail for the fourth period from K to Ar. With some practice using a periodic table along with Figure 8-16, we can predict the expected outer electron configuration of any element.

**FIGURE 8-16** Electron Configuration and the Periodic Table The electron configuration of an element can be determined from its position in the periodic table. The value of  $n$  shown in each box is the shell of the outermost subshell.

| IA<br>$s^1$    |                 | IIA<br>$s^2$    |                 | VIII<br>$d^6$ $d^7$ $d^8$ |                      |                 |                 |                 |                 |                         |                    |                 |                 | IIIA<br>$p^1$   | IVA<br>$p^2$    | VA<br>$p^3$     | VIA<br>$p^4$    | VIIA<br>$p^5$ | VIIIA<br>$p^6$ |  |
|----------------|-----------------|-----------------|-----------------|---------------------------|----------------------|-----------------|-----------------|-----------------|-----------------|-------------------------|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------------|----------------|--|
| 1s             |                 |                 |                 |                           |                      |                 |                 |                 |                 |                         |                    |                 |                 |                 |                 |                 |                 |               |                |  |
| 2s             | 2s              |                 |                 |                           |                      |                 |                 |                 |                 |                         |                    |                 |                 |                 |                 |                 |                 |               |                |  |
| 3s             | 3s              | III B<br>$d^1$  | IV B<br>$d^2$   | V B<br>$d^3$              | VI B<br>$d^5$        | VII B<br>$d^5$  | VIII B<br>$d^6$ | VIII B<br>$d^7$ | VIII B<br>$d^8$ | IB<br>$d^{10}$          | II B<br>$d^{10}$   | III A<br>$p^1$  | IV A<br>$p^2$   | V A<br>$p^3$    | VI A<br>$p^4$   | VII A<br>$p^5$  | VIII A<br>$p^6$ |               |                |  |
| 19 K<br>$4s^1$ | 20 Ca<br>$4s^2$ | 21 Sc<br>$3d^1$ | 22 Ti<br>$3d^2$ | 23 V<br>$3d^3$            | 24 Cr<br>$4s^1 3d^5$ | 25 Mn<br>$3d^5$ | 26 Fe<br>$3d^6$ | 27 Co<br>$3d^7$ | 28 Ni<br>$3d^8$ | 29 Cu<br>$4s^1 3d^{10}$ | 30 Zn<br>$3d^{10}$ | 31 Ga<br>$4p^1$ | 32 Ge<br>$4p^2$ | 33 As<br>$4p^3$ | 34 Se<br>$4p^4$ | 35 Br<br>$4p^5$ | 36 Kr<br>$4p^6$ |               |                |  |
| 5s             | 5s              | 4d              | 4d              | 4d                        | 4d                   | 4d              | 4d              | 4d              | 4d              | 4d                      | 4d                 | 5p              | 5p              | 5p              | 5p              | 5p              | 5p              |               |                |  |
| 6s             | 6s              | 5d              | 5d              | 5d                        | 5d                   | 5d              | 5d              | 5d              | 5d              | 5d                      | 5d                 | 6p              | 6p              | 6p              | 6p              | 6p              | 6p              |               |                |  |
| 7s             | 7s              | 6d              | 6d              | 6d                        | 6d                   | 6d              | 6d              | 6d              | 6d              | 6d                      | 6d                 |                 |                 |                 |                 |                 |                 |               |                |  |
|                |                 |                 |                 |                           |                      |                 |                 |                 |                 |                         |                    |                 |                 |                 |                 |                 |                 |               |                |  |
|                |                 |                 |                 |                           |                      |                 |                 |                 |                 |                         |                    |                 |                 |                 |                 |                 |                 |               |                |  |
|                |                 |                 |                 |                           |                      |                 |                 |                 |                 |                         |                    |                 |                 |                 |                 |                 |                 |               |                |  |

\* These groups have  $s^1$  configuration rather than  $s^2$ .

### 8-3.5 Electron Configurations of Specific Groups

As we will see in the next chapter, the electrons beyond the previous noble gas core are the ones commonly involved in the formation of chemical bonds. It will be these electrons that we will be mostly concerned with. To focus on these outer electrons, we use the noble gas shorthand in expressing electron configurations. In the following discussion, we designate a general noble gas configuration as [NG] and a general shell as  $n$ . For example, [NG] $ns^1$  means a noble gas configuration followed by one electron in the  $n$  shell and the  $s$  subshell.

#### Representative Elements: [NG] $ns^xnp^y$

These are the elements shown in blue in Figure 8-16. Four of the groups within this category have family names. The general electron configurations of each group are as follows.

**IA: [NG] $ns^1$**  Except for hydrogen, these are the *alkali metals*. All have one electron beyond a noble gas configuration. Notice that the numbering for the  $s$  subshell begins at 1 for hydrogen and is consecutive down the table.

**IIA: [NG] $ns^2$**  These are the *alkaline earth metals*. All have two electrons beyond a noble gas. The numbering begins at 2 in this column with Be. He ( $1s^2$ ) is located to the far right with the noble gases.

**IIIA: [NG] $ns^2np^1$**  Notice that boron (B) is the first element with an electron in a  $p$  subshell. The numbering of the  $p$  subshells begins with 2  $p$  at B and continues consecutively down the table. The elements Ga (#31) and In (#49), as well as all of those to the right of these elements, also have filled  $d$  subshells beyond the previous noble gas. Tl (#81) and the elements directly to the right of Tl also have filled  $4f$  subshells as well as a filled  $6d$  subshell beyond the noble gas. The electron configurations of In (#49) and Tl (#81) are shown below. So as to emphasize the outermost shell, the filled inner subshells are sometimes listed first in order of  $n$ , the shell number.



**IVA: [NG] $ns^2np^2$**

**VA: [NG] $ns^2np^3$**

**VIA: [NG] $ns^2np^4$**  These elements are sometimes referred to as the *chalcogens*, but this title is rarely used anymore. They are all nonmetals except for Po.

**VIIA: [NG] $ns^2np^5$**  These elements are known as the *halogens*. The halogens are all nonmetals and one electron short of having a noble gas configuration.

**VIIIA Noble Gases: [NG]ns<sup>2</sup>np<sup>6</sup>**

This category of elements (VIIIA) is shown in green in Figure 8-16. These elements are so named because they rarely form chemical bonds. They are characterized by filled outer *s* and *p* subshells. He has only 1s<sup>2</sup>.

**Transition Metals: [NG]ns<sup>2</sup>(n - 1)d<sup>x</sup>**

These 40 elements are shown in yellow in Figure 8-16. The element scandium (#21) is the first element with an electron in a *d* subshell. *The numbering for the d subshell begins at 3.* Thus Sc has a 4s<sup>2</sup>3d<sup>1</sup> configuration, and the next element in Group IIIB has a 5s<sup>2</sup>4d<sup>1</sup> configuration, and so forth down the group. As mentioned previously, there are many exceptions to the expected order of filling in the transition metals, but two important examples involve the VIB and IB elements. For example, Ag (#47) has the configuration [Kr] 5s<sup>1</sup>4d<sup>10</sup>. The 6*d* series of elements are not naturally occurring but have been synthesized in various laboratories. In most cases, only a few atoms of each element have been produced. Still, there is enough evidence to indicate that these elements belong in their appropriate positions in the periodic table.

**Inner Transition Metals: [NG]ns<sup>2</sup>(n - 1)d<sup>1</sup>(n - 2)f<sup>x</sup>**

These elements are shown in orange in Figure 8-16. The orange bar in the transition metals indicates where they would fit in if the periodic table were extended fully to include these elements. *These elements involve the filling of the f subshell, which begins with shell 4.* There are two series of these elements: the *lanthanides*, which have the general configuration [Xe]6s<sup>2</sup>5d<sup>1</sup>4f<sup>x</sup>, and the *actinides*, which have the configuration [Rn]7s<sup>2</sup>6d<sup>1</sup>5f<sup>x</sup>.

The filling of the *f* orbitals is somewhat unusual and needs elaboration. Notice in Figure 8-3 that the 57th electron of La and the 89th electron of Ac go into the 5*d* and 6*d* subshells, respectively, rather than the 4*f* and 5*f*. Their correct configurations are



Thus, these two elements are shown in the periodic table in Group IIIB under Sc and Y, which also have one electron in a *d* subshell. Notice that the next two elements after La and Ac are shown as inner transition elements, however, which are characterized by the filling of the 4*f* and 5*f* subshells, respectively. These two electron configurations can be written as



In fact, the configurations of these elements may not be exactly as shown here because the outer *d* and *f* subshells are very close in energies. This leads to various deviations from an orderly filling of the *f* subshells. In any case, the elements Lu and Lr complete the filling of the 4*f* and 5*f* subshells. The next elements after these, Hf and Rf, return to the 5*d* and 6*d* subshells, respectively. If we use the periodic table to determine electron configuration and follow the atomic numbers faithfully, we don't have to remember the exceptions relating to *d* versus *f* orbitals.

**EXAMPLE 8-1****Writing a Complete Electron Configuration**

Write the complete electron configuration of iron.

**PROCEDURE**

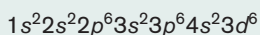
Use the periodic table as a reference. Note the atomic number of iron and build up to there. Start at the beginning of the table and write the subshells in the order of filling plus a running summation of the total number of electrons involved with respect to iron.

**SOLUTION**

From the table inside the front cover, we find that iron has an atomic number of 26, which means that the neutral atom has 26 electrons.

| SUBSHELL | NUMBER OF ELECTRONS IN SUBSHELL | TOTAL NUMBER OF ELECTRONS |
|----------|---------------------------------|---------------------------|
| 1s       | 2                               | 2                         |
| 2s       | 2                               | 4                         |
| 2p       | 6                               | 10                        |
| 3s       | 2                               | 12                        |
| 3p       | 6                               | 18 [Ar]                   |
| 4s       | 2                               | 20                        |
| 3d       | 6                               | 26                        |

Iron has 6 electrons past the filled 4s subshell, but they do not completely fill the 3d subshell, which could accommodate 10 electrons. The complete electron configuration of iron is

**ANALYSIS**

Full electron configurations are tedious and repetitive; they need to be done only by students beginning their study of electron configurations. Once you understand the general principles and patterns behind configurations, noble gas shorthand notations are all that's required to get a complete analysis of the electronic structure of elements. That's because they distinguish between *core* electrons, which are not involved in chemical bonding and are incorporated into the noble gas symbol, and the electrons that are the ones listed beyond the noble gas and have a profound effect on the chemistry of that particular element.

**SYNTHESIS**

Based on this configuration, can we now understand why iron favors formation of +2 and +3 ions? If you had to remove two electrons to make a +2 cation, which two would you remove? Everything up to the 3p is a core electron and so shouldn't be affected. That leaves 2 electrons in the 4s and 6 in the 3d. Removing the two electrons from the 4s gives us a configuration that looks closer to a noble gas than taking only two of the six from the 3d, so that's where these two electrons come from. For the +3 ion, an additional electron needs to be removed, this time from the 3d, leaving 5. This, too, is advantageous, as 5 is half-filled and has some additional stability. Many charges of nonrepresentative elements that were previously a mystery become more understandable when viewed in reference to electron configurations.

**EXAMPLE 8-2****Writing Electron Configurations Using Noble Gas Shorthand**

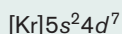
Write the electron configuration for (a) rhodium and (b) bismuth using the noble gas shorthand.

**PROCEDURE**

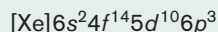
Using the periodic table, locate the noble gas directly preceding the elements in question. Proceed with the configurations as before.

**SOLUTION****(a) Rhodium**

Locate rhodium (#45) in the periodic table on the inside back cover. Now locate Rh in the periodic table shown in Figure 8-16. Rh is the next element below Co, so the highest energy subshell for this element is the 4d. Counting over from the first 4d element (Y), the configuration is 4d<sup>7</sup>. Starting then with the previous noble gas, notice that the 5s fills before the 4d. The configuration becomes

**(b) Bismuth**

The electron configuration of bismuth using the noble gas shorthand that begins with the noble gas xenon (with 54 electrons) is



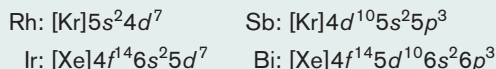


**ANALYSIS**

The completeness of the examples above is provided as an instructional tool. Most students, after a little practice, can turn out accurate electron configurations with only the periodic table and a pencil. List the noble gas preceding the element in question, and begin with the next *s* subshell down the column. What you are then listing are the outermost electrons in an atom.

**SYNTHESIS**

What would the electron configurations of the elements directly below rhodium or directly above bismuth look like? The noble gas core would change, of course. And so would the numbers on the shell designations. They'd advance or lower by 1. But the numbers of electrons in each subshell would be identical for each set, as they would for all other elements in that column. Note the presence of the *4f* subshell below rhodium and its absence above bismuth.



Mendeleev originally organized the periodic table so that elements in the same column had similar chemical properties. We are now beginning to see the structural basis for this consistency in reactivity.

**EXAMPLE 8-3****Identifying an Element on the Table from its Electron Configuration**

What element has the electron configuration  $[\text{Kr}]4d^{10}5s^25p^5$ ?

**PROCEDURE**

Begin with the noble gas and work across the next period of the table until you reach the fifth element of the *p* subshell (column VIIA).

**SOLUTION**

The element after Kr in the  $p^5$  column in Figure 8-16 has atomic number 53, which is iodine.

**ANALYSIS**

This is a good time to draw specific parallels between the periodic table and the electronic structure of atoms. Electrons in atoms are organized into shells, subshells, and orbitals. On the periodic table, the shells translate, roughly, into rows or periods. There are seven rows on the periodic table, and there are seven shells in the ground state of the largest atoms. The regions of the periodic table, then, represent different subshells. The IA and IIA columns represent the *s* subshell. The remaining six columns of representative elements fill the *p* subshell. The ten columns of transition metals represent the ten electrons it takes to fill up a *d* subshell, and the fourteen lanthanides and actinides have their outermost electrons in *f* subshells. The *s* and *p* subshells appear in the row for which they are numbered; the *s* beginning in the first row and the *p* in the second row. Due to the increases in energy, the *d* subshell falls one period and the *f* subshell falls two. Specifically, elements filling the  $3d$  subshell are found in the fourth period and those filling the  $4f$  subshell are in the sixth period.

**SYNTHESIS**

We've already worked our way through the  $4p$  (elements 31 through 36). From there the order continues as we've laid it out above:  $5s$ ,  $4d$ ,  $5p$ ,  $6s$ ,  $4f$ ,  $5d$ ,  $6p$ ,  $7s$ ,  $5f$ ,  $6d$ ,  $7p$ . It would be a worthwhile exercise to open your text to the periodic table inside the back cover and confirm that you can duplicate that series from the beginning of the table ( $1s$ ) right through to the known end ( $7p$ ).

**ASSESSING THE OBJECTIVE FOR SECTION 8-3**

**EXERCISE 8-3(a) KNOWLEDGE:** Fill in the blanks.

The electron configuration  $4d^5$  indicates that there are \_\_\_\_\_ electrons in the \_\_\_\_\_ subshell in the \_\_\_\_\_ shell.

**EXERCISE 8-3(b) ANALYSIS:** Using the periodic table only, give the electron configurations for the elements Zn (#30) and W (#74).

**EXERCISE 8-3(c) ANALYSIS:** Using the periodic table only, give the symbol of the element with the electron configuration  $[\text{Ar}]4s^23d^{10}4p^3$ .

**EXERCISE 8-3(d) SYNTHESIS:** Give the general electron configurations for the elements in Groups VIA and VIB.

**EXERCISE 8-3(e) SYNTHESIS:** Based on electron configurations, what charges would you assign to the monatomic ions formed from the following, and why?

(a) sulfur (b) copper (c) gallium

For additional practice, work chapter problems 8-23, 8-25, 8-30, 8-32, 8-33, 8-34, and 8-35.

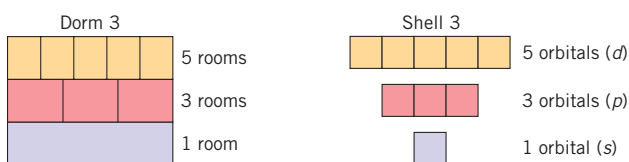
► **OBJECTIVE FOR SECTION 8-4**

Using orbital diagrams, determine the distribution of electrons in an atom.

## 8-4 ORBITAL DIAGRAMS OF THE ELEMENTS (OPTIONAL)



**LOOKING AHEAD!** The number of bonds an atom can be involved in sometimes relates to how many orbitals contain a single electron. In this section, we will take a closer look at how electrons exist within a specific subshell. ■



**FIGURE 8-17 Dorm Rooms and Orbitals** The rooms represent different regions of space on each floor of a dorm, analogous to the orbitals of each subshell.

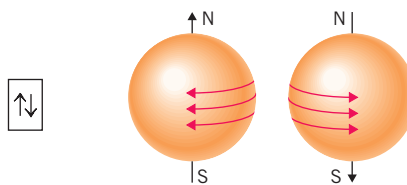
Recall that subshells are composed of one or more orbitals, which are regions of space in which electrons reside. Each orbital can hold a maximum of two electrons.

The orbitals in a subshell are analogous to the rooms on a certain floor. The dorm and the floor within the dorm are analogous to the shell and subshell. (See Figure 8-17.) In the following scheme, we will represent an individual orbital by a box. Therefore, an *s* subshell will have one box, and the three orbitals in a *p* subshell will be represented by three boxes. Likewise, a *d* subshell will be represented by five boxes and an *f* subshell, by seven. Individual electrons will be represented by arrows.

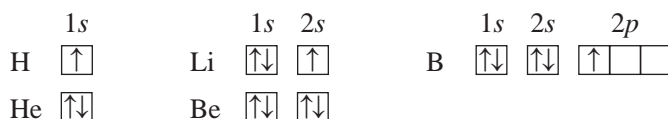
### 8-4.1 The Pauli Exclusion Principle and Orbital Diagrams

As mentioned earlier, an electron has a dual nature. In some respects it has properties of a wave, and in other respects it has properties of a particle. One particle property is that the electron behaves like a charged particle, spinning in either a clockwise or a counterclockwise direction. A spinning charged particle is like a tiny magnet. What if there are two electrons in the same orbital? *The Pauli exclusion principle states that no two electrons in the same orbital can have the same spin.*

We will represent the electrons in orbitals by means of orbital diagrams. *The orbital diagram of an element represents the orbitals in a subshell as boxes and its electrons as arrows. The spin of an electron is indicated by the direction of the arrow, pointing either up or down. Two electrons with opposite spins in the same orbital are said to be paired. Thus, a doubly occupied orbital is represented as follows:*

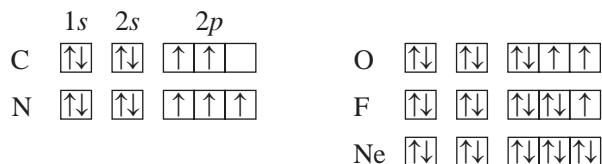


We will now expand on the electron configuration of the first five elements by including their orbital diagrams.



## 8-4.2 Hund's Rule

Before going on, we need to consider the placement of the sixth electron in carbon. There are three possibilities. Does it pair with the first  $2p$  electron in the same orbital or have an opposite spin in a different orbital, or does it go into a different orbital with the same spin? We have one more rule to guide us. **Hund's rule** states that *electrons occupy separate orbitals in the same subshell with parallel (i.e., identical) spins*. At least part of this rule is understandable. Since electrons have the same charge, they will repel each other to different regions of space. Electrons “want their space,” so they prefer separate orbitals rather than pairing in the same orbital. This is analogous to students wanting their own room rather than having to tolerate a roommate. Pairing occurs when separate empty orbitals in the same subshell are not available. With Hund's rule in mind, we can now write the orbital diagrams of the next five elements.



A similar phenomenon occurs with elements that have electrons occupying  $d$  or  $f$  orbitals. For example, Mn (#25) has the following electron configuration and orbital diagram.



Although we will not pursue the topic in this text, orbital diagrams give us important information about the magnetic properties of elements. Orbital diagrams are also relevant to the types of bonds that a particular element forms.

### EXAMPLE 8-4

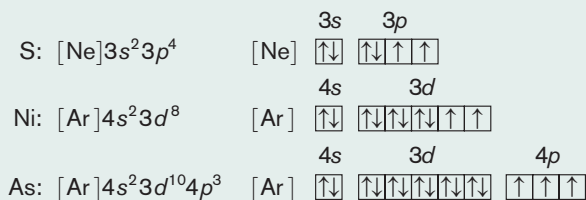
#### Writing Orbital Diagrams

Determine the electron configuration and write the orbital diagram of the electrons beyond the noble gas core for the elements S, Ni, and As.

#### PROCEDURE

Use Figure 8-16 to determine the electron configuration of the element as in Example 8-2. Identify the type of subshells that exist beyond the noble gas core for each element. Draw the number of boxes indicated for each subshell (1 for  $s$ , 3 for  $p$ , 5 for  $d$ , 7 for  $f$ ). Fill up all boxes with paired arrows until the outermost subshell. Apply Hund's rule for the remaining electrons in the outermost shell.

#### SOLUTION



#### ANALYSIS

These orbital diagrams give us an intuitive feel for why filled and half-filled orbitals have an energetic stability associated with them. It's as if we wouldn't want to disturb the nice symmetrical arrangement that nature has provided. Chemical reactivity involves adjustments in electron configurations. More than likely, those electrons will come from subshells that have yet to achieve a stable configuration.

**SYNTHESIS**

We will find out later how bonds are able to form by using electrons in half-filled orbitals. How many bonds would we predict oxygen might form? The orbital diagram for oxygen:



indicates that there is the opportunity for two bonds to form, one to each unpaired electron. How many would you predict for hydrogen? Answer: just one possible bond. We will deal with bond formation in detail in the next chapter.

**ASSESSING THE OBJECTIVE FOR SECTION 8-4**

**EXERCISE 8-4(a) KNOWLEDGE:** What is the name of each of the following rules/principles?

- The spin of the electrons in the same orbital must be paired.
- Electrons go into separate orbitals with parallel spins.
- Fill orbitals starting with the lowest energy orbital first.

**EXERCISE 8-4(b) ANALYSIS:** Show the electron configuration and orbital diagram of all of the electrons beyond the previous noble gas for Nb (#41).

**EXERCISE 8-4(c) SYNTHESIS:** Carbon is known to form four bonds. Bonds form when half-filled orbitals overlap. Draw the orbital diagram for carbon. How will it be possible for carbon to make four bonds?

*For additional practice, work chapter problems 8-60, 8-61, and 8-64.*

**OBJECTIVE FOR SECTION 8-5**

Using the periodic table, predict trends in atomic and ionic radii, ionization energy, and electron affinity.

**8-5 PERIODIC TRENDS**

**LOOKING AHEAD!** Besides electron configuration, there are other characteristics of the atoms of an element that follow trends in the periodic table. These properties relate directly to the chemical properties of elements that we will pursue in the next chapter. The first characteristic that we will consider in this section is the size of neutral atoms. ■

We have seen that electron configurations correspond to the position of an element in the periodic table. But there is much more. The number and types of chemical bonds that an element forms are perhaps the most fundamental properties that the periodic table can help us predict and understand. The basis for these trends, however, lies first in the size, or radius, of the atoms of an element and then in other considerations that relate directly to the atomic size.

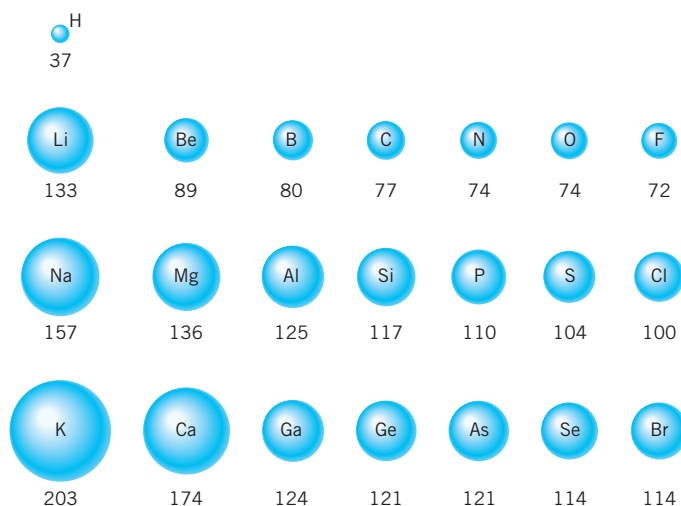
**8-5.1 Atomic Radius**

The **radius** of an atom is the distance from the nucleus to the outermost electrons. It is not an easy task to measure the radius of an atom. There are both experimental and theoretical problems (e.g., electrons are not at a fixed distance from the nucleus). Despite all these difficulties, consistent values for the radii of neutral atoms have been compiled. Some generally accepted values are shown in Figure 8-18 for the first three rows of representative elements. Two units of measurement are most often used for such small distances—the *nanometer* ( $1\text{nm} = 10^{-9}\text{m}$ ) and the *picometer* ( $1\text{pm} = 10^{-12}\text{m}$ ). We will

use picometers because the numbers are easier to express and compare (e.g., 37 pm rather than 0.037 nm).

Notice that there is a general decrease in the radii from left to right across representative element groups and an increase in radii down a group. Not surprisingly, the radii of atoms increase down a group simply because the outermost electron is in a shell farther from the nucleus. On the other hand, it may seem surprising that the radii decrease from Li to F and from Na to Cl, even though the atoms are heavier, since they have more electrons and nucleons as we move to the right. Since electrons are being added to the same outer subshell as we move from Li to F (i.e., the  $2p$ ), one may at first predict that the size of the atoms would not change. However, an additional proton (positive charge) is also being added to each successive nucleus. This increased positive charge increases the attraction between the nucleus and all the negatively charged electrons. As a result, all the outer electrons are drawn in tighter around the nucleus and we observe a decrease in radii of the atoms of successive elements as a subshell is filling.

These same trends are also demonstrated in the transition metals. The radius of Sc (#21), with one  $3d$  electron, is 144 pm, and the radius of Zn (#30), with ten  $3d$  electrons (and nine more protons), is 125 pm.



**FIGURE 8-18 Atomic Radii** Radii of these atoms are given in picometers (pm).

## 8-5.2 Ionization Energy

The energy required to form a cation from an atom is an important periodic property. **ionization energy (I.E.)** is the energy required to remove an electron from a gaseous atom to form a gaseous ion. Since the outermost electron is generally the least firmly attached, it will be the first to go.

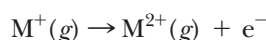


$M(g)$ , a gaseous atom, forms a gaseous cation and an electron.

Because the electrons are held in the atom by electrostatic attractions for the nucleus, it requires energy (an *endothermic* process) to remove an electron. The ionization energy generally increases across a period but decreases down a group. The ionization energies for the second and third periods are shown in Table 8-2. The energy unit is abbreviated kJ/mol, which stands for kilojoules per mole, the energy for a defined quantity of atoms. Notice that the trends in ionization energy follow from the discussion of atomic radius. That is, the smaller the atom, the harder it is to remove an electron. This makes sense according to Coulomb's law. Coulomb's law states that the forces of attraction increase as the charges increase but decrease as the distance between the charges increase. In smaller atoms, the positive protons and negative electrons are closer together and are thus attracted to each other more strongly.

Notice that ionization energy generally decreases to the left and down. It is no coincidence that this is the same direction as increasing metallic properties. *In fact, the most significant chemical property of metals is that they lose electrons relatively easily to form cations in compounds.* However, some metals have considerably higher ionization energies than others. The chemical reactivity of a metal relates to this energy. For example, the ionization energy of sodium is 496 kJ/mol and of gold is 890 kJ/mol. As a result, sodium is a very reactive metal (i.e., it reacts dramatically with water), yet gold is called the *eternal metal* because of its relative unreactivity. Nonmetals also have very high ionization energies and so do not form positive ions in compounds. Instead they form negative ions, as we will discuss next.

The second ionization energy for an ion involves removal of an electron from a +1 ion to form a +2 ion.



**TABLE 8-2**

**Ionization Energy of Some Elements**

| ELEMENT | I.E. (kJ/mol) |
|---------|---------------|
| Li      | 520           |
| Be      | 900           |
| B       | 801           |
| C       | 1086          |
| N       | 1402          |
| O       | 1314          |
| F       | 1681          |
| Na      | 496           |
| Mg      | 738           |
| Al      | 578           |
| Si      | 786           |
| P       | 1102          |
| S       | 1000          |
| Cl      | 1251          |



**TABLE 8-3** Ionization Energies (kJ/mol)

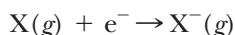
| ELEMENT | FIRST I.E. | SECOND I.E. | THIRD I.E. | FOURTH I.E. |
|---------|------------|-------------|------------|-------------|
| Na      | 496        | 4565        | 6912       | 9,540       |
| Mg      | 738        | 1450        | 7732       | 10,550      |
| Al      | 577        | 1816        | 2744       | 11,580      |

In a similar manner, the third ionization energy forms a +3 ion, and so forth. In all cases it becomes increasingly difficult to remove each succeeding electron. The trends in consecutive ionization energies for Na through Al are shown in Table 8-3.

Note that the second I.E. for Na, the third I.E. for Mg, and the fourth I.E. for Al are all very large compared to the preceding number. For example, it takes 2188 kJ (1450 + 738) to remove the first two electrons from Mg (to form  $\text{Mg}^{2+}$ ) but about three times as much energy to remove the third electron (7732 kJ to form  $\text{Mg}^{3+}$ ). Why is there such a big jump? The answer lies in the electron configuration of magnesium, which is  $[\text{Ne}]3s^2$ . The first two electrons are removed from the outer  $3s$  subshell. To form  $\text{Mg}^{3+}$ , however, the third electron must be removed from the filled inner shell of the neon configuration (the  $2p$ ). Because the second shell is closer to the nucleus than the third shell, this is very difficult and requires a large amount of energy. The same reasoning holds for the second electron from Na and the fourth from Al. We will refer to this observation in the next chapter. For now, it is important to note that a filled shell represents a very stable arrangement. Thus, the magnitude of the positive charge that a representative metal can form is limited by the number of electrons beyond a noble gas configuration.

### 8-5.3 Electron Affinity

Atoms can also gain electrons as well as lose them. *The tendency of a gaseous atom to gain an electron is termed electron affinity (E.A.)* (*affinity* means “an attraction for something”). This process is represented symbolically as



Whereas ionization energy is always an endothermic process, electron affinity can also be exothermic, meaning a favorable process. In this case, energy is released as an electron is added to an orbital of an atom. The electron will enter into an empty orbital according to Hund’s rule in the same manner as the other electrons in the subshell.

The larger negative values (the *higher* electron affinities) are found to the upper right on the periodic table. This is the direction of nonmetallic behavior. This confirms what we already knew—that the representative element nonmetals have a tendency to form anions. They do so because there are one to three vacancies in their outermost  $p$  orbitals. Table 8-4 lists the electron affinities for the second period of the table.

Beryllium and neon show positive electron affinities because they each have a filled subshell ( $2s$  and  $2p$ , respectively), and so they actually have no tendency to add an electron. Nitrogen also has a positive affinity because its  $2p$  subshell is half-filled and somewhat stable. An additional electron would disrupt this. Otherwise, there is a general trend to increase electron affinity from left to right, corresponding to the greater number of protons pulling on the electron and the smaller size of the atom. Electron affinity also decreases going down in the periodic table.

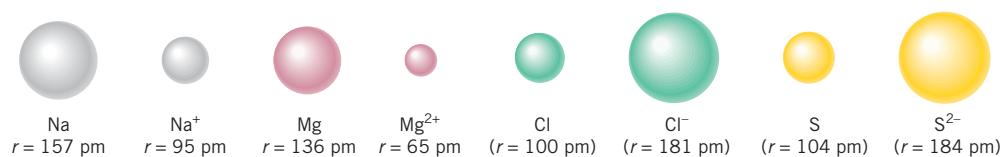
**TABLE 8-4**

### Electron Affinities (kJ/mol)

| ELEMENT | E.A. (kJ/mol) |
|---------|---------------|
| Li      | −60           |
| Be      | >0            |
| B       | −27           |
| C       | −122          |
| N       | >0            |
| O       | −141          |
| F       | −328          |
| Ne      | >0            |

### 8-5.4 Ionic Radii

When an electron is removed from an atom, the resulting cation is smaller than the parent atom. The loss of an electron from an outer subshell results in an increased attraction between the nucleus and the remaining electrons. As a result, the loss of electrons results in a contraction. Also, if the electrons in the outer shell are removed, the remaining inner shells reside closer to the nucleus. If all the electrons in the out-



**FIGURE 8-19 Ionic Radii** A positive ion is always smaller than the original neutral atom. A negative ion is always larger than the original atom.

When the outermost shell are removed, the resulting ion will be considerably smaller, as is the case of the two cations shown in Figure 8-19. Just as a cation is smaller than its parent atom, an anion is larger than its neutral parent atom. When an electron is added to an atom, the added repulsions between the electrons cause the radius of the ion to expand. Just as a metal cation becomes smaller as the positive charge increases, a non-metal anion becomes larger as the negative charge increases.

**ASSESSING THE  
OBJECTIVE FOR  
SECTION 8-5**

**EXERCISE 8-5(a) KNOWLEDGE:** Where on the periodic table (upper/lower, right/left) would you find atoms with the following?

- (a) largest atomic radius                                  (c) largest electron affinity  
(b) smallest ionization energy

**EXERCISE 8-5(b) ANALYSIS:** Given the following four elements: Ga, Ge, In, and Sn.

- (a) Which has the smallest radius?  
(b) Which has the lowest first ionization energy?  
(c) Which is most likely to form a positive ion?

**EXERCISE 8-5(c) ANALYSIS:** Na<sup>+</sup>, Mg<sup>2+</sup>, F<sup>-</sup>, O<sup>2-</sup>, and Ne represent an isoelectronic series (they all have 10 electrons). Rank them from largest to smallest.

**EXERCISE 8-5(d) SYNTHESIS:** Explain why aluminum's first ionization energy is lower than silicon's. Explain why aluminum's first ionization energy is lower than boron's.

**EXERCISE 8-5(e) SYNTHESIS:** Only the first E.A. (adding the first electron to form the  $-1$  anion) of most atoms is exothermic. The second, third, and higher are all endothermic. Why?

*For additional practice, work chapter problems 8-67, 8-70, 8-73, 8-76, 8-77, and 8-81.*

**PART B  
SUMMARY**

**KEY TERMS**

- 8-3.1** **Electron configuration** is determined as a result of the **Aufbau principle**. p. 233  
**8-4.1** **Orbital diagrams** are written with direction from the **Pauli exclusion principle**. p. 240  
**8-4.2** **Hund's rule** determines the spin orientation of electrons in the same subshell. p. 241  
**8-5.1** The **atomic radius** of an element is the distance to the outermost electrons. p. 242  
**8-5.2** **Ionization energy (I.E.)** relates to the relative ease of formation of positive ions. p. 243  
**8-5.3** **Electron affinity (E.A.)** relates to the formation of negative ions. p. 244

**SUMMARY CHART**

| <i>Electron Configuration</i>                                       |   |   |
|---|---|---|
| Aufbau principle  | Pauli exclusion principle   | Hund's rule   |
| ↓   | ↓   | ↓   |
| order of filling  | electron spin in same orbital                                     | electron spin in same subshell  |
| ↓   | ↓   | ↓   |
| i.e., [Ar] 4s <sup>2</sup> 3d <sup>2</sup> not [Ar] 3d <sup>4</sup> | i.e., $\boxed{\uparrow\downarrow}$ not $\boxed{\uparrow\uparrow}$ | i.e., $\boxed{\uparrow}\boxed{\uparrow}$ not $\boxed{\uparrow\downarrow}$ |

## CHAPTER SUMMARY

This chapter starts us on a journey that ultimately leads to an explanation of why and how atoms of elements bond to each other. The periodic basis of chemical bonding lies in the nature of the electrons and the various regions of space within atoms where they exist. Our journey started with a theoretical explanation of the **discrete**, or **line, spectrum of electromagnetic radiation** (light) emitted by hot, gaseous hydrogen atoms. This is quite unlike the **continuous spectrum** seen in a rainbow. The **wavelength** of light is inversely related to its energy. In 1913, Niels Bohr proposed a theory, known as **Bohr's model**, in which the hydrogen electron orbits the nucleus in **quantized energy levels**. He assigned a **principal quantum number** ( $n$ ) to each energy level, in which the first energy level ( $n = 1$ ) is lowest in energy and known as the **ground state**. In hydrogen, the energy levels higher than  $n = 1$  are the **excited states**. Light is emitted from an atom when an electron falls from an excited state to a lower state. The difference in energy between the states becomes the energy of the light wave. If the energy of the light is within the visible part of the spectrum, we see a specific color.

Eventually, Bohr's model had to be adjusted and then mostly discarded as newer, more inclusive theories were advanced. Modern atomic theory, which is known as **wave mechanics**, takes into account the wave nature of the electron. Thus, the electron is viewed as having a certain probability of existing in a region of space known as an **orbital**. There are four different types of orbitals, known as **s**, **p**, **d**, and **f orbitals**. All four have distinctive shapes for the regions of highest probability. The simplest are **s orbitals**, which have a spherical shape. If the principal energy levels are designated as **shells**, then the orbitals of one type within a particular shell make up what is known as a **subshell**. Just as the shells increase in energy from  $n = 1$  on, the subshells within a shell increase in energy in the order **s**, **p**, **d**, and **f**.

Each shell holds  $2n^2$  electrons and has  $n$  different subshells. The electrons in any atom can be assigned to a given shell and subshell. This is known as the element's **electron configuration**. Electrons fill subshells according to the **Aufbau principle**, which simply means that the lowest energy subshells fill first. As we proceed through the electron configurations of the elements, one fact makes itself apparent. Atoms of elements in vertical columns or groups have the same outermost subshell

configuration. The next higher shell is indicated as one goes down the table. Since the periodic table and electron configuration are interrelated, we now put the periodic table to work in writing electron configurations. We see that various groups can be identified by their specific configurations as well as their properties.

By using **orbital diagrams**, we can expand the representation of electron configuration to include assignment of electrons to orbitals. Two other rules are required to do this successfully. The **Pauli exclusion principle** relates to the spin of electrons in the same orbital, and **Hund's rule** relates to the electron distribution in separate orbitals of the same subshell.

The periodic table tells us even more. There are general trends in the **radii** of atoms. In general, atomic radii decrease up and to the right on the table. The radius of an atom is related to the shell of the outermost electrons and to the number of electrons in the outermost subshell. The higher the energy of the shell and the fewer electrons in the outermost subshell, the larger the atom. Thus, atoms to the lower left are the largest atoms.

The opposite trend occurs if we compare the energy required to remove the outermost electron, which is known as the element's **ionization energy (I.E.)**. The same factors that affect the size of an atom affect the ionization energy. That is, in general, larger atoms have lower ionization energies than smaller atoms. Metal atoms tend to have larger atoms than nonmetal atoms, so they have lower ionization energies. How many electrons can be easily removed from a metal is determined by its outer electron configuration.

Opposite to ionization energy is **electron affinity (E.A.)**, the energy released when an electron is added to an atom. The general trend is that smaller atoms will release more energy than larger atoms as an electron is added, meaning that the smaller nonmetals form anions more easily.

Finally, the radius of an ion depends on the position of the element in the periodic table, the sign of the charge, and the magnitude of the charge. Generally, the more positive the ion, the smaller its radius. If we compare species in the same period, a monatomic anion is larger than a neutral atom, which in turn is larger than a monatomic positive ion.

| SECTION | YOU SHOULD BE ABLE TO...   | OBJECTIVES    |                    |  |
|---------|--|---------------|--------------------|--|
|         |  | EXAMPLES      | EXERCISES          | CHAPTER PROBLEMS                               |
| 8-1     | Describe the relationships among the wavelengths of light, energy, and color.  |               | 1a, 1b             | 1  |
|         | Describe the relationship between emission spectra and the electronic structure of the hydrogen atom as explained by Bohr's model. |               | 1c, 1d, 1e         | 3, 4   |
| 8-2     | Differentiate among a shell, a subshell, and an orbital.   |               | 2a, 2b, 2d         | 6, 11, 12, 13, 15, 16, 17                      |
|         | Identify an <i>s</i> , <i>p</i> , or <i>d</i> type orbital from its shape.   |               | 2c, 2d             | 8, 9, 10                                       |
| 8-3     | Using the periodic table, write the outer electron configuration of the atoms of a specific element.                               | 8-1, 8-2, 8-3 | 3a, 3b, 3c, 3d, 3e | 21, 23, 26, 28, 32, 33, 36, 39, 40, 44, 45, 55 |
| 8-4     | Using orbital diagrams, determine the distribution of electrons in an atom.  | 8-4           | 4a, 4b, 4c         | 60, 61, 64, 65, 66                             |
| 8-5     | Using the periodic table, predict trends in atomic and ionic radii, ionization energy, and electron affinity.                      |               | 5a, 5b, 5c, 5d, 5e | 68, 70, 71, 73, 75, 77, 81, 82                 |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**8-1(a)** Long wavelengths of light have low (high/low) frequencies and low (high/low) energies. The color of visible light with the highest energy is violet, and the color of visible light with the longest wavelength is red. White light contains all colors of light, called a continuous spectrum. Light from heated gaseous element sources gives off only discrete energies to form a line spectrum. Niels Bohr suggested that the orbits of an electron were quantized, or set to specific values. The lowest energy state is the ground state, and the higher states are the excited states.

**8-1(b)** (high energy/short wavelength) gamma rays—X-rays—ultraviolet—visible—infrared—microwaves—radio waves (low energy/long wavelength)

**8-1(c)** Electrons absorb energy and jump a quantized distance to an energy level in an excited state. When the electrons return to lower energy states, this excess energy is released at a specific value that shows up as a single wavelength in a line spectrum. Different lines represent transitions between different energy states.

**8-1(d)** It is reasonable to assume that all atoms are fundamentally designed similarly. They differ only in numbers of nucleons and electrons. So the structure found in the hydrogen atom is going to be similar to the structure of larger atoms. Understanding hydrogen allows us to understand these larger atoms as well.

**8-1(e)** We use different elements to make different colors. For example, argon produces a red color.

**8-2(a)** Wave mechanics tell us that the electron exists in a region of space known as an orbital. The four types of these regions are labeled *s*, *p*, *d*, and *f*. The lowest in energy of these four has a spherical shape. A principal energy level, called a shell, can be subdivided into subshell. Such a subdivision contains all of the same type of orbital in that particular energy level.

**8-2(b)** (a) 18 (b) *s*, *p*, and *d* (c) 2, 6, and 10, respectively (d) 1, 3 and 5, respectively

**8-2(c)** The pattern of one lobe for *s*, two for *p*, and four for *d* lets us assume that the *f* orbital has 8 lobes (doubling each time). Eight lobes would be arranged most symmetrically by having them point toward the corners of a cube. The actual *f* orbitals are a small modification of this.

**8-2(d)** (a) 5 (b) 9 (c) 18 (d) 50

## PART B

## EXERCISES

**8-3(a)** The electron configuration  $4d^5$  indicates that there are five electrons in the *d* subshell in the fourth shell.

**8-3(b)** Zn:  $[\text{Ar}] 4s^2 3d^{10}$  W:  $[\text{Xe}] 4f^{14} 6s^2 5d^4$

**8-3(c)** As (arsenic)

**8-3(d)** Group VIA:  $[\text{NG}] ns^2(n-1)d^{10}np^4$ ;  
Groups VIB:  $[\text{NG}] ns^2(n-1)d^5$

**8-3(e)** (a) -2. It takes two more electrons to fill up the  $3p$  subshell. (b) +1. Lose one electron from the  $4s$  subshell. (It also forms a +2 ion that can't be explained by subshell structure.) (c) +3. Remove the electrons from the  $4p$  and the  $4s$  subshell, leaving a filled  $3d$ .

**8-4(a)** (a) Pauli exclusion principle (b) Hund's rule (c) Aufbau principle

**8-4(b)** electron configuration:  $[\text{Kr}] 5s^2 4d^3$   
orbital diagram:



**8-4(c)** Carbon:  $2s \qquad 2p$  If one electron is moved from the  $2s$  to the  $2p$ , that will create four half-filled orbitals.



**8-5(a)** (a) lower left (b) lower left (c) right

**8-5(b)** (a) Ge (b) In (c) In

**8-5(c)**  $O^{2-} > F^- > Ne > Na^+ > Mg^{2+}$

**8-5(d)** Aluminum's first ionization energy is lower than silicon's because aluminum has one fewer proton in the nucleus attracting its outer electron, making that electron

easier to remove. Aluminum's first I.E. is lower than boron's because aluminum has an extra shell that places its outer electrons farther away from its nucleus, reducing the attraction and making it easier to remove.

**8-5(e)** Once an electron is added, the resulting species has a negative charge. This charge repels additional electrons, making them progressively harder to add.

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Atomic Theory and Orbitals (SECTION 8-1)

**8-1.** Ultraviolet light causes sunburns, but visible light does not. Explain.

**8-2.** The  $n = 8$  and  $n = 9$  energy levels are very close in energy. Using the Bohr model, describe how the wavelengths of light compare as an electron falls from these two energy levels to the  $n = 1$  energy level.

**8-3.** The  $n = 3$  energy level is of considerably greater energy than the  $n = 2$  energy level. Using the Bohr model, describe how the wavelengths of light compare as an electron falls from these two energy levels to the  $n = 1$  energy level.

**8-4.** An electron in the lithium atom is in the third energy level. Is the atom in the ground or excited state? Can the atom emit light? If so, how?

**8-5.** Which of the following types of orbitals do not exist?

6s 3p 1p 4d 3f

**8-6.** Which of the following types of orbitals do not exist?

5f 2d 7p 6d 1s

**8-7.** What is meant by the "shape" of an orbital?

**8-8.** Describe the shape of the  $4p$  orbitals.

**8-9.** Describe the shape of the  $3s$  orbital. How does it differ from that of a  $2s$  orbital?

**8-10.** Describe the shape of the  $4d$  orbital. How does it differ from a  $4p$  orbital?

**8-11.** How many total orbitals are in the third energy level?

**8-12.** How many total orbitals are in the fourth energy level?

### Shells and Subshells (SECTION 8-2)

**8-13.** How many orbitals are in the following subshells?

(a)  $3p$  (b)  $4d$  (c)  $6s$

**8-14.** How many orbitals are in the following subshells?

(a)  $5f$  (b)  $6p$  (c)  $2d$

**8-15.** What are the total electron capacities of the  $n = 3$  and the  $n = 2$  shells?

**8-16.** What is the total electron capacity of the fourth shell?

**8-17.** What is the total electron capacity of each subshell in the fourth shell?

**8-18.** What is the total electron capacity of the fifth shell?

**8-19.** The fifth shell (theoretically) contains a fifth subshell designated the  $5g$  subshell. What is the total electron capacity of the  $g$  subshell?

**8-20.** How many orbitals are in the  $5g$  subshell? (See problem 8-19.)

### Electron Configuration (SECTION 8-3)

**8-21.** Which subshell always fills first?

**8-22.** Which subshell fills second and which subshell fills third?

**8-23.** Explain how a subshell in a particular shell can be lower in energy than a subshell in a lower shell.

**8-24.** Which of the following subshells fills first? (Refer to Figure 8-16.)

(a)  $6s$  or  $6p$  (b)  $5d$  or  $5p$  (c)  $4p$  or  $4f$  (d)  $4f$  or  $4d$

**8-25.** Which of the following subshells is lower in energy? (Refer to Figure 8-16.)

(a)  $6s$  or  $5p$  (c)  $5s$  or  $4d$  (e)  $4f$  or  $6d$   
(b)  $6s$  or  $4f$  (d)  $4d$  or  $5p$  (f)  $3d$  or  $4p$

**8-26.** Write the following subshells in order of increasing energy. (Refer to Figure 8-16.)

$4s, 5p, 4p, 5s, 4f, 4d, 6s$

**8-27.** Write the total electron configuration for each of the following elements. (Refer to Figure 8-16.)

(a) Mg (b) Ge (c) Pd (d) Si

**8-28.** Write the total electron configuration for each of the following elements. (Refer to Figure 8-16.)

(a) B (b) Ag (c) Se (d) Sr

**8-29.** Write the electron configuration that is implied by [Ar]. (Refer to Figure 8-16.)

**8-30.** Write the electron configuration that is implied by [Xe]. (Refer to Figure 8-16.)

**8-31.** Using the noble gas shorthand, write the electron configurations for the following elements. (Refer to Figure 8-16.)

(a) S (b) Zn (c) Pu (d) I

**8-32.** Using the noble gas shorthand, write the electron configurations for the following elements. (Refer to Figure 8-16.)

(a) Sn (b) Ni (c) Cl (d) Au

**8-33.** Write the symbol of the first element that has the following.

(a) a  $5p$  electron (c) a  $4f$  electron  
(b) a  $4d$  electron (d) a filled  $3p$  subshell

**8-34.** Write the symbol of the first element that has the following.

(a) a filled  $4d$  subshell (c) a  $6s$  electron  
(b) a half-filled  $4p$  subshell (d) a filled fourth shell

**8-35.** Which subshell begins to fill for each of the following elements?

(a) Al (b) In (c) La (d) Rb

**8-36.** Which subshell begins to fill for each of the following elements?

(a) Y (b) Th (c) Cs (d) Ga



**8-37.** What do Groups IIIA and IIIB have in common? How are they different?

**8-38.** What do the elements Al and Ga have in common? How are they different?

**8-39.** Which elements have the following electron configurations? (Use only the periodic table.)

- (a)  $1s^2 2s^2 2p^5$  (d)  $[\text{Xe}] 6s^2 5d^1 4f^7$   
 (b)  $[\text{Ar}] 4s^2 3d^{10} 4p^1$  (e)  $[\text{Ar}] 4s^1 3d^{10}$  (exception to rules)  
 (c)  $[\text{Xe}] 6s^2$

**8-40.** Which elements have the following electron configurations?

- (a)  $[\text{He}] 2s^2 2p^3$  (d)  $[\text{Rn}] 7s^2 6d^1$   
 (b)  $[\text{Kr}] 5s^2 4d^2$  (e)  $[\text{Xe}] 6s^2 5d^{10} 4f^{14} 6p^1$   
 (c)  $[\text{Ar}] 4s^2 3d^{10} 4p^6$  (f)  $[\text{Ar}] 4s^2 3d^{10}$

**8-41.** If any of the elements in problem 8-39 belong to a numerical group (e.g., Group IA) in the periodic table, indicate the group.

**8-42.** Write the number designation of the two groups that may have five electrons beyond a noble gas configuration.

**8-43.** Write the number designation of a group that has 2 electrons beyond a noble gas configuration. Write the number designation of a group with 12 electrons beyond a noble gas configuration.

**8-44.** Which two configurations belong to the same group in the periodic table?

- (a)  $[\text{Kr}] 5s^2$  (d)  $[\text{Ar}] 4s^2 3d^2$   
 (b)  $[\text{Kr}] 5s^2 4d^{10} 5p^2$  (e)  $[\text{Ne}] 3s^2 3p^2$   
 (c)  $[\text{Xe}] 6s^2 5d^1 4f^2$

**8-45.** Which two configurations belong to the same group in the periodic table?

- (a)  $[\text{Kr}] 5s^2 4d^{10}$  (d)  $[\text{Xe}] 6s^2$   
 (b)  $[\text{Ar}] 4s^1 3d^{10}$  (e)  $[\text{Xe}] 6s^2 4f^{14} 5d^{10}$   
 (c)  $[\text{Ne}] 3s^1$

**8-46.** Which group in the periodic table has the following general electron configuration? ( $n$  is the principal quantum number.)

- (a)  $ns^2 np^2$  (c)  $ns^1(n-1)d^{10}$  (e.g.,  $4s^1 3d^{10}$ )  
 (b)  $ns^2 np^6$  (d)  $ns^2(n-1)d^1(n-2)f^2$  (two elements)

**8-47.** Write the general electron configurations for the following groups.

- (a) IIA (b) IIB (c) VIA (d) IVB

**8-48.** How does He differ from the other elements in Group VIIIA?

**8-49.** Which of the following elements fits the general electron configuration  $ns^2(n-1)d^{10}np^4$ ?

- (a) Cr (b) Te (c) S (d) O (e) Si

**8-50.** What is the electron configuration of the noble gas at the end of the third period?

**8-51.** What is the electron configuration of the noble gas at the end of the fourth period?

**\*8-52.** What would be the atomic number of an element with one electron in the  $5g$  subshell?

**\*8-53.** Element number 114 forms a comparatively long-lived isotope. What would be its electron configuration and in what group would it be?

**\*8-54.** How many elements would be in the seventh period if it were complete?

**\*8-55.** How many elements would be in a complete eighth period? (*Hint:* Consider the  $5g$  subshell.)

**\*8-56.** Classify the following electron configurations into one of the four main categories of elements.

- (a)  $[\text{Ar}] 4s^2 3d^2$  (c)  $[\text{Ar}] 4s^2 3d^{10} 4p^6$   
 (b)  $[\text{Kr}] 5s^2 4d^{10} 5p^5$  (d)  $[\text{Rn}] 7s^2 6d^1 5f^3$

**\*8-57.** Classify the following electron configurations into one of the four main categories of elements.

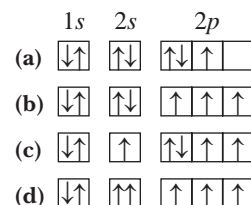
- (a)  $[\text{Ne}] 3s^2 3p^6$  (c)  $[\text{Xe}] 6s^2 4f^{14} 5d^2$   
 (b)  $[\text{Ne}] 3s^2 3p^5$  (d)  $[\text{Xe}] 6s^2 5d^1 4f^7$

**\*8-58.** What would be the atomic number and group of the next nonmetal after element number 112?

**\*8-59.** What is the atomic number of the heaviest metal that would appear in the periodic table after element number 112?

### Orbital Diagrams (SECTION 8-4)

**8-60.** Which of the following orbital diagrams is excluded by the Aufbau principle? Which by the Pauli exclusion principle? Which by Hund's rule? Which is correct? Explain how a principle or rule is violated in the others.



**8-61.** Write the orbital diagrams for electrons beyond the previous noble gas core for the following elements. (Refer to Figure 8-16.)

- (a) S (b) V (c) Br (d) Pm

**8-62.** Write the orbital diagrams for electrons beyond the previous noble gas core for the following elements. (Refer to Figure 8-16.)

- (a) As (b) Ar (c) Tc (d) Tl

**8-63.** How many unpaired electrons are in the atoms of elements in Groups IIB, VB, VIA, and VIIA? An atom with electron configuration given by  $[ns^1(n-1)d^5]$ ; and Pm (atomic number 61)?

**8-64.** The atoms of the elements in three groups in the periodic table have all their electrons paired. What are the groups?

**8-65.** What group or groups have two unpaired  $p$  electrons?

**8-66.** What group or groups have five unpaired  $d$  electrons?

### Periodic Trends (SECTION 8-5)

**8-67.** Which of the following elements has the larger radius?

- (a) As or Se (b) Ru or Rh (c) Sr or Ba (d) F or I

**8-68.** Which of the following elements has the larger radius?

- (a) Tl or Pb (b) Sc or Y (c) Pr or Ce (d) As or P

**8-69.** Four elements have the following radii (in pm): 117, 122, 129, and 134. The elements, in random order, are V, Cr, Nb, and Mo. Which element has a radius of 117 pm? Which has a radius of 134 pm?

**8-70.** Four elements have the following radii: 180 pm, 154 pm, 144 pm, and 141 pm. The elements, in random order, are In, Sn, Tl, and Pb. Which element has a radius of 141 pm? Which has a radius of 180 pm?

**8-71.** Which of the following elements has the higher ionization energy?

- (a) Ti or V            (c) Mg or Sr            (e) B or Br  
(b) P or Cl            (d) Fe or Os

**8-72.** Four elements have the following first ionization energies (in kJ/mol): 762, 709, 579, and 558. The elements, in random order, are Ga, Ge, In, and Sn. Which element has an ionization energy of 558 kJ/mol? Which element has an ionization energy of 762 kJ/mol?

**8-73.** Four elements have the following first ionization energies (in kJ/mol): 869, 941, 1010, and 1140. The elements, in random order, are Se, Br, Te, and I. Which element has an ionization energy of 869 kJ/mol? Which element has an ionization energy of 1140 kJ/mol?

**8-74.** The first four ionization energies for Ga are 578.8, 1979, 2963, and 6200 kJ/mol. How much energy is required to form each of the following ions:  $\text{Ga}^+$ ,  $\text{Ga}^{2+}$ ,  $\text{Ga}^{3+}$ , and  $\text{Ga}^{4+}$ ? Why does the formation of  $\text{Ga}^{4+}$  require a comparatively large amount of energy?

**8-75.** Which of the following monatomic cations is the easiest to form, and which is the hardest to form?

- (a)  $\text{Cs}^+$     (b)  $\text{Rb}^{2+}$     (c)  $\text{Ne}^+$     (d)  $\text{Sc}^{3+}$

**8-76.** Which of the following atoms would most easily form a cation?

- (a) B    (b) Al    (c) Si    (d) C

**8-77.** Which of the following atoms would most likely form an anion?

- (a) Be    (b) Al    (c) Ga    (d) I

**8-78.** Noble gases form neither anions nor cations. Why?

**8-79.** Which of the following would have the highest second ionization energy?

- (a) Rb    (b) Pb    (c) Ba    (d) Al    (e) Be

**8-80.** Which of the following would have the lowest third ionization energy?

- (a) Na    (b) B    (c) Ga    (d) Mg    (e) N

**8-81.** Arrange the following ions and atoms in order of increasing radii.

- (a) Mg                      (c) S                      (e)  $\text{K}^+$   
(b)  $\text{S}^{2-}$                     (d)  $\text{Mg}^{2+}$                 (f)  $\text{Se}^{2-}$

**8-82.** Arrange the following ions and atoms in order of increasing radii.

- (a) Br                      (c) K                      (e)  $\text{Br}^-$   
(b)  $\text{K}^+$                     (d)  $\text{I}^-$                     (f)  $\text{Ca}^{2+}$

**\*8-83.** Zirconium and hafnium are in the same group and have almost the same radius despite the general trend down a group. As a result, the two elements have almost identical chemical and physical properties. The fact that these elements have almost the same radius is due to what is referred to as the *lanthanide contraction*. With the knowledge that atoms get progressively smaller as a subshell is being filled, can you explain this phenomenon? (*Hint:* Follow all the expected trends between the two elements.)

**8-84.** The first five ionization energies for carbon are 1086, 2353, 4620, 6223, and 37,830 kJ/mol. How much energy is required to form the following ions:  $\text{C}^+$ ,  $\text{C}^{2+}$ ,  $\text{C}^{3+}$ ,  $\text{C}^{4+}$ , and

$\text{C}^{5+}$ ? In fact, even  $\text{C}^+$  does not form in compounds. Compare the energy required to form this ion with that needed to form some metal ions. Explain.

## General Problems

**8-85.** Write the symbol of the element that corresponds to the following.

- (a) the first element with a  $p$  electron  
(b) the first element with a filled  $4p$  subshell  
(c) three elements with only one electron in the  $4s$  subshell  
(d) the first element with one  $p$  electron that also has a filled  $d$  subshell  
(e) the element after Xe that has two electrons in a  $d$  subshell

**8-86.** Write the symbol of the element that corresponds to the following.

- (a) the first element with a half-filled  $p$  subshell  
(b) the element with only three electrons in a  $4d$  subshell  
(c) the first two elements with a filled  $3d$  subshell  
(d) the element with only three electrons in a  $5p$  subshell

**8-87.** Write the symbol of the element that corresponds to the following.

- (a) a nonmetal with only one electron in a  $p$  subshell  
(b) an element that is a liquid at room temperature that has five  $p$  electrons  
(c) the first metal to have three  $p$  electrons  
(d) a metalloid with two  $p$  electrons and no  $d$  electrons

**8-88.** Write the symbol of the element that corresponds to the following.

- (a) a transition metal in the fifth period with three unpaired electrons  
(b) a representative metal with three unpaired electrons with no  $f$  electrons  
(c) an element that is a liquid at room temperature with no unpaired electrons  
(d) a metalloid with two unpaired electrons and a filled  $d$  subshell

**8-89.** Identify the first element that has the following total number of electrons and indicate whether the element is a metal or nonmetal, its category, and its group number.

- (a) 10  $s$  electrons                      (c) 15  $p$  electrons  
(b) 28  $d$  electrons

**8-90.** Identify the first element that has the following total number of electrons and indicate whether the element is a metal or nonmetal, its category, and its group number.

- (a) 15  $f$  electrons                      (c) 24  $p$  electrons  
(b) 36  $d$  electrons

**8-91.** A certain isotope has a mass number of 30. The element has three unpaired electrons. What is the element?

**8-92.** A certain isotope has a mass number of 196. It has two unpaired electrons. What is the element?

**8-93.** Given two elements, X and Z, identify them from the following information.

- (a) They are both metals, but one is a representative element.  
(b) The first ionization energy of Z is greater than that of X.  
(c) They are both in the same period that does not have  $f$  electrons.  
(d) They both have two unpaired electrons and neither is used in jewelry.  
(e) A nonmetal in the same period is a diatomic solid.

**8-94.** Given two elements, Q and R, identify them from the following information.

- One is a gas and one is a solid.
- One forms a +1 ion and the other does not.
- Q is larger than R, but both elements are the first elements that have full shells.
- One is used in coins and the other in fluorescent lights.

**8-95.** Which of the following monatomic cations would require a particularly large amount of energy to form? If a certain ion requires a large amount of energy to form, give the reason.

- (a)  $\text{In}^{3+}$     (b)  $\text{I}^+$     (c)  $\text{Ca}^{2+}$     (d)  $\text{K}^+$     (e)  $\text{B}^{3+}$

**8-96.** Which of the following atoms would not be likely to form a +2 cation? Explain.

- (a) Sr    (b) Li    (c) B    (d) Ba

**8-97.** Chemical reactivity relates to the size of the atom or ion. In the following pairs, which has the larger radius?

- (a) Be or Ca    (d)  $\text{S}^{2-}$  or  $\text{Cl}^-$   
 (b) Br or  $\text{Br}^-$     (e)  $\text{Na}^+$  or  $\text{Mg}^{2+}$   
 (c) Cl or S

**8-98.** In the following pairs, which has the larger radius?

- (a)  $\text{Na}^+$  or  $\text{K}^+$     (d) Si or Ge  
 (b)  $\text{O}^{2-}$  or  $\text{Se}^{2-}$     (e)  $\text{K}^+$  or K  
 (c) Ga or Ge

**\*8-99.** On the planet Zerk, the periodic table of elements is slightly different from ours. On Zerk, there are only two  $p$

orbitals, so a  $p$  subshell holds only four electrons. There are only four  $d$  orbitals, so a  $d$  subshell holds only eight electrons. Everything else is the same as on Earth, such as the order of filling ( $1s$ ,  $2s$ , etc.) and the characteristics of noble gases, metals, and nonmetals. Construct a Zerkian periodic table using numbers for elements up to element number 50. Then answer these questions.

- How many elements are in the second period? In the fourth period?
- What are the atomic numbers of the noble gases at the ends of the third and fourth periods?
- What is the atomic number of the first inner transition element?
- Which element is more likely to be a metal: element number 5 or element number 11? element number 17 or element number 27?
- Which element has the larger radius: element number 12 or element number 13? element number 6 or element number 12?
- Which element has a higher ionization energy: element number 7 or element number 13? element number 7 or element number 5? element number 7 or element number 9?
- Which ions are reasonable?
 

|               |            |               |           |
|---------------|------------|---------------|-----------|
| (1) $16^{2+}$ | (3) $7^+$  | (5) $17^{4+}$ | (7) $1^-$ |
| (2) $9^{2+}$  | (4) $13^-$ | (6) $15^+$    |           |

## STUDENT WORKSHOP

### Plotting Periodic Trends

**Purpose:** To graphically represent several periodic trends and predict expected behavior based on those trends. (Work in groups of three or four. Estimated time: 45 min.)

**Equipment:** Several sheets of graph paper; several different colors of pens or markers.

**Procedure:** We will make line graphs even though the data more properly belongs on bar graphs. This way we can put two sets of data on the same graph.

#### Graph 1: First Ionization Energies of the Second- and Third-Period Elements

- Refer to the data in Table 8-2. The  $x$ -axis will be seven separate points labeled for the seven columns on the periodic table, IA through VIIA. The  $y$ -axis needs to range from 0 kJ/mol to 1700 kJ/mol. Scale accordingly.
- In one color ink, plot the points for the elements Li through F from Table 8-2. Connect the points in that color.
- In a second color ink, plot the points for the elements Na through Cl, and connect those points as well.
- Answer the following questions:
  - Which series of elements has the higher ionization energies? Why?
  - What is the general trend as you move from left to right? Why?
  - There are two dips in the graph. Can you explain why they are there?

#### Graph 2: First to Fourth Ionization Energies for Third-Period Elements


- Refer to the data in Table 8-3. The  $x$ -axis will be four separate points labeled I, II, III, and IV. The  $y$ -axis will range from 0 kJ/mol to 12,000 kJ/mol. Scale as needed.
- In one color ink, plot the points for the first through fourth ionization energies of Na.
- In separate color inks, do the same thing for Mg and Al.
- Answer the following questions:
  - Is it clear from this graph what the most favorable number of electrons to remove from each atom is?
  - How does that relate to the electronic structure of the atom?
  - How does it relate to the atom's position on the periodic table?

#### Graph 3: Atomic Radii for Second- and Third-Period Elements

- Refer to Figure 8-18 for the data. The  $x$ -axis will be the same as in graph 1. The  $y$ -axis can range from 50 pm to 200 pm (graphs do not necessarily have to start at 0).
- Plot the data using the same color ink as in graph 1. Make one line for the data of Li through Ne and a second line for Na through Ar.
- Answer the following questions:
  - How does graph 3 compare to graph 1?
  - Is this a coincidence, or are the two trends related? If so, why?



# The Chemical Bond

A photograph of Earth from space, showing the curvature of the planet, the blue atmosphere, and the dark space with stars. A bright sun is visible on the left side, creating a lens flare effect.

**T**his is our home as seen from far-out space. Its surface and atmosphere are composed of some free elements as well as ionic and molecular compounds. We look deeper into the nature of compounds in this chapter.



**PART A**  
**CHEMICAL BONDS AND  
THE NATURE OF IONIC  
COMPOUNDS**

**9-1** Bond Formation and Representative  
Elements

**9-2** Formation of Ions and Ionic  
Compounds

**PART B**  
**CHEMICAL BONDS AND THE  
NATURE OF MOLECULAR  
COMPOUNDS**

**9-3** The Covalent Bond



**MAKING IT REAL**

*Nitrogen: From the Air to Proteins*

**9-4** Writing Lewis Structures

**9-5** Resonance Structures

**PART C**  
**THE DISTRIBUTION OF  
CHARGE IN CHEMICAL  
BONDS**

**9-6** Electronegativity and Polarity  
of Bonds

**9-7** Geometry of Simple Molecules

**9-8** Polarity of Molecules

**9-9** Formal Charge (Optional)



**MAKING IT REAL**

*Enzymes—The Keys of Life*

**SETTING THE STAGE** Earth is a complex world of chemicals. Consider the air. It is composed of molecular elements—nitrogen and oxygen—as well as smaller quantities of the solitary atoms of noble gases—argon, helium, and neon. In addition there are trace amounts of several molecular compounds such as carbon dioxide and water. The surface of Earth is largely composed of water containing dissolved compounds. The solid surface of Earth contains compounds of living things, rocks, and fossils.

We will focus on two compounds that occur in nature and are necessary in life processes—salt and water. These two compounds are examples of the two basic types of compounds: ionic and molecular. Salt (specifically, sodium chloride) is typical of ionic compounds. It is a hard, brittle solid with a high melting point. Water, on the other hand, is typical of many molecular compounds in that it is a liquid at or near room temperature. What is there about these two compounds that make them so distinct? Even though both are composed of just two elements, there actually is an important difference. Sodium chloride is a binary compound formed from a metal, sodium, and a nonmetal, chlorine. Water is also a binary compound, but it is formed from two nonmetals, hydrogen and oxygen. In this chapter we will discover why the combination of a metal and a nonmetal results in an ionic compound, whereas the combination of two nonmetals results in a molecular compound.

In Part A in this chapter, we will examine the ionic compounds formed from the combination of metals and nonmetals. Nonmetals combine to form molecular compounds. The structure of these compounds is the subject of Part B. Finally, in Part C, we will examine some of the many implications that follow from the structure of molecular compounds.



**PART A**  
**CHEMICAL BONDS AND**  
**THE NATURE OF IONIC**  
**COMPOUNDS**

**SETTING A GOAL**

- You will learn how the octet rule is used to determine the charge on ions and the formulas of ionic compounds.

**OBJECTIVES**

- 9-1 (a)** Explain the significance of the octet rule. **(b)** Write the Lewis dot symbol of the atoms of any representative element.
- 9-2** Using the Lewis dot structure and the octet rule, predict the charges on the ions of representative elements and the formulas of binary ionic compounds.

▶ **OBJECTIVES FOR SECTION 9-1**

**(a)** Explain the significance of the octet rule. **(b)** Write the Lewis dot symbol of the atoms of any representative element.

## 9-1 BOND FORMATION AND REPRESENTATIVE ELEMENTS



**LOOKING AHEAD!** All the elements in the periodic table interact with other elements to form compounds except for some of the noble gases. Why these elements do not form bonds with other elements provides a clue to understanding the bonding of the representative elements. ■

### 9-1.1 The Octet Rule

The noble gases exist as solitary atoms, since they have little or no tendency to form chemical bonds. Why is this so? It has been known for some time that the formation of chemical bonds involves changes in the electron configurations of the atoms involved. Apparently, the noble gases have stable electron configurations with little or no tendency to change. All the noble gases except for helium have filled outer  $s$  and  $p$  subshells (e.g.,  $ns^2np^6$ ). Since this is a total of eight electrons, it is referred to as an *octet* of electrons. An octet of electrons forms a particularly stable configuration, as we discussed in the previous chapter. In fact, the bonding we will discuss in this chapter is dictated by the **octet rule**, which states that elements of the representative elements form bonds so as to have access to eight outer electrons. Note that helium is a noble gas but has only a filled  $1s$  subshell containing two electrons. Thus, helium has a stable electron configuration, with only two electrons, compared to the other noble gases, with an octet of electrons.

### 9-1.2 Valence Electrons and Dot Symbols

The outer  $s$  and  $p$  electrons in the atoms of a representative element are referred to as the **valence electrons**. Since only the valence electrons are involved in bonding, we can focus on these electrons exclusively. **Lewis dot symbols** represent valence electrons as dots around the symbol of the element. Table 9-1 shows the Lewis dot symbols for the first four periods of representative elements and noble gases. The first four valence electrons are shown placed around the symbol, one dot at a time, on each of the four sides. The next four valence electron

**TABLE 9-1** Lewis Dot symbols<sup>a</sup>

| IA | IIA | IIIA | IVA | VA | VIA | VIIA | VIIIA |
|----|-----|------|-----|----|-----|------|-------|
| H  |     |      |     |    |     |      | He    |
| Li | Be  | B    | C   | N  | O   | F    | Ne    |
| Na | Mg  | Al   | Si  | P  | S   | Cl   | Ar    |
| K  | Ca  | Ga   | Ge  | As | Se  | Br   | Kr    |

<sup>a</sup>Named after the American Chemist G. N. Lewis (1875–1946), who developed this theory of bonding.

dots then pair up with each of the originals. Notice that the elements in each group have the same number of valence electrons and thus the same number of dots.

The Roman numeral of the group number also represents the number of valence electrons (dots) for a neutral atom. In some periodic tables, the groups are labeled 1 through 18. In this case the last digit of the group number represents the number of valence electrons. For example, Group 14 has four valence electrons.

If an octet of electrons is a particularly stable configuration, how can the atoms of elements other than the noble gases alter their electron configuration so as to obtain an octet? There are three ways.

1. A metal may *lose* one to three electrons to form a cation with the electron configuration of the previous noble gas (i.e., the one with the next-lowest atomic number).
2. A nonmetal may *gain* one to three electrons to form an anion with the electron configuration of the next noble gas (i.e., the one with the next-highest atomic number).
3. Atoms (usually two nonmetals) may *share* electrons with other atoms to obtain access to the number of electrons in the next noble gas.

Notice that the octet rule must be modified somewhat for the elements H, Li, and Be. They can obtain the stable noble gas configuration of helium with only two electrons. For these elements, it would be more appropriate to call it a “duet” rule.

Processes 1 and 2 complement each other in the formation of ionic compounds. Process 3 produces molecular compounds. We will consider the formation of ions first and molecular compounds in Part B of this text.

### ASSESSING THE OBJECTIVES FOR SECTION 9-1

**EXERCISE 9-1(a) KNOWLEDGE:** How many valence electrons are found in the following atoms:

- (a) Ga    (b) S    (c) Kr

**EXERCISE 9-1(b) KNOWLEDGE:** What is the Lewis dot symbol for the following?

- (a) Mg    (b) N    (c) I

**EXERCISE 9-1(c) ANALYSIS:** Where does the reference to eight in the “octet rule” come from?

**EXERCISE 9-1(d) SYNTHESIS:** In advanced chemistry courses, students study complicated molecules that follow the “18-electron rule.” Which subshells need to be filled in these compounds?

*For additional practice, work chapter problems 9-1, 9-2, and 9-4.*

## 9-2 FORMATION OF IONS AND IONIC COMPOUNDS



**LOOKING AHEAD!** In Chapter 4, we made use of the periodic table to assign charges to representative metals and nonmetals. In this section we will describe how the octet rule leads us to the expected charge on representative element ions. ■

### OBJECTIVE FOR SECTION 9-2

Using the Lewis dot structure and the octet rule, predict the charges on the ions of representative elements and the formulas of binary ionic compounds.

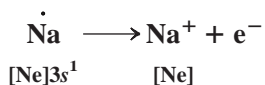


**FIGURE 9-1** Reaction of Sodium with Chlorine Sodium reacts with chlorine to form sodium chloride.

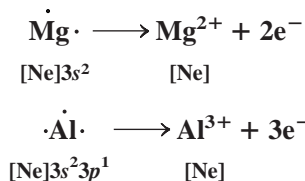
When a small piece of sodium metal is placed in a bottle containing chlorine gas, a chemical change is obvious. (See Figure 9-1.) The sodium ignites, and a white coating of sodium chloride forms on the sides of the bottle. In this chemical reaction, electrons from sodium atoms are transferred to chlorine atoms to form an ionic compound, sodium chloride.

### 9-2.1 Formation of Binary Ionic Compounds

First we will focus on what happens to metals such as sodium when they react to form cations. In the previous chapter, we indicated that metals have low ionization energies and can lose outer electrons relatively easily. The octet rule tells us how many electrons will be lost and from this the magnitude of the positive charge. *If a representative metal loses all its valence electrons, it acquires the octet of the previous noble gas.* We also found in the previous chapter that the ionization energies of core electrons are very high, so these electrons are not lost in compound formation. Thus, only valence electrons are lost in the formation of positive ions. We can illustrate the octet rule and cation formation using the Lewis dot symbol of sodium.

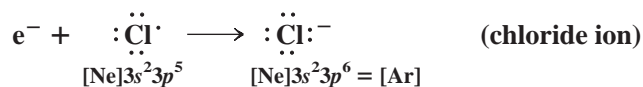


The Lewis representation of the  $\text{Na}^+$  ion does not include any electrons (dots) because the octet of electrons of  $\text{Na}^+$  occupy filled inner subshells. All the metals in Group IA have analogous dot symbols, so each can lose one electron to form a +1 ion with the electron configuration of the preceding noble gas. The ionizations of a IIA metal to form a +2 ion and a IIIA metal to form a +3 ion are represented as follows.

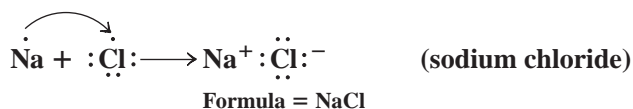


Positive ions do not exist alone in compounds. Negative ions must be present to balance the positive charge. In Chapter 2, we found that representative nonmetals complement metals by forming negative ions. In the previous chapter, we noticed that nonmetals add electrons exothermically. First, we will consider ions formed by the VIIA nonmetals such as chlorine.

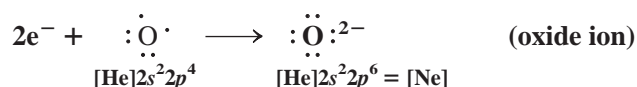
Chlorine and all the other atoms of the halogens in Group VIIA are one electron short of a noble gas configuration. An octet of electrons can be achieved by adding one electron. The result is an anion with a -1 charge and the electron configuration of the next noble gas.



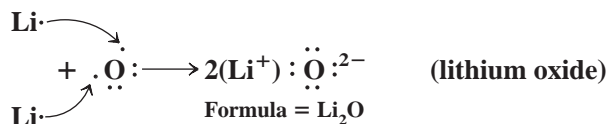
When we bring sodium in contact with chlorine, an exchange of the single valence electron occurs. The exchange of the electron means that both of the ions formed have octets of electrons.



Consider what happens to the electrons when lithium metal comes into contact with the oxygen in the air. An oxygen atom needs two electrons to achieve an octet and form an anion with a  $-2$  charge.

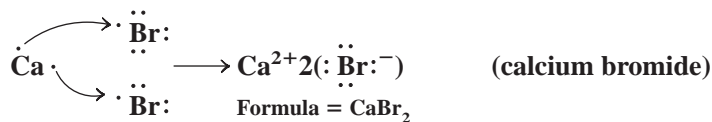


Since a lithium atom can lose only one electron, two lithium atoms are needed to supply the two electrons. Recall that the two  $+1$  ions balance the charge of the one  $-2$  ion [i.e.,  $2(+1) - 2 = 0$ ]. The chemical formula of the compound lithium oxide is therefore  $\text{Li}_2\text{O}$ .

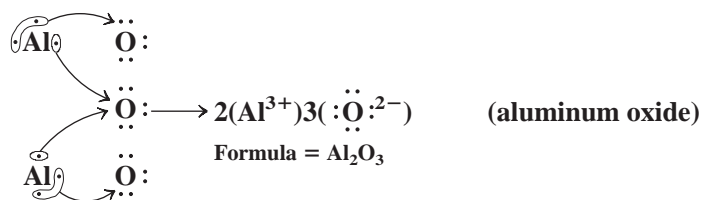


Now consider a reaction involving calcium, an alkaline earth metal (IIA), with bromine, a halogen. Calcium atoms can attain the noble gas configuration of the previous noble gas (neon) by losing two electrons. (All other metals in this group form  $+2$  ions in the same manner.)

Two bromine atoms are needed to accept the two electrons from the one calcium atom.

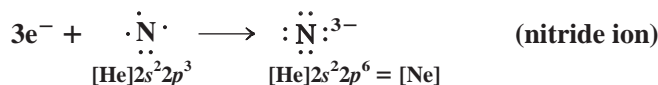


Finally, we will include the reaction of aluminum with oxygen to form aluminum oxide. Group IIIA metals (Al and lower) can lose three electrons in order to form an octet of electrons.\* Boron is not a metal and does not form a  $+3$  ion in its compounds. Boron bonds by electron sharing, which is discussed later in this chapter. In this reaction, two Al atoms give up six electrons, which are then accepted by three O atoms. The formula is thus  $\text{Al}_2\text{O}_3$ , and the charges cancel [ $2(+3) + 3(-2) = 0$ ].

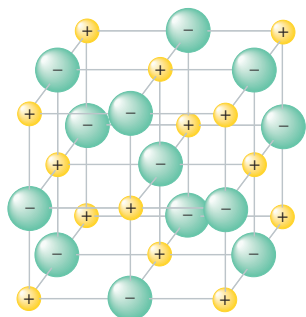
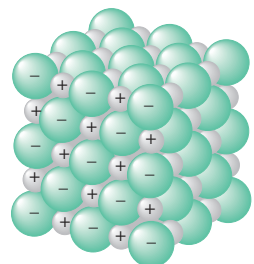


## 9-2.2 Other Representative Element Ions

Two nonmetals (N and P) in Group VA gain three electrons to form  $-3$  ions.



\*Ions such as  $\text{Tl}^{3+}$  and  $\text{Ga}^{3+}$  have a filled  $d$  subshell in addition to a noble gas configuration. This is sometimes referred to as a pseudo-noble gas configuration. The filled  $d$  subshell does not seem to affect the stability of these ions. In this text, we do not distinguish between noble gas and pseudo-noble gas electron configurations. Transition metals also form positive ions, but for the most part, these ions do not relate to a noble gas configuration. Some of these ions were discussed in Chapter 4.



**FIGURE 9-2 An Ionic Solid**  
Table salt (photo) is composed of cations and anions in a specific geometric lattice.

Group IVA metals such as tin and lead have four electrons in their outer subshells. Loss of all four of these electrons to produce a  $+4$  ion requires a rather large amount of energy. Instead, these metals can lose two of their four outer electrons to form a  $+2$  ion that does not follow the octet rule. They do form compounds where all four of their outer electrons are involved, but the bonding in these compounds is best described by electron sharing rather than ion formation. For the most part, Group IVA nonmetals also bond by electron sharing rather than forming monatomic ions. Although there is some evidence for a  $C^{4-}$  ion with an octet of electrons, formation of such highly charged ions is an energetically unfavorable process.

In Group VA, bismuth forms a  $+3$  ion that does not follow the octet rule.

### 9-2.3 The Physical State of Ionic Compounds

Ionic compounds are solids at room temperature. They tend to have high melting points and are usually hard and brittle. If we look into the basic structure of a crystal of table salt, we can see why. Ionic compounds do not exist as discrete molecular units with one  $Na^+$  attached to one  $Cl^-$ . As shown in Figure 9-2, each  $Na^+$  is actually surrounded by six  $Cl^-$  ions, and each  $Cl^-$  ion is surrounded by six  $Na^+$  ions in a *three-dimensional array of ions called a lattice*. Recall from Chapter 8 that cations are smaller than their parent atoms, while anions are larger. Thus, in most cases, we can assume that the anion is larger than the cation. The lattice is held together strongly and rigidly by electrostatic interactions. *These electrostatic attractions are known as ionic bonds*. There are several other arrays of ions (lattices) used to accommodate both the size differences and varying ratios of cations to anions found in all of the possible ionic compounds. For example, in  $CsCl$  both the  $Cs^+$  and the  $Cl^-$  are surrounded by eight oppositely charged ions.

Besides the monatomic ions, polyatomic ions exist where two or more atoms are bound together by electron sharing, and the total species carries a net charge [e.g., the carbonate ion ( $CO_3^{2-}$ )]. These species exist as ions because they have an imbalance of electrons compared to the total number of protons in their nuclei. We will discuss the bonding within a polyatomic ion later in this chapter, but for now we acknowledge their presence in ionic compounds.



Rubies and sapphires are hard substances found in nature. They are ionic compounds.

#### EXAMPLE 9-1

##### Writing Formulas of Binary Ionic Compounds

Using the Lewis dot symbols, determine the formulas of the ionic compounds formed between (a) aluminum and fluorine and (b) barium and sulfur.

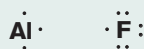
##### PROCEDURE

Use the octet rule and the Lewis dot symbol to determine the number of electrons to be lost by the metal and to be gained by the nonmetal. Determine the correct ratio of cation to anion so that the total number of electrons transferred from cations to anions is the same.

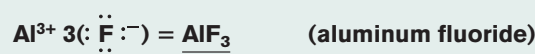


**SOLUTION**

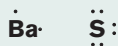
(a) Aluminum is in Group IIIA and fluorine is in Group VIIA. Their dot symbols are



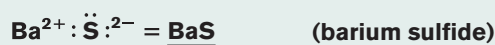
To have a noble gas configuration (an octet), the Al, a metal, must lose all three outer electrons to form a +3 ion. Fluorine can add only one electron, which forms a -1 ion and gives the F<sup>-</sup> ion an octet. Three fluorine atoms are needed to balance the charge. The compound formed is



(b) Barium is in Group IIA and sulfur is in Group VIA, and they have the dot symbols



One Ba atom gives up two electrons, and one S atom takes up two electrons, forming the compound

**ANALYSIS**

This example is less about teaching you something new than it is about providing stronger evidence for something we've already learned. Back in Chapter 4, we illustrated for the first time how to write the formulas of ionic compounds by assuming that certain elements would have specific charges. Now, based on the octet rule, valence electrons, and Lewis dot formulas, we provide the underlying rationale for these charges that previously we asked you to accept without discussion.

**SYNTHESIS**

Tying this in with other previously learned material, we realize that the strength of the ionic bonds we're forming affects whether an ionic solid is soluble or insoluble in water. When the ions are held together more tightly, it becomes harder to break them apart, and so harder to get them to dissolve. Certainly other factors are present, but the strength of the ionic bond is a major component to the calculation. Would you expect bigger or smaller ions to be held together more tightly? +1's with -1's or +2's with -2's? Clearly, the higher charges lead to a stronger attraction between the ions in the lattice (known as the *lattice energy*). Less intuitively, smaller ions generate higher attractions than larger ones because the ions can get closer to each other. According to Coulomb's law, the closer charges (ions) are to each other, the greater the attraction and the harder to break apart.

**ASSESSING THE OBJECTIVE FOR SECTION 9-2**

**EXERCISE 9-2(a) KNOWLEDGE:** What are the charges on the ions formed by Be and As?

**EXERCISE 9-2(b) ANALYSIS:** What is the formula of the compound formed when Be combines with As?

**EXERCISE 9-2(c) SYNTHESIS:** When we write a formula for an ionic compound such as aluminum oxide, what do we mean when we write Al<sub>2</sub>O<sub>3</sub>?

*For additional practice, work chapter problems 9-8, 9-9, 9-14, 9-19, 9-22, and 9-25.*

**PART A SUMMARY****KEY TERMS**

- 9-1.1** The formulas of binary ionic compounds can be understood by reference to the **octet rule**. p. 254
- 9-1.2** The **valence electrons** of the atoms of representative elements can be displayed as **Lewis dot symbols**. p. 254
- 9-2.3** The **lattice** of an ionic compound is the arrangement of ions in a crystal. p. 258
- 9-2.3** The electrostatic interactions of the oppositely charged ions in a crystal are known as **ionic bonds**. p. 258

The summary of ionic compounds is included in the Summary Chart after Part B.

**PART B**  
**CHEMICAL BONDS AND THE**  
**NATURE OF MOLECULAR**  
**COMPOUNDS**

**SETTING A GOAL**

- You will learn how to apply the octet rule to draw structures that form the basis of our understanding of bonding in most molecular compounds.

**OBJECTIVES**

- 9-3** Describe the covalent bond and how the octet rule determines the number of such bonds for simple compounds.
- 9-4** Draw Lewis structures of a number of molecular compounds and polyatomic ions.
- 9-5 (a)** Discuss the significance of resonance. **(b)** Write resonance structures of appropriate molecules or ions.

► **OBJECTIVE FOR SECTION 9-3**

Describe the covalent bond and how the octet rule determines the number of such bonds for simple compounds.

**9-3 THE COVALENT BOND**

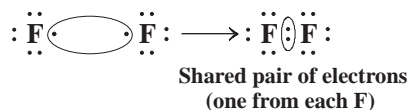


**LOOKING AHEAD!** We are now ready to turn our attention to compounds that may exist as gases and liquids as well as solids. Since metals are not involved in these compounds, an exchange of electrons does not occur. In these cases, the octet rule applies to the sharing of electrons. ■

In binary ionic compounds, octets are achieved when metals lose electrons and nonmetals gain electrons. But what if both elements are nonmetals, so neither has a tendency to give up electrons? In that case, octets are obtained by electron sharing. The shared electrons are counted toward each element's octet of electrons. For example, hydrogen and oxygen (both nonmetals) combine in a dramatic chemical reaction (i.e., an explosion) to form water if initiated by a spark. In the formation of water, electrons are not completely exchanged but instead are shared between each of the two hydrogen atoms and the oxygen atom, resulting in a neutral molecule. Compounds composed of neutral molecules such as water and carbon dioxide have properties very different from compounds composed of ions such as sodium chloride.

**9-3.1 Lewis Structures**

The fluorine atom (Group VIIA) has seven valence electrons. Fluorine can achieve an octet in two ways. It can gain one electron to form the fluoride ion as described previously, or it can share one electron with another atom to have access to eight electrons. For example, two fluorine atoms can achieve an octet of electrons by sharing two electrons, one from each fluorine. *The sharing of two electrons between two atoms is known as a covalent bond.* The bonding in the  $F_2$  molecule, which is like that of all of the other diatomic halogens, is illustrated as follows.

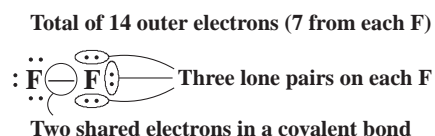


It is easy to appreciate how a complete exchange of electrons can satisfy the octet rule, but the concept of electron sharing and the octet rule is more subtle. A simple analogy may help. Assume we have a young man (Henry) who has \$7. Henry wishes to have access to \$8 and, for some strange reason, no more than \$8. Now let Henry happen on to an even weirder person who also wishes to have no more than \$8 but instead has \$9. An exchange of \$1 to Henry leaves them both happy. This is analogous to a metal and a nonmetal forming an ionic bond, with the metal giving its extra

electron to the nonmetal. In a second situation, assume that two people have only \$7 each and, again, both wish access to \$8. There is a solution to the dilemma. If they keep \$6 in their own pockets and contribute \$1 each (for a total of \$2) to a joint checking account, then both can claim access to \$8 (but no more than \$8). That is, each has \$6 plus access to the \$2 in the joint account.

We can now extend the concept of Lewis dot representations to molecular compounds containing covalent bonds. A **Lewis structure** for a molecule shows the order and arrangement of atoms in a molecule (the structural formula) as well as all of the valence electrons for the atoms involved. There are several variations of how Lewis structures represent molecules. A pair of electrons is sometimes shown as a pair of dots (:) or as a dash (—). In this text, we use a pair of dots to represent unshared pairs (also called *lone pairs*) of electrons on an atom and a dash to represent a pair of electrons that are shared between atoms. In this way, shared and unshared electrons can be distinguished.

The Lewis structure of  $F_2^*$  is illustrated as follows:

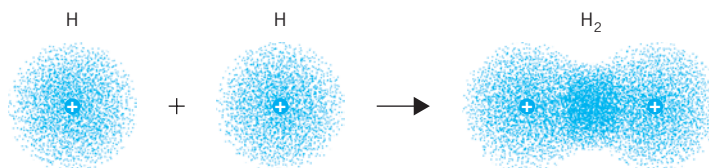


Similarly, other halogens exist as diatomic molecules like  $F_2$  and have the same Lewis structures. Hydrogen, which forms the simplest of all molecules, also exists as a diatomic gas with one covalent bond between atoms:



Recall that hydrogen follows a duet rule in order to attain the noble gas configuration of He.

Why do two H atoms combine to form an  $H_2$  molecule? The answer is “because that is a more stable arrangement.” A simple way of viewing a covalent bond is as arising from the overlapping of half-filled atomic orbitals, one from each atom. To be more descriptive, two hydrogen atoms alone have one electron in a  $1s$  orbital, which is spherically diffuse. The electron has a probability of existing in any direction from the nucleus in the separate atoms. When two hydrogen atoms come together, however, the two electrons become more localized between the two nuclei in a region where the two  $1s$  orbitals overlap. Each positive hydrogen nucleus is attracted to two negative electrons between the atoms, rather than just one. Although there are also forces of repulsion between the two electrons, the mutual attraction of two nuclei for two electrons predominates and holds them together. (See Figure 9-3.) It is like why two people get married. They each may be OK alone, but the forces of attraction are stronger than the forces of repulsion—and that bonds them together.



**FIGURE 9-3 A Covalent Bond** The high electron density between the two nuclei holds the two atoms together.

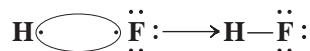
### 9-3.2 Hydrogen Compounds with Other Nonmetals

Just as we were able to justify the formulas of simple binary ionic compounds by the octet rule, we can do the same with simple binary molecular compounds. In fact, this works so well that we can predict the formulas of compounds based on the octet rule.

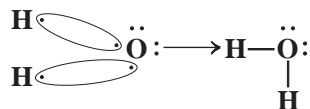
First, we will consider the compounds formed by hydrogen with the halogens in Group VIIA. For example, consider the compound formed from hydrogen and

\*An F atom has one unpaired electron in a  $2p$  orbital. Formation of a covalent bond pairs the electrons in the two F atoms so that the  $F_2$  molecule has no unpaired electrons. Although most atoms of the representative elements have unpaired electrons, most molecules or ions formed from these elements do not have unpaired electrons.

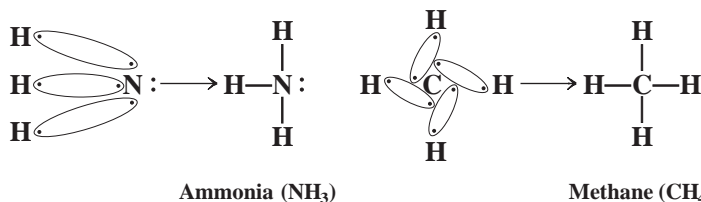
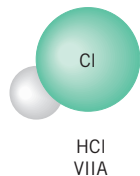
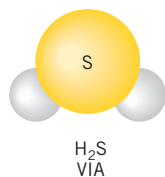
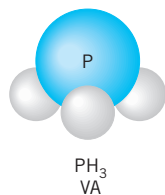
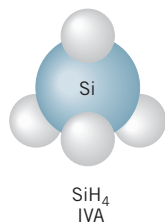
fluorine, which has the formula HF. A shared pair of electrons (one from each atom) gives both atoms access to the same number of electrons as a noble gas.



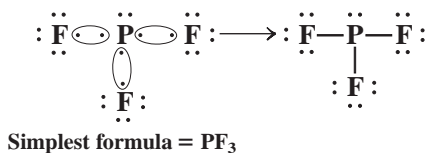
Now consider the compounds formed between hydrogen and the Group VIA elements. Our primary example, of course, is water. Since one oxygen atom needs access to two more electrons to have an octet, two hydrogen atoms are required to form two covalent bonds to one oxygen atom.



As we move across the periodic table to consider the hydrogen compounds formed between Group VA and Group IVA nonmetals, we see that the octet rule serves us well. Three hydrogen atoms are needed by N (Group VA) and four by C (Group IVA). Recall that hydrogen is written second in binary compounds with Group IVA and VA elements but is written first with Group VIA and VIIA elements. (See also some hydrogen compounds of third-period elements in Figure 9-4.)



Let's try to predict the formula of the simplest compound formed between phosphorus (Group VA) and fluorine (Group VIIA). Since the dot symbol of P indicates that it needs access to three more electrons and F needs access to one more, the solution points to one P sharing a pair of electrons with each of three different F atoms.



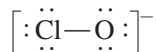
**FIGURE 9-4** Formulas of Hydrogen Compounds The formulas of some simple hydrogen compounds can be predicted from the octet rule.

### 9-3.3 The Electrons in Polyatomic Ions

In addition to molecular compounds, atoms within polyatomic ions share electrons in covalent bonds. For example, consider the hypochlorite ion (ClO<sup>-</sup>). The -1 charge on the ion tells us that there is one more electron present in this species than the valence electrons provided by one Cl atom and one O atom. The total number of electrons is calculated as follows.

$$\begin{array}{r} \text{from a neutral Cl} = 7 \\ \text{from a neutral O} = 6 \\ \text{additional electron indicated by charge} = \underline{1} \\ \text{total number of electrons} = 14 \end{array}$$

Two atoms bonded together with 14 electrons have a Lewis structure like F<sub>2</sub>, which also has 14 electrons.



The brackets indicate that the total ion has a  $-1$  charge. The extra electron has not been specifically identified because all electrons are identical and belong to the ion as a whole.

### 9-3.4 Double and Triple Bonds

In the examples illustrated so far, two atoms share one pair of electrons. There are also examples, especially among the second-period nonmetals (B through O), where two or even three pairs of electrons are shared between two atoms. *The sharing of two pairs of electrons between the same two atoms is known as a double bond. The sharing of three pairs is known as a triple bond.* A double bond is illustrated as  $=$ , and a triple bond is illustrated as  $\equiv$ . The use of a double bond to satisfy the octet rule is analogous to two people who wish to have access to \$8 but only have a total of \$12 between them. In this case, each person could have \$4 in a private account while sharing \$4 in a joint account. A triple bond would be analogous to the two people having only \$10 between them. Each could have only \$2 in a private account while sharing \$6 in the joint account.

The molecules of carbon dioxide have double bonds. In the Lewis structure shown below, notice that the octets of both carbon and oxygen are satisfied by the sharing



#### Nitrogen: From the Air to Proteins



Field of soybeans.

Our bodies are literally held together by proteins. In the form of enzymes, proteins are involved in virtually every chemical reaction that occurs inside us. Proteins, which are composed of various amino acids such as glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ),

contain nitrogen. Therefore, nitrogen is essential to life. Fortunately, we literally live in a sea of nitrogen, since about 80% of our atmosphere is in the form of  $\text{N}_2$ . Unfortunately, the change from the elemental form of nitrogen into the chemical bonds in proteins is not an easy path, since  $\text{N}_2$  is very hard to break down.

Elemental nitrogen ( $\text{N}_2$ ) contains a triple bond. Triple bonds between the same two elements are stronger than double bonds and much stronger than single bonds. The triple bond must be broken, however, before nitrogen can be taken from the air and incorporated into compounds. Nature breaks down nitrogen so it can form compounds in two ways, both of which are known generally as *nitrogen fixation*.

One way that nitrogen can be fixed is with the energy from a powerful bolt of lightning strong enough to break its triple bond. When the  $\text{N}_2$  bond is broken, the free nitrogen atoms combine with oxygen in the air to form nitric oxide (NO), which eventually falls to earth dissolved in the rain. However, this path does not provide nearly enough fixed nitrogen for plants and animals. The second more important

way is through the action of certain plants, such as beans and peas (legumes), that have bacteria attached to their roots. These bacteria contain an enzyme known as *nitrogenase*, which has the unusual ability to break the  $\text{N}_2$  triple bond and produce nitrogen compounds that can be used by their host plants. This is how nature fertilizes crops. With over 6 billion people on Earth, nature isn't nearly enough, however, so farmers must now supplement their crops with huge amounts of ammonia ( $\text{NH}_3$ ). This compound is manufactured from its elements in a difficult and expensive process that is discussed in chapter 15.

Both academic and industrial chemists are looking for an inexpensive and continuous way to fix nitrogen. The goal is to duplicate the action of *nitrogenase* in plants, but the process is very complex and only partially understood. Nevertheless, there is active research at various laboratories where scientists are searching for an agent (known as a catalyst) that will absorb atmospheric nitrogen, form bonds between nitrogen and other elements (i.e., hydrogen and oxygen), release the new compound, and then regenerate the original agent. The right process has been elusive, but the benefits of future success are enormous.

Imagine the formation of a solid compound that could be spread on the surface of a field or garden that would use solar energy to continually generate nitrogen fertilizers directly from the air. Crop yields would increase, and overused and misused farmland could be made fertile again. The payoff for such a substance would be immeasurable.



of two pairs of electrons in each carbon–oxygen bond. Elemental nitrogen,  $N_2$ , is an example of a molecule that satisfies the octet rule with a triple bond.



**ASSESSING THE  
OBJECTIVE FOR  
SECTION 9-3**

**EXERCISE 9-3(a) KNOWLEDGE:** Based on Lewis dot structures, how many bonds must the following make in order to have an octet?

(a) P      (b) Br      (c) Si

**EXERCISE 9-3(b) ANALYSIS:** Based on Lewis dot structures, what is the formula of the simplest molecule that can be formed from the following?

(a) As and H      (b) C and Cl      (c) Cl and F

**EXERCISE 9-3(c) SYNTHESIS:** We've seen examples of single, double, and triple bonds. Could a quadruple bond exist?

*For additional practice, work chapter problems 9-26, 9-27, and 9-28.*

**▶ OBJECTIVE FOR  
SECTION 9-4**

Draw Lewis structures of a number of molecular compounds and polyatomic ions.

## 9-4 WRITING LEWIS STRUCTURES



**LOOKING AHEAD!** The Lewis structures of simple binary compounds with single covalent bonds can be written without too much difficulty by following the octet rule. The writing of other structures can be more complex, so a set of rules or guidelines is most helpful. In this section, we will see how a sequential approach will make this important task quite manageable. ■

The octet rule is the key that allows us to write the correct Lewis structures for many compounds and polyatomic ions. From this we not only justify the formulas of compounds (e.g.,  $H_2O$ , not  $H_3O$ ) but can predict other formulas as well. Other features of a compound follow from the correct Lewis structure. For example, later in this chapter we will use the Lewis structure to predict the geometry of some simple molecules. Many physical and chemical properties of a compound are directly related to its geometry. As we progress in the study of chemistry, we will continually refer to the Lewis structures of many compounds. Therefore, writing Lewis structures correctly is considered a fundamental skill to be acquired early in the study of chemistry.

### 9-4.1 Rules for Writing Lewis Structures

Writing Lewis structures according to the octet rule is quite straightforward when certain guidelines or rules are systematically applied. These rules, of course, require considerable practice in their application. Starting with the formula of a compound (either ionic or molecular), the rules are as follows.

1. Check to see whether any ions are involved in the compounds. Write any ions present.
  - a. Metal–nonmetal binary compounds are mostly ionic.
  - b. If Group IA or Group IIA metals (except Be) are part of the formula, ions are present. For example,  $KClO$  is  $K^+ ClO^-$  because *K is a Group IA element and forms only a + 1 ion*. If K is +1, the ClO must be  $-1$  to have a neutral compound. Likewise,  $Ba(NO_3)_2$  contains ions because *Ba is a Group IIA element and forms only a + 2 ion*. The formula also indicates the presence of two nitrate ions. The ions are represented as  $Ba^{2+} 2(NO_3^-)$ .
  - c. Compounds composed of nonmetals contain only covalent bonds.

2. For a molecule, add all of the outer (valence) electrons of the neutral atoms. Recall that the number of valence electrons is the same as the column number (or last digit when columns are labeled 1–18). For an ion, add (if negative) or subtract (if positive) the number of electrons indicated by the charge.
3. Write the symbols of the atoms of the molecule or ion in a skeletal arrangement.
  - a. A hydrogen atom can form only one covalent bond and therefore bonds to only one atom at a time. Hydrogen atoms are situated on the periphery of the molecule.
  - b. The atoms in molecules and polyatomic ions tend to be arranged symmetrically around a central atom. The central atom is generally a nonmetal other than oxygen or hydrogen. Oxygen atoms usually do not bond to each other. Thus  $\text{SO}_3$  has an S surrounded by three O's.



rather than such structures as



In most cases, the first atom in a formula is the central atom, and the other atoms are bound to it. Usually the central atom is the atom found farther to the right or lower down on the periodic table.

4. Place a dash representing a shared pair of electrons between adjacent atoms that have covalent bonds (not between ions). Subtract the electrons used for this (two for each bond) from the total calculated in step 2.
5. Distribute the remaining electrons among the atoms so that no atom has more than eight electrons, starting with the atoms on the outside of the structure first.
6. Check all atoms for an octet (except H). If an atom has access to fewer than eight electrons (usually the central atom), put an electron pair from an adjacent atom into a double bond. Each double bond increases by two the number of electrons available to the atom needing electrons without taking them away from the other atom. Remember that you cannot satisfy an octet for an atom by adding any electrons at this point.

### EXAMPLE 9-2

#### Writing the Lewis Structure of a Molecular Compound

Write the Lewis structure for  $\text{NCl}_3$ .

#### PROCEDURE

Follow the procedure as outlined above.

#### SOLUTION

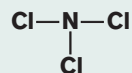
1. This is a binary compound between two nonmetals. Therefore, it is not ionic.
2. The total number of electrons available for bonding is

$$\begin{array}{r} \text{N } 1 \times 5 = 5 \\ \text{Cl } 3 \times 7 = \underline{21} \\ \text{Total} = 26 \end{array}$$

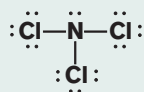
3. The skeletal arrangement is



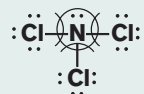
4. Use 6 electrons to form bonds.



5. Distribute the remaining 20 electrons ( $26 - 6 = 20$ ).



6. Check to make sure that all atoms satisfy the octet rule.

**EXAMPLE 9-3****Writing the Lewis Structure of an Ion**

Write the Lewis structure of the cyanide ion ( $\text{CN}^-$ ).

**SOLUTION**

- This is an ion.
- The total number of electrons available is

$$\begin{array}{r} \text{N } 1 \times 5 = 5 \\ \text{C } 1 \times 4 = 4 \\ \text{From charge} = \underline{1} \\ \text{Total} = 10 \end{array}$$

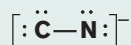
- The skeletal arrangement is



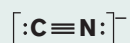
- Use two electrons to form a bond.



- Distribute the remaining eight electrons ( $10 - 2 = 8$ ).



- Notice that both carbon and nitrogen have access to only six electrons each. Use two electrons from the carbon and two electrons from nitrogen to make a triple bond. Now the octet rule is satisfied.

**EXAMPLE 9-4****Writing the Lewis Structure of an Ionic Compound**

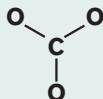
Write the Lewis structure for  $\text{CaCO}_3$ .

**SOLUTION**

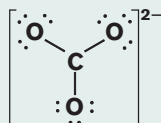
- This is an ionic compound composed of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions. (Since you know that Ca is in Group IIA, it must have a +2 charge; therefore, the polyatomic anion must be  $-2$ .) A Lewis structure can be written for  $\text{CO}_3^{2-}$ .
- For the  $\text{CO}_3^{2-}$  ion, the total number of outer electrons available is

$$\begin{array}{r} \text{C } 1 \times 4 = 4 \\ \text{O } 3 \times 6 = 18 \\ \text{From charge} = \underline{2} \\ \text{Total} = 24 \end{array}$$

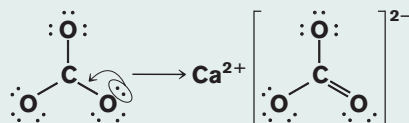
4. The skeletal structure with bonds is



5. Add the remaining 18 electrons ( $24 - 6 = 18$ ).



6. The C needs two more electrons, so one double bond is added using one lone pair from one oxygen.



### EXAMPLE 9-5

#### Writing the Lewis Structure of an Oxyacid

Write the Lewis structure for  $\text{H}_2\text{SO}_4$ .

#### SOLUTION

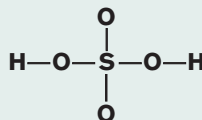
- All three atoms are nonmetals, which means that all bonds are covalent.
- The total number of outer electrons available is

$$\begin{array}{r} \text{H } 2 \times 1 = 2 \\ \text{S } 1 \times 6 = 6 \\ \text{O } 4 \times 6 = \underline{24} \\ \text{Total} = 32 \end{array}$$

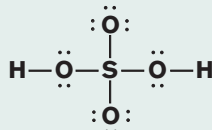
- In most molecules containing H and O, the H is bound to an O and the O to some other atom, which in this case is S. The skeletal structure is



- Use 12 electrons for the six bonds.



- Add the remaining 20 electrons ( $32 - 12 = 20$ ).



- All octets are satisfied.

#### ANALYSIS

The Lewis structure of a molecule clearly shows how atoms are attached to each other and with what types of bonds. It also tells us how many unshared electrons are found in the valence shell of each atom in the structure. Later in this chapter, we'll examine the other information contained in a Lewis structure that begins to build on itself and serves as a basis for the next several chapters of the text. Your success in studying chemistry from this point onward is going to depend on your ability to accurately draw Lewis structures. You're encouraged to work as many examples as are necessary to become proficient at the procedure.

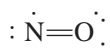
#### SYNTHESIS

These simple examples of Lewis structures illustrate the concepts that chemists use to picture the structures of the largest and most complicated covalent molecules known. Hemoglobin, DNA, proteins, and all sorts of other biologically significant chemicals can be modeled with Lewis structures not dramatically more complex than the several we've drawn here. This fact suggests the strength and utility of Lewis structures in general. A stepwise procedure that adequately generates models of both a simple and complex nature has deservedly become one of the fundamental backbones of chemistry.

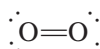
### 9-4.2 Exceptions to the Octet Rule

The octet rule is very useful in describing the bonding in most compounds of the representative elements. A significant number of compounds, however, do not follow the octet rule. For example, some molecules have an odd number of valence electrons, such as nitric oxide (NO—11 valence electrons) and nitrogen dioxide ( $\text{NO}_2$ —17 valence electrons). In both of these cases the nitrogen has access to fewer than 8 electrons. *When there are an odd number of electrons in a molecule it is known as a free radical.* It turns out that free radicals such as these are very reactive because they are missing the stability associated with a filled octet and paired electrons.

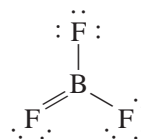
In other molecules, a Lewis structure may be written that follows the octet rule, but other evidence suggests that the situation is more complex. For example, the ordinary  $\text{O}_2$  molecule with 12 valence electrons could be written with a double bond as shown below. This representation implies that all electrons are in pairs. However, we know from experiments that  $\text{O}_2$  is also a free radical with two unpaired electrons. We just need to remember that the Lewis structure is simply the representation of a theory; in the case of  $\text{O}_2$ , the theory doesn't work perfectly. There are other theories of bonding that explain the case of  $\text{O}_2$  quite well, although these theories are more complicated. Another example of the conflict between theory and experiments is illustrated by the molecule  $\text{BF}_3$ . Experiments indicate that the B—F bond has little to no double-bond character. Thus, the correct structure shows the boron with access to only 6 electrons.



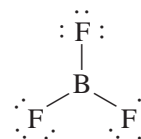
A correct Lewis representation that *does not* follow octet rule



A Lewis representation of  $\text{O}_2$  that *does not* correspond with experiments



A Lewis representation of  $\text{BF}_3$  that *does not* correspond with experiments



A Lewis representation of  $\text{BF}_3$  that *does* correspond with experiments

There are a significant number of compounds involving representative elements where the central atoms are in the third and higher periods. In some of these compounds the central atom has access to more than eight electrons (e.g.,  $\text{SF}_4$  and  $\text{ClF}_5$ ). The bonding in these compounds will not be discussed in this text.

#### ASSESSING THE OBJECTIVE FOR SECTION 9-4

**EXERCISE 9-4(a) ANALYSIS:** Draw Lewis structures for the following.

- (a)  $\text{SF}_2$   
 (b)  $\text{NO}_2\text{Cl}$  (with N as the central atom)  
 (c)  $\text{Mg}(\text{ClO}_2)_2$

**EXERCISE 9-4(b) ANALYSIS:** Draw Lewis structures for the following.

- (a) HCN    (b)  $\text{C}_2\text{H}_4$     (c)  $\text{PO}_3^{3-}$

**EXERCISE 9-4(c) SYNTHESIS:** Two compounds of oxygen are named oxygen difluoride and dioxygen difluoride. Write the Lewis structures of these two compounds. (The latter compound contains an O—O bond.) Oxygen is usually written and named second in binary compounds. Why not here?

*For additional practice, work chapter problems 9-33, 9-34, and 9-35.*



## 9-5 RESONANCE STRUCTURES

## OBJECTIVES FOR SECTION 9-5

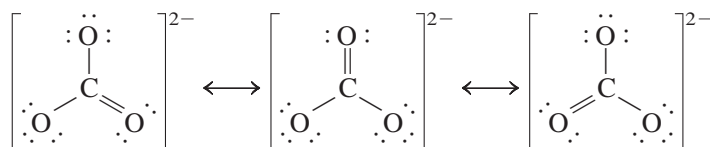
(a) Discuss the significance of resonance. (b) Write resonance structures of appropriate molecules or ions.



**LOOKING AHEAD!** Glance again at the Lewis structure of the carbonate ion shown in Example 9-4. The structure that is displayed implies that the three carbon–oxygen bonds are not all identical in that one bond is double and the other two are single. Is that true? Actually, the answer is no, but we need to explore this phenomenon in more detail. ■

If we compare a double bond to a single bond between the same two elements, we find there are significant differences. The sharing of four electrons holds two atoms together more strongly, and thus more closely, than the sharing of two electrons. Likewise, a triple bond is even stronger and shorter than a double bond. The one Lewis structure of the  $\text{CO}_3^{2-}$  ion, shown in Example 9-4, implies that one carbon–oxygen bond is shorter and stronger than the other two. We know from experiment, however, that the ion is perfectly symmetrical, meaning that all three bonds are identical and just as likely to contain the extra electrons. Experiments also tell us that the lengths of the three identical bonds are somewhere between those expected for a single and a double bond.

One Lewis representation of the  $\text{CO}_3^{2-}$  ion does not convey this information, but three representations (connected by double-headed arrows) illustrate that all three bonds are just as likely to be a double bond. *The three structures as shown below are known as resonance structures.* The actual structure of the molecule can be viewed as a **resonance hybrid**, or average, of the three structures.



Resonance structures exist for molecules where equally correct Lewis structures can be written without changing the basic skeletal geometry or the position of any atoms. An example of a molecule with resonance structures is a form of elemental oxygen known as ozone ( $\text{O}_3$ ). (Different forms of the same element are known as *allotropes*.) Ozone has very different properties than the other allotrope of oxygen,  $\text{O}_2$ , which maintains life. Ozone is a critical component in the stratosphere because it absorbs ultraviolet light from the sun. The resonance structures of ozone are illustrated in the following example.

## EXAMPLE 9-6

## Writing Resonance Structures

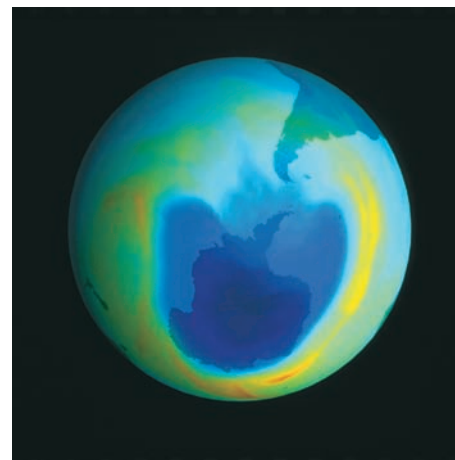
Write a Lewis structure and any equivalent resonance structures for ozone ( $\text{O}_3$ ), where one oxygen serves as the central atom.

## PROCEDURE

Follow the procedure for writing Lewis structures. When the time comes to form double or triple bonds, draw all possibilities separately, and connect the structures with double-headed arrows.

## SOLUTION

1. No ions are involved.
2. There are 18 ( $3 \times 6$ ) outer electrons.



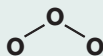
The pale blue over Antarctica (dark blue) in October 1999 shows the area of ozone depletion.

3. The skeletal structure is

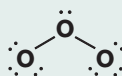


(Later in the chapter, we will discuss why we write the basic structure as bent rather than linear.)

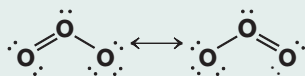
4. Use 4 electrons for the two bonds.



5. Add the remaining 14 electrons.



6. Notice that the central oxygen does not have an octet. A double bond must be made from one of the outer oxygen atoms. Notice that it doesn't matter which oxygen is chosen; the two structures are equivalent. Draw both possibilities, which are the two resonance structures. The resonance structures indicate that each oxygen–oxygen bond is a hybrid between a single and a double bond.



### ANALYSIS

Molecules with double or triple bonds somewhere in the structure have the possibility of resonance. Once the skeletal structure is in place, see if the double or triple bonds can be placed in the structure in more than one way to make a valid Lewis structure. If so, the molecule has resonance structures.

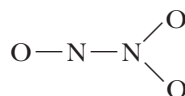
### SYNTHESIS

Resonance is an important concept for chemists because it is used to explain many observations in the lab. For example, it is found that molecules and ions that have resonance structures are inherently more stable than molecules that do not. Where normal bonds hold only two atoms together (the two that share the electrons), the electrons used in resonating bonds can hold three, four, or more atoms together at the same time. A chain is only as strong as its weakest link, and a molecule is only as stable as its weakest bond. A bond is stronger if it is halfway between a single and a double bond rather than just a single bond. Chemists often invoke resonance to explain why some molecules' formation is more favorable than others. When the choice is between two, the one that has resonance is highly favored.

The word *resonance* is often associated with vibration or a constantly changing situation. That concept can be misleading in this case. The two oxygen–oxygen bonds in ozone are not changing rapidly back and forth between a single and a double bond. In fact, both bonds exist *at all times* as intermediate between a single and a double bond. It is much like a large, sweet hybrid tomato that you grow in the garden or buy in the grocery store. This tomato is a hybrid of a large tomato and a small but sweet tomato. It isn't changing rapidly back and forth between these two forms but has properties intermediate between the two original species of tomatoes. When we view resonance structures, we try to visualize the molecule as a combination of the two or more structures. This is analogous to trying to taste the hybrid tomato by combining a piece of the large tomato with a piece of the small, sweet tomato in your mouth at the same time.

### ASSESSING THE OBJECTIVES FOR SECTION 9-5

**EXERCISE 9-5(A) ANALYSIS:** Draw four resonance structures for  $\text{N}_2\text{O}_3$ . Notice that not all these structures are equivalent. The skeletal structure is



**EXERCISE 9-5(B) ANALYSIS:** Which of the following molecules have resonance structures?

- (a) HCN    (b) SO<sub>2</sub>    (c) PCl<sub>3</sub>    (d) OCN<sup>-</sup>

**EXERCISE 9-5(C) SYNTHESIS:** A possible Lewis structure for CO<sub>2</sub> involves a triple bond and a single bond between C and the O's. Write the two resonance structures involving the triple bond. What is implied about the nature of the C—O bond by these two structures? How does this relate to the common Lewis structure for CO<sub>2</sub> involving two double bonds?

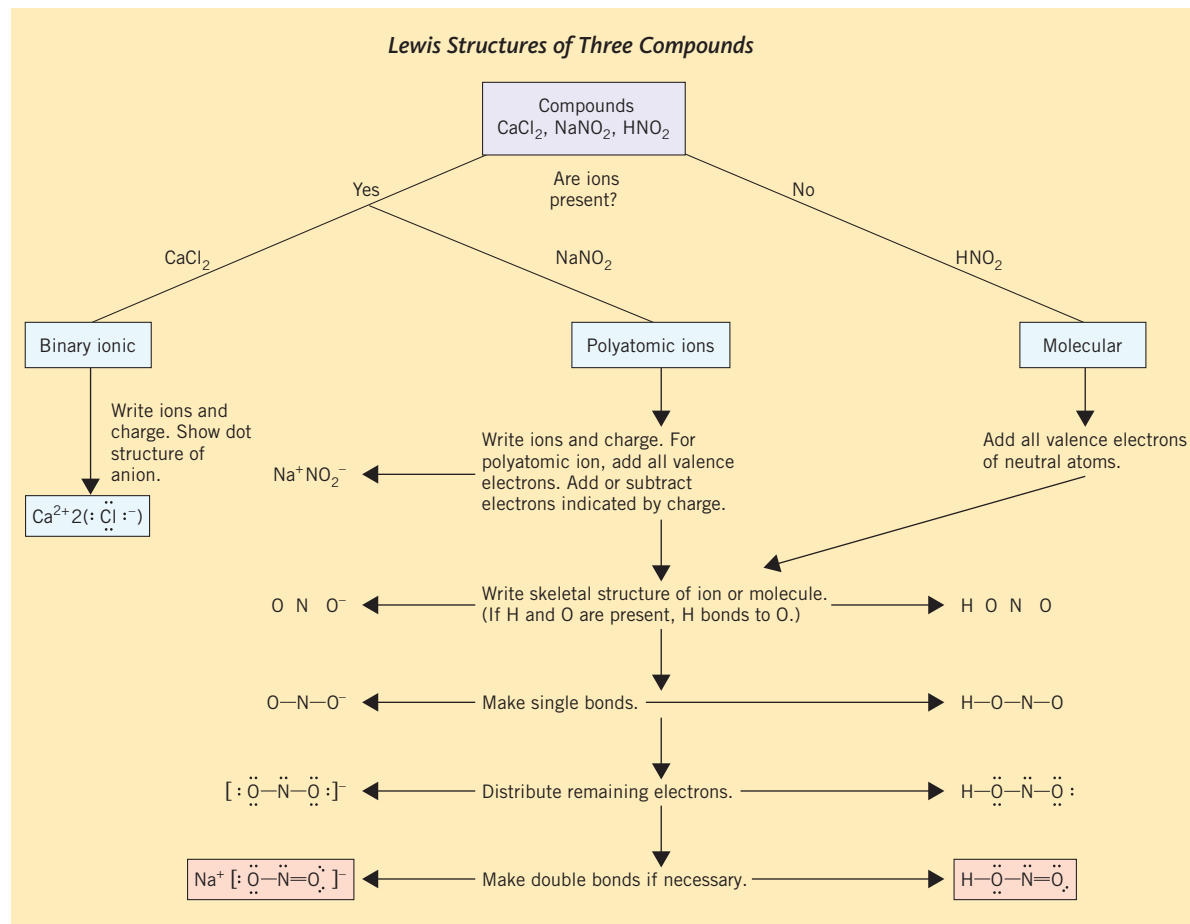
For additional practice, work chapter problems 9-42, 9-43, and 9-46.

## PART B SUMMARY

### KEY TERMS

- 9-3.1** A **covalent bond** between two atoms consists of a shared pair of electrons and is represented as a dash in a **Lewis structure**. pp. 260–261
- 9-3.4** Two pairs of electrons are shared in a **double bond** and three pairs are shared in a **triple bond**. p. 263
- 9-4.2** A **free radical** is a molecule with unpaired electrons. p. 268
- 9-5** **Resonance structures** indicate the presence of a **resonance hybrid** structure. p. 269

### SUMMARY CHART



**PART C**  
**THE DISTRIBUTION OF  
 CHARGE IN CHEMICAL  
 BONDS**

**SETTING A GOAL**

- You will learn how the correct Lewis structure of a compound allows chemists a thorough understanding of its properties.

**OBJECTIVES**

- 9-6** Classify a bond as being nonpolar, polar, or ionic.
- 9-7** Determine the bond angles and geometries present in simple molecules or ions from the Lewis structure.
- 9-8** Classify a molecule as polar or nonpolar based on geometry and electronegativity.
- 9-9** Determine the validity of a Lewis structure based on formal charge considerations. (Optional)

**OBJECTIVE FOR  
 SECTION 9-6**

Classify a bond as being nonpolar, polar, or ionic.

**9-6 ELECTRONEGATIVITY AND POLARITY  
 OF BONDS**



**LOOKING AHEAD!** In the formation of a covalent bond, electrons are shared. However, atoms of different elements rarely share electrons equally in a covalent bond. This unequal sharing leads to a partial charge, as we will see in this section. ■

**9-6.1 Electronegativity**

You are probably aware that *sharing* a carton of popcorn at a movie rarely means *equal sharing*. The hungrier, faster popcorn eater usually gets the lion's share.

Likewise, in a chemical bond between the atoms of two different elements, the pair of electrons is not shared equally, and one atom gets a larger share of the electrons. *The ability of an atom of an element to attract electrons to itself in a covalent bond is known as the element's electronegativity.* The value assigned for the electronegativity of many elements is shown in Figure 9-5. The most electronegative element is fluorine, which is assigned an electronegativity value of 4.0. Notice that nonmetals tend to have higher values of electronegativity than metals. The values shown in Figure 9-5 were first calculated by Linus Pauling (winner of two Nobel Prizes). Although more refined values are now available, the actual numbers are not as important as how the electronegativity of one element compares with that of another.

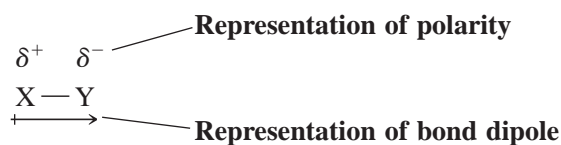
|             |                 |                 |                 |                 |                 |                 |                 |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|             | Increases →     |                 |                 |                 |                 |                 |                 |
| Decreases ↓ | 1<br>H<br>2.1   |                 |                 |                 |                 |                 |                 |
|             | 3<br>Li<br>1.0  | 4<br>Be<br>1.5  | 5<br>B<br>2.0   | 6<br>C<br>2.5   | 7<br>N<br>3.0   | 8<br>O<br>3.5   | 9<br>F<br>4.0   |
|             | 11<br>Na<br>0.9 | 12<br>Mg<br>1.2 | 13<br>Al<br>1.5 | 14<br>Si<br>1.8 | 15<br>P<br>2.1  | 16<br>S<br>2.5  | 17<br>Cl<br>3.0 |
|             | 19<br>K<br>0.8  | 20<br>Ca<br>1.0 | 31<br>Ga<br>1.6 | 32<br>Ge<br>1.8 | 33<br>As<br>2.0 | 34<br>Se<br>2.4 | 35<br>Br<br>2.8 |
|             | 37<br>Rb<br>0.8 | 38<br>Sr<br>1.0 | 49<br>In<br>1.7 | 50<br>Sn<br>1.8 | 51<br>Sb<br>1.9 | 52<br>Te<br>2.1 | 53<br>I<br>2.5  |
|             | 55<br>Cs<br>0.7 | 56<br>Ba<br>0.9 | 81<br>Tl<br>1.8 | 82<br>Pb<br>1.8 | 83<br>Bi<br>1.9 | 84<br>Po<br>2.0 | 85<br>At<br>2.2 |
|             | 87<br>Fr<br>0.7 | 88<br>Ra<br>0.9 |                 |                 |                 |                 |                 |

**FIGURE 9-5** Electronegativity

**9-6.2 Representing Polar Bonds**

Electrons carry a negative charge. When there is a complete exchange of an electron between atoms, as in the formation of an ionic bond, one atom acquires a full negative charge. In a covalent bond between two atoms of different electronegativity, the more electronegative atom attracts the electrons in the bond partially away from the other atom and thus acquires a *partial* negative charge (symbolized by  $\delta^-$ ). This leaves the less electronegative atom with a partial positive charge (symbolized by  $\delta^+$ ).

A covalent bond that has a partial separation of charge due to the unequal sharing of electrons is known as a **polar covalent bond** (or simply, a **polar bond**). A polar bond has a negative end and a positive end and is said to contain a **dipole** (two poles). A polar bond is something like Earth itself, which contains a magnetic dipole with a north and south magnetic pole. (The poles in a bond dipole are electrostatic rather than magnetic.) The dipole of a bond is represented by an arrow pointing from the positive to the negative end ( $\leftrightarrow$ ).



The polarity of bonds has a significant effect on the chemical properties of compounds. For example, the polarity of the H—O bonds in water accounts for many of its familiar properties that we take for granted. We will discuss the chemistry of water in more detail in Chapter 11.

### 9-6.3 Predicting the Polarity of Bonds

When electrons are shared between atoms of the same element, they are obviously shared equally. *If electrons are shared equally, the bond is known as a nonpolar bond.* The greater the difference in electronegativity between two elements, the more polar the bond between them. In fact, if the difference in electronegativity is 1.8 or greater on the Pauling scale, it indicates that one atom has gained complete control of the pair of electrons. In other words, the bond is most likely ionic.

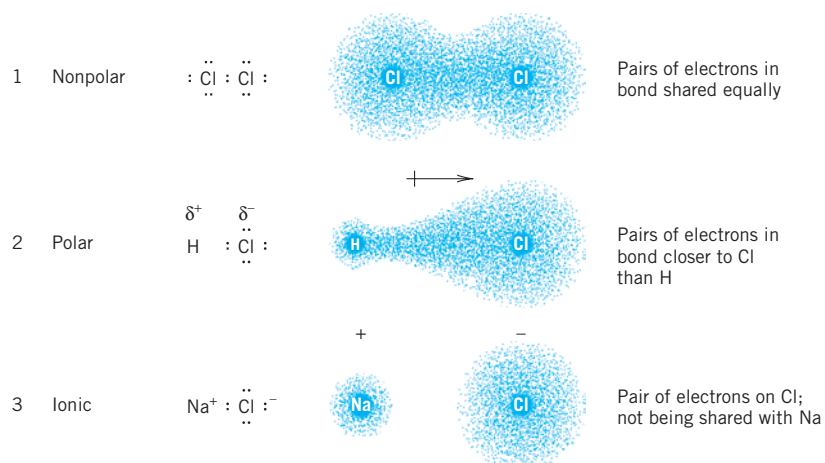
In summary, when two atoms compete for a pair of electrons in a bond, there are three possibilities for the pair of electrons.

1. Both atoms share the electrons equally, forming a nonpolar bond (an electronegativity difference between the two atoms of zero or near zero).
2. The two atoms share electrons unequally, forming a polar bond. This is intermediate between purely ionic and equal sharing (an electronegativity difference of less than 1.8).
3. The electron pair is not shared, since one atom acquires the electrons. This is an ionic bond, in which each atom acquires a complete charge (an electronegativity difference greater than about 1.8).

These three cases are illustrated in Figure 9-6. The bond in Cl<sub>2</sub> is nonpolar (case 1), since both atoms are identical. To determine the charge on each Cl, we will assign electrons to the two Cl atoms. In this case, each Cl is assigned the six electrons from its three lone pairs. Since the two atoms share the pair evenly, we can assign exactly one-half of the shared electrons to each Cl for a total of seven each [ $6 + (1/2 \times 2) = 7$ ]. Since Cl is in Group VIIA, seven valence electrons leave each Cl exactly neutral. Thus there is not a positive and a negative end.

The molecule HCl illustrates case 2. There is a significant difference in electronegativity between H and Cl (0.9), indicating a polar bond, but not so much as to indicate an ionic bond. Since the Cl is more electronegative than H, it has a partial negative charge. In this case, the Cl is still assigned six electrons from its three lone pairs but more than one-half of the pair of electrons in the bond. Since it is assigned more than seven electrons but less than eight, it acquires a *partial negative charge*. The hydrogen, with less than one-half of the electron pair, has fewer than one electron and thus has an equal but opposite *partial positive charge*. On the other hand, the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is relatively small (0.4), so the bond is considered essentially nonpolar. The nonpolar nature of the C—H bond is an important concept in the chemistry of the compounds of life.

The bond in NaCl illustrates case 3. As mentioned earlier in this chapter, there is a complete exchange of the valence electron from Na to Cl, producing charged



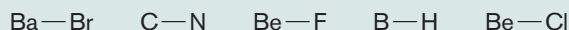
**FIGURE 9-6 Nonpolar, Polar, and Ionic Bonds** In case 1, the bond is nonpolar covalent; in case 2, the bond is polar covalent; in case 3, the bond is ionic.



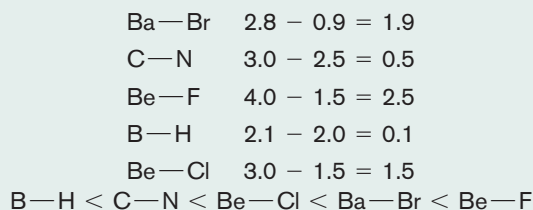
ions. Eight electrons on Cl form an anion with a  $-1$  charge. Notice that the difference in electronegativity between Na and Cl is large (2.1), predicting an ionic nature.

**EXAMPLE 9-7****Comparing the Polarity of Bonds**

Referring to Figure 9-5, rank the following bonds in order of increasing polarity. The positive end of the dipole is written first. On the basis of electronegativity differences, indicate whether any of the bonds are predicted to be ionic.

**PROCEDURE**

Determine the difference in electronegativity between the elements. The smaller the difference, the less polar the bond. Higher differences make the bonds more ionic.

**SOLUTION****ANALYSIS**

The differences in electronegativity suggest that Ba—Br and Be—F have ionic bonds. Notice that the difference in electronegativity suggests that the Be—Cl bond is polar covalent rather than ionic. This is confirmed by a profound difference in the physical properties of Be compounds containing these two bonds. Despite being a binary compound between a metal and a nonmetal, the  $\text{BeCl}_2$  species has a molecular nature rather than an ionic one.

**SYNTHESIS**

It is important to realize that the distinctions nonpolar, polar, and ionic do not represent three cut-and-dried ways of sharing electrons, but rather a continuum of increasingly unequal sharing from the even 50/50 sharing found in purely nonpolar molecules all the way to the 100/0 sharing (or lack of it) found in the most ionic substances—and everything in between. While we give approximate cutoffs for electronegativity differences between polar and ionic bonds, these are guidelines only. Two elements whose difference is 1.5, for example, can be expressed as having a certain amount of ionic character and a certain amount of covalent character. Experimental evidence is the final arbiter.

**ASSESSING THE OBJECTIVE FOR SECTION 9-6**

**EXERCISE 9-6(a) KNOWLEDGE:** Fill in the blanks.

The most electronegative element is: \_\_\_\_\_. The second most electronegative element is: \_\_\_\_\_. In a covalent bond between unlike atoms, the more electronegative element has a partial \_\_\_\_\_ charge. This type of bond is said to be a \_\_\_\_\_ covalent bond. A large difference in electronegativity between two atoms leads to an \_\_\_\_\_ bond.

**EXERCISE 9-6(b) ANALYSIS:** Indicate with a dipole arrow from the partially positive atom to the partially negative atom if any of these bonds is polar.



**EXERCISE 9-6(c) ANALYSIS:** Based on electronegativity differences, label each bond as being nonpolar, polar, or ionic.



**EXERCISE 9-6(d) SYNTHESIS:** Explain how differences in electronegativity play a role in whether a bond is ionic, nonpolar covalent, or polar covalent.

*For additional practice, work chapter problems 9-48, 9-48, 9-51, and 9-52.*

## 9-7 GEOMETRY OF SIMPLE MOLECULES

## ▶ OBJECTIVE FOR SECTION 9-7

Determine the bond angles and geometries present in simple molecules or ions from the Lewis structure.

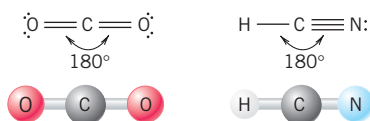


**LOOKING AHEAD!** Because the covalent bonds in most molecules are polar, does that mean the molecule itself is polar? Surprisingly, the answer is not necessarily. The polarity of a molecule depends on its geometry as well as the polarity of its bonds. In this section, we will use Lewis structures to tell us about the geometry of some simple molecules and then use this information to discuss molecular polarity in the next section. ■

## 9-7.1 VSEPR Theory

Every blink of the eye requires the action of a certain enzyme (a protein) in our body. An enzyme may interact with a specific receptor site in a muscle like a specific key fits into a lock. Like a key, the action of an enzyme is determined by its configuration, or geometry. Consider also ordinary water. If water were a linear molecule rather than bent, this would drastically affect its properties. For example, water would be a gas at room temperature rather than a liquid. Life as we know it could not exist under those conditions. When properly interpreted, however, the Lewis structure of water indicates its bent nature. The approximate geometry of the atoms around a central atom can be predicted by the **valence shell electron-pair repulsion theory (VSEPR)**. *This theory tells us that electron pairs, either unshared pairs or electrons localized in a bond, repel each other to the maximum extent.* In other words, the negatively charged electron groups get as far away from each other as possible (without breaking the bonds) because of their electrostatic repulsion. *The geometry assumed by the unshared electron pairs and the electrons in the bond is known as the **electronic geometry**.*

Consider the  $\text{CO}_2$  molecule. Its Lewis structure indicates two double bonds to each of the two oxygen atoms. There are two groups of electrons surrounding the carbon, with each group containing four electrons. To place the two groups as far apart as possible, the electrons in the bonds must lie on opposite sides of the carbon atom at an angle of  $180^\circ$ . This creates an electronic geometry of the molecule that is said to be *linear*. Another linear molecule is HCN, shown below. Notice that *double and triple bonds are treated the same as single bonds when determining the geometry of a molecule.* That is, all three types of bonds are counted as one group of electrons (even though double and triple bonds constitute larger groups).



The  $\text{BF}_3$  molecule has three groups of electrons. In this case, the three groups get as far away from each other as possible by assuming the geometry of an equilateral triangle with an  $\text{F}-\text{B}-\text{F}$  angle of  $120^\circ$ . The electronic geometry of this molecule is said to be *trigonal planar*.

Finally, consider the molecule  $\text{CH}_4$ . This molecule consists of four bonds around the central atom, the most for a molecule following the octet rule. The farthest apart four groups of electrons can move is a three-dimensional structure called a *tetrahedron* with an internal angle of  $109.5^\circ$ .

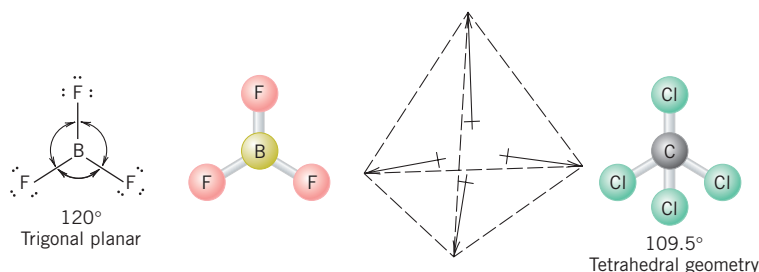


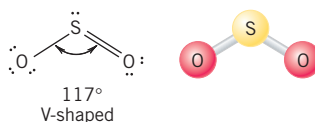
TABLE 9-2 Electronic Geometries

| NUMBER OF ELECTRON GROUPS | ELECTRONIC GEOMETRY | BOND ANGLE |
|---------------------------|---------------------|------------|
| 2                         | linear              | 180°       |
| 3                         | trigonal planar     | 120°       |
| 4                         | tetrahedral         | 109.5°     |

The electronic geometry of a molecule, then, is directly related to the number of groups surrounding the central atom of a molecule. The three electronic geometries discussed are listed in Table 9-2.

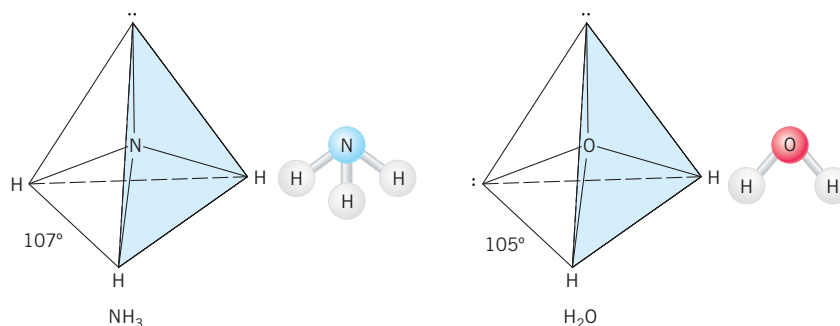
### 9-7.2 Molecular Geometry

Now consider molecules where there are one or two unshared electron pairs in place of covalent bonds. The  $\text{SO}_2$  molecule, which has three electron groups, has the same electronic geometry as  $\text{BF}_3$ , described above. The central sulfur atom is bonded to two oxygen atoms, and it has one unshared pair of electrons. (Remember that the two  $\text{S}-\text{O}$  bonds are actually identical, since two resonance structures can be written.) The  $\text{O}-\text{S}-\text{O}$  angle is approximately that of an equilateral triangle. *The molecular geometry of a molecule is the geometry described by the bonded atoms and does not include the unshared pairs of electrons.* Thus we describe the molecular geometry of the three atoms in  $\text{SO}_2$  as *V-shaped* or *bent*.




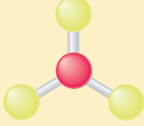
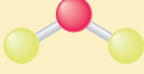
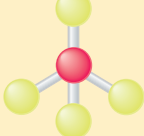
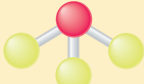

Ammonia ( $\text{NH}_3$ ) has four groups of electrons, so it has the same electronic geometry as  $\text{CH}_4$ . In the case of  $\text{NH}_3$ , however, one group is an unshared pair of electrons. The  $\text{H}-\text{N}-\text{H}$  angle is found to be  $107^\circ$ , which is in good agreement with the angle predicted by this theory. (The angle is somewhat less than  $109^\circ$  because lone pairs of electrons take up more space than bonded pairs.) The molecular geometry of the  $\text{NH}_3$  molecule is described as *trigonal pyramidal*. Finally, the familiar  $\text{H}_2\text{O}$  molecule also has four groups but with two unshared pairs of electrons. The  $\text{H}-\text{O}-\text{H}$  angle is known to be  $105^\circ$ , which also agrees with this theory. The molecular geometry of  $\text{H}_2\text{O}$  is described as *V-shaped* or *bent*. (In the V-shaped structure of  $\text{SO}_2$ , the angle of  $117^\circ$  is near the expected trigonal angle of  $120^\circ$ ; in the V-shaped structure of  $\text{H}_2\text{O}$ , the angle of  $105^\circ$  is near the tetrahedral angle of  $109^\circ$ .)

Notice that when a molecule has no unshared electrons, the electronic and molecular geometry are the same. *When discussing the geometry of a molecule in the future, however, we will be referring to the molecular geometry.*



The molecular geometries for all of these molecules are summarized in Table 9-3.

**TABLE 9-3** Molecular Geometry

| NUMBER OF ELECTRON GROUPS ON CENTRAL ATOM (BONDED ATOMS + UNSHARED PAIRS) | NUMBER OF ATOMS BONDED TO CENTRAL ATOM | NUMBER OF UNSHARED PAIRS OF ELECTRONS ON CENTRAL ATOM | MOLECULAR GEOMETRY   | MODEL   |
|---|--|---|----------------------|---|
| 2   | 2                                      | 0   | linear               |  |
| 3   | 3                                      | 0   | trigonal planar      |  |
| 3   | 2                                      | 1   | V-shaped (near 120°) |  |
| 4   | 4                                      | 0   | tetrahedral          |  |
| 4   | 3                                      | 1   | trigonal pyramidal   |  |
| 4   | 2                                      | 2   | V-shaped (near 109°) |  |

**EXAMPLE 9-8**
**Predicting the Geometry of Molecules**

What is the electronic and molecular geometry of each of the following ions and molecules?

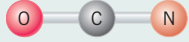
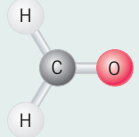
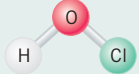
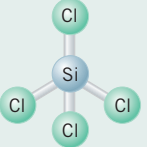
(a)  $\text{OCN}^-$     (b)  $\text{H}_2\text{CO}$     (c)  $\text{HClO}$     (d)  $\text{SiCl}_4$

In (a) and (b), the middle atom in the formula is the central atom. In (c), oxygen is the central atom.

**PROCEDURE**

First write the correct Lewis structure. Then count the number of electron groups [bonded atoms (connected to the central atom) + the number of unshared pairs of electrons]. This provides the electronic geometry. For atoms with unshared electron pairs on the central atom, evaluate the molecular geometry as well.

**SOLUTION**

|                           | LEWIS STRUCTURE  | NUMBER OF ELECTRON GROUPS | MOLECULAR GEOMETRY   |
|---------------------------|--|---------------------------|--|
| (a) $\text{OCN}^-$        | $\text{:}\ddot{\text{O}}=\text{C}=\text{N:}^-$   | 2                         | linear ( $180^\circ$ )    |
| (b) $\text{H}_2\text{CO}$ | $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\ddot{\text{O}} \\ \diagup \\ \text{H} \end{array}$  | 3                         | trigonal planar           |
| (c) $\text{HClO}$         | $\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}:$   | 4                         | V-shaped ( $109^\circ$ )  |
| (d) $\text{SiCl}_4$       | $\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \\   \\ \text{:}\ddot{\text{Cl}}-\text{Si}-\ddot{\text{Cl}}\text{:} \\   \\ \text{:}\ddot{\text{Cl}}\text{:} \end{array}$ | 4                         | tetrahedral               |

**ANALYSIS**

The molecular geometries where there are unshared pairs of electrons are best reasoned out rather than memorized. Learn and picture the three basic electronic geometries, and then ask yourself what shape is left as one or two bonds are “removed” from the geometry (and replaced with an unshared pair). The resulting molecular geometries readily become apparent.

Also, consider the answer in (d) above. Based on electron repulsions, what’s the farthest apart that four groups of electrons should be able to get? Many students’ immediate response is  $90^\circ$ , which is  $360^\circ$  divided by 4. This would be a square plane with a central atom. What we fail to realize is that all three dimensions are in play, and the bonds can actually spread out even farther than that. In three-dimensional space, the maximum bond angle that can be achieved is  $109.5^\circ$ , and the electronic geometry created is described as tetrahedral, a result directly from Euclidean geometry.

**SYNTHESIS**

While it is beyond the scope of this book to provide a detailed description of geometries resulting from molecules with more than an octet of electrons, a quick look into one possible geometry is instructive as regards the application of VSEPR theory. What should the bond angles be for a molecule with six pairs of electrons on a central atom? What’s the farthest apart you can place six groups on a sphere? The answer is along each of the three mathematical axes, the  $x$ ,  $y$ , and  $z$ . These axes are  $90^\circ$  apart from each other, and so we’d predict  $90^\circ$  bond angles in the molecule. What would the *molecular* geometries look like for one or two sets of unshared electrons in these types of molecules? Picture a three-dimensional axis, and remove one bond. That geometry is described as being *square pyramidal*. Removal of the second bond creates a *square planar* arrangement. Can you picture these structures?

**ASSESSING THE OBJECTIVE FOR SECTION 9-7**

**EXERCISE 9-7(a) KNOWLEDGE:** How many groups of electrons are found in the following, for the purpose of determining geometries? [Note: At first glance (a) may be considered as an ionic compound. However, after comparing the electronegativities of Be and Cl, you can understand that it is actually most likely a molecular compound.]



**EXERCISE 9-7(b) ANALYSIS:** From the Lewis structure, what is the bond angle in  $\text{PBr}_3$ ?

**EXERCISE 9-7(c) ANALYSIS:** What is the electronic geometry of  $\text{COCl}_2$  (C is central atom)?

**EXERCISE 9-7(d) ANALYSIS:** What is the molecular geometry of  $\text{SCl}_2$ ?

**EXERCISE 9-7(e) SYNTHESIS:** Give the bond angle and the electronic and molecular geometries for the following.



For additional practice, work chapter problems 9-57, 9-58, and 9-60.

**OBJECTIVE FOR SECTION 9-8**

Classify a molecule as polar or nonpolar based on geometry and electronegativity.

**9-8 POLARITY OF MOLECULES**

**LOOKING AHEAD!** A molecule such as  $\text{CO}_2$  is composed of two polar bonds, but the molecule itself is nonpolar. This sounds contradictory, but it is actually predictable. We will unite our discussion of bond polarity and geometry in this section of the chapter to discuss the polarity of the entire molecule. ■

When a person pushes on a table, how easily or quickly it moves and in what direction depends on the force applied. A polar bond in a molecule can also be



considered a force with both direction and magnitude. The magnitude of the force of the polar bond depends on the degree of polarity, which relates to the difference in electronegativity of the two atoms in the bond. The greater the difference in electronegativities, the greater the partial charges on the two atoms in the bond and the larger the magnitude of the dipole.

### 9-8.1 Nonpolar Molecules

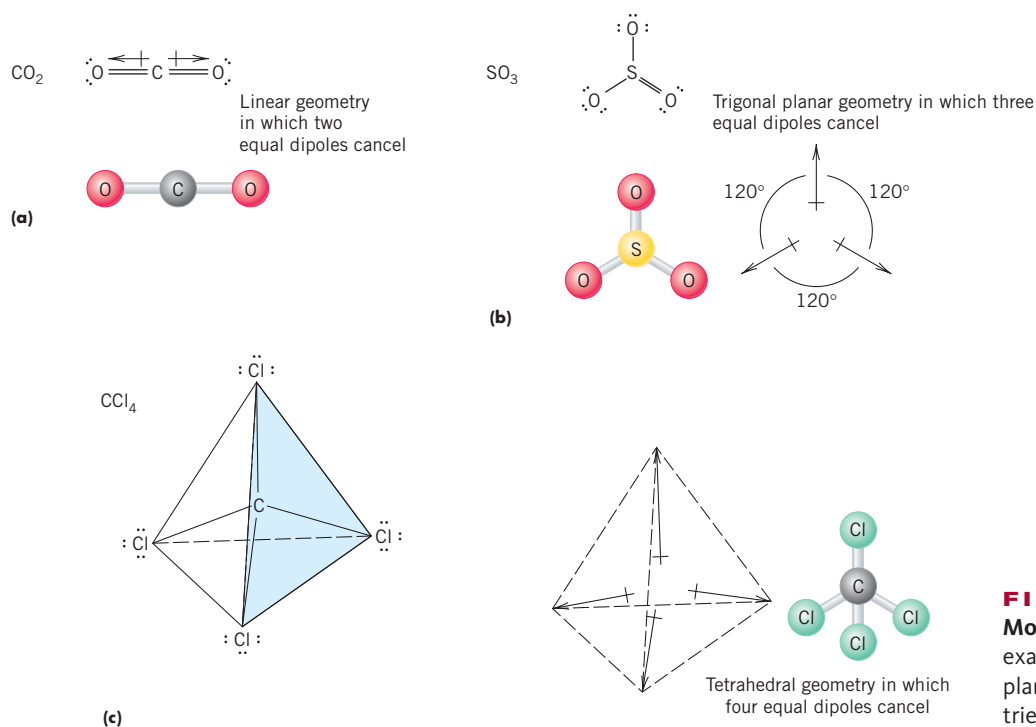
Force has direction as well as magnitude. Consider what would happen if someone of exactly equal strength was pushing on the table described above in exactly the opposite direction (i.e., an angle of  $180^\circ$ ). The two forces would exactly cancel and there would be no movement of the table. In such a shoving match, it would be a standoff. In a molecule, *the combined effects of the bond dipoles (the net dipole) are known collectively as the molecular dipole*. If the geometry of the molecule is such that equal dipoles cancel, *there is no molecular dipole, which means that the molecule is nonpolar*. For example, in  $\text{CO}_2$  the bond dipoles are equal and are orientated in exactly opposite directions.  $\text{CO}_2$  is thus a nonpolar molecule. The same is true for trigonal planar (e.g.,  $\text{BF}_3$ ) and tetrahedral molecular geometries (e.g.,  $\text{CCl}_4$ ), where all terminal atoms are the same. (See Figure 9-7.)

A molecule is also nonpolar if it is made entirely of nonpolar bonds, regardless of its geometry. Since we view the  $\text{C}-\text{H}$  bond as being essentially nonpolar, then any molecule composed entirely of carbon and hydrogen (a *hydrocarbon*) needs to be considered nonpolar as well. This fact is very important in the chemistry of living systems.

### 9-8.2 Polar Molecules

Polar molecules occur when the dipole forces do not cancel. There are two reasons that the dipole forces do not cancel.

(1) The molecule has a symmetrical geometry (i.e., linear, trigonal pyramid, or tetrahedral), but the terminal atoms are not all the same. This would be the case where two people of different strengths were in a tug of war. The stronger predominates, and the weaker is forced to move in the direction opposite to the force he or she is



**FIGURE 9-7 Nonpolar Molecules** If resultant forces exactly cancel in linear (a), trigonal planar (b), and tetrahedral geometries (c), the molecule is nonpolar.

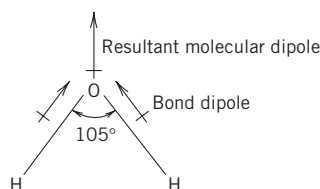
applying. For example, HCN is linear and  $\text{CHCl}_3$  (chloroform) is tetrahedral, but both molecules are polar because the unequal dipoles in the bonds do not cancel.



(2) The geometry of the molecule is V-shaped or trigonal pyramid. The geometry of the molecule leads to forces that do not cancel. Such a thing occurs in V-shaped or trigonal pyramidal molecules regardless of the identity of the terminal atoms.

In the analogy of the forces applied by two people on a table, if forces are equal but at an angle, the table will move. The direction of movement and the amount of movement depend on the strength of the two people pushing and the angle between them.

The most important example of a molecule that is polar because it is V-shaped is water. The two  $\text{O}-\text{H}$  bonds are at an angle of about  $105^\circ$ , so the equal bond dipoles do not cancel. As we will see again in later chapters, the fact that water is polar (has a molecular dipole) is of critical importance to its role as a room-temperature liquid that can dissolve many ionic compounds.



### ASSESSING THE OBJECTIVE FOR SECTION 9-8

**EXERCISE 9-8(a) ANALYSIS:** Indicate whether the following molecules are polar or nonpolar.

- (a)  $\text{CH}_2\text{Cl}_2$     (b)  $\text{NI}_3$     (c)  $\text{BeCl}_2$     (d)  $\text{SiH}_4$

**EXERCISE 9-8(b) ANALYSIS:** Rank the following molecules by increasing polarity.

- (a)  $\text{CH}_2\text{O}$     (b)  $\text{HF}$     (c)  $\text{CS}_2$     (d)  $\text{SO}_2$

**EXERCISE 9-8(c) SYNTHESIS:** One piece of evidence we have for the tetrahedral geometry for four electron pairs over a square arrangement is the polarity of molecules. Consider the molecule  $\text{CH}_2\text{F}_2$ . What is its polarity? If the square arrangement existed, when would it be polar?

For additional practice, work chapter problems 9-62, 9-63, 9-65, and 9-68.

### OBJECTIVE FOR SECTION 9-9

Determine the validity of a Lewis structure based on formal charge considerations.

## 9-9 FORMAL CHARGE (OPTIONAL)



**LOOKING AHEAD!** Sometimes a properly written Lewis structure may not actually represent the true structure of the molecule. How would we know this? It turns out that there is a way we can determine whether a structure is indeed correct. The concept of formal charges in the molecule can give us information in these cases. ■

### 9-9.1 Resonance Structures That Violate the Octet Rule

The representation of the sulfuric acid molecule ( $\text{H}_2\text{SO}_4$ ), as shown in Example 9-5, follows the octet rule quite nicely. However, if one proceeds to the study of organ-

## MAKING IT REAL

### Enzymes—The Keys of Life



Enzymes work like a lock and key.

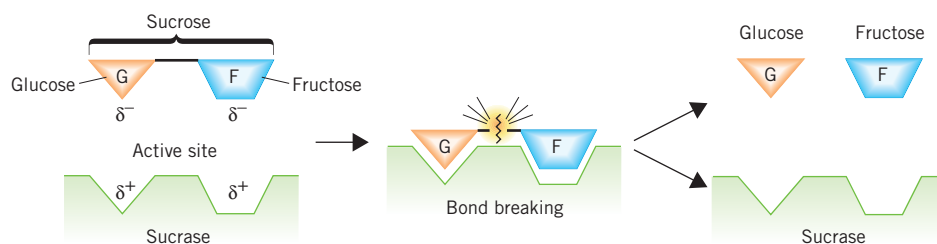
You can't blink your eye or digest a slice of pizza without the help of enzymes. Enzymes demonstrate quite dramatically the importance of geometry in how they function while doing so many jobs. Enzymes are rather complex molecules made from proteins that serve as catalysts. A catalyst is an agent that causes or speeds up a chemical reaction but is not itself consumed in the reaction. Catalysts will be discussed in more detail in later chapters. In effect, an enzyme is much like a specific key that unlocks a specific door. If the shape of the key is not exact, it does not work. The action of an enzyme in doing a particular job has to do with the geometry and polarity of a part of the molecule known as its *active site*.

Glucose, blood sugar, is the only sugar that we can use in our body in metabolism. It is used in the combustion reaction that provides the energy to keep us alive. Carbohydrates and other sugars, including sucrose (table sugar), must be broken down, or converted, into glucose before they can be used.

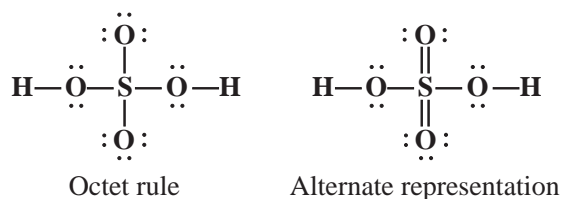
Sucrose is actually composed of two simpler sugars, fructose and glucose, chemically bonded together. An enzyme known as *sucrase* is responsible for breaking sucrose into its components. The sucrase molecule has a specific molecular geometry that is complementary to the sucrose molecule. The polarity of the bonds in the enzyme are also such that they attract the sucrose molecule so as to form an exact fit between the two geometries. The enzyme then causes the sucrose to break into its two components, which are then released. The sucrase enzyme can then seek out another sucrose molecule and repeat the process. This is illustrated in the accompanying figure. Other enzymes cause the fructose to be converted into glucose so that it, too, is used in metabolism.

Dairy products contain milk sugar (lactose), which can be broken down into its two component sugars, glucose and galactose. The enzyme that causes this reaction is known as *lactase*. However, some people are lactose intolerant, which means that they lack the lactase enzyme. To avoid discomfort, they must avoid dairy products or take a lactase tablet (i.e., Lactaid) before they can enjoy a dish of ice cream.

The list of enzymes seems endless. There is a specific enzyme in our body for every biochemical function. In fact, we are just now learning about many of the enzymes that make life possible.



ic chemistry and biochemistry, the molecule is usually represented with two double bonds in violation of the octet rule, as shown below.



Why represent the molecule in this manner? The answer is that the later structure represents a more favorable formal charge distribution. **Formal charge** is the charge that each atom in a molecule would have if the electrons in the bonds were divided equally between the two atoms. In other words, all bonds are treated as if they were nonpolar. Formal charge is a method of electron bookkeeping. It is not meant to imply that

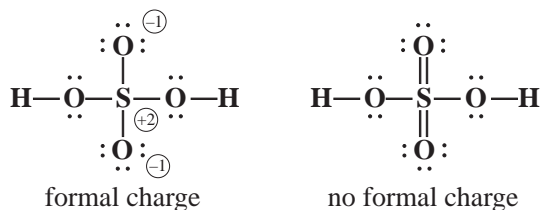
it is the actual charge on the atom in question. Formal charge is calculated by subtracting the number of lone-pair electrons on the atom in question and half of the shared electrons from the group number. (The group number represents the number of valence electrons in a neutral atom.) For example, consider the structure above, which follows the octet rule.

The formal charge on the S is  $[6 \text{ (group number)} - 1/2 \times 8 \text{ (four bonded pairs)}] = +2$ .

The two O atoms bonded to both S and H have formal charges of zero [i.e.,  $6 - 4 \text{ (two lone pairs)} - 1/2 \times 4 \text{ (two bonded pairs)} = 0$ ].

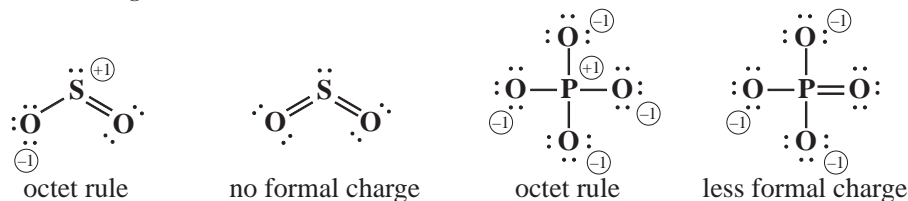
The two O atoms bonded only to S each have a formal charge of  $-1$  [i.e.,  $6 - 6 \text{ (three lone pairs)} - 1/2 \times 2 \text{ (one bonded pair)} = -1$ ].

The formal charge is represented as the charge in a circle, as follows. Zero formal charge is not shown. *All the formal charges add to zero for a molecule or to the charge on an ion.*



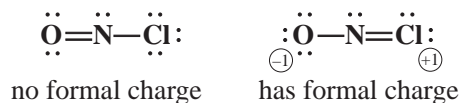
Now consider the alternate structure. None of the atoms have any formal charge; that is, for the S,  $6 - 1/2 \times 12 = 0$ , and for the O atoms with double bonds,  $6 - 4 \text{ (two lone pairs)} - 1/2 \times 4 \text{ (two bonded pairs)} = 0$ . The other two oxygen atoms also have no formal charge. Many chemists consider the structure with the least amount of formal charge to be the more favorable structure. The point remains controversial, however.

Other sulfur and phosphorus compounds are often represented by favorable formal charge structures at the expense of the octet rule. For example,  $\text{SO}_2$  and the  $\text{PO}_4^{3-}$  ion can be represented with a structure that follows the octet rule or has a favorable formal charge distribution that violates the octet rule. Note that ozone,  $\text{O}_3$  (Example 9-6), which has the same geometry as  $\text{SO}_2$ , cannot have the more favorable formal charge representation. Oxygen, which is in the second period, cannot have access to more than eight electrons. As mentioned earlier, only elements in the third period and higher can form compounds where the central atom has access to more than eight electrons.



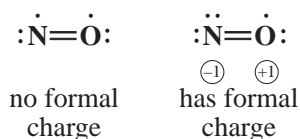
### 9-9.2 Other Applications of Formal Charge

Formal charge has one other very useful application. It can be very helpful in answering questions regarding the ordering of bonds. In other cases, it can help us decide whether a specific Lewis structure is legitimate or not. Just because we can write a structure that follows the octet rule does not necessarily mean that the structure actually represents the bonding in the molecule. For example, consider the compound nitrosyl chloride, which has the formula  $\text{NOCl}$  (despite the way it is written, N is the central atom). One can write two resonance structures for this compound.



If both were important, we would expect both bonds to have double-bond character (i.e., length). In the structure on the left, there are no formal charges on the atoms. In the structure on the right, there is a formal charge of  $-1$  on the oxygen and  $+1$  on the chlorine. Recall that structures with the least amount of formal charge are most important in determining the actual bonding. Thus, the structure with the formal charge does not represent the actual bonding in the molecule. Experiments tell us that only the structure on the left, which has an  $\text{N}=\text{O}$  double bond and an  $\text{N}-\text{Cl}$  single bond, represents the bonding in  $\text{NOCl}$ . The resonance structure on the right does not contribute to the true resonance hybrid of the molecule.

For another example of the utility of formal charge, consider the free radical  $\text{NO}$ .  $\text{NO}$  has an important role in the biological chemistry of the body. It bonds at the location of the unpaired electron. Is the unpaired electron on the nitrogen or on the oxygen atom? The structure with the least formal charge points to the answer. The Lewis structures of the two possibilities are shown below.



The structure on the left has no formal charge, indicating that the unpaired electron is on the nitrogen. Experiments indicate that this is the case.

### EXAMPLE 9-9

#### Using Formal Charge

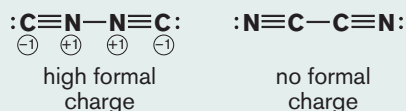
Cyanogen  $(\text{CN})_2$  is known as a *pseudohalogen* because it has some properties similar to halogens. It is composed of two  $\text{CN}$ 's joined together. Do the two  $\text{CN}$ 's join through the carbon or the nitrogen (i.e.,  $\text{C}-\text{N}-\text{C}$  or  $\text{N}-\text{C}-\text{C}-\text{N}$ )?

#### PROCEDURE

1. Draw the two Lewis structures following the rules given in Section 9-4.
2. Assign formal charges to the atoms in each structure.
3. The one with less formal charge is the actual structure.

#### SOLUTION

1. Only one structure that follows the octet rule can be written for each structure.



2. In the structure on the left, the formal charge on the C is  $2 - 1/2(6) = -1$ . The formal charge on the N is  $5 - 1/2(8) = +1$ . In the structure on the right, the formal charge on the C is  $4 - 1/2(8) = 0$ . The N also has a formal charge of zero.
3. In cyanogen, the two  $\text{CN}$ 's are bonded through the carbons.

#### ANALYSIS

With formal charge, we are determining the best distribution of electrons within a molecule. Some molecules will show formal charges regardless of how we draw them. Our task is to minimize the amount of formal charge present. The formal charges on all the atoms of a molecule will add to the charge on that molecule. So an ion such as  $\text{OCN}^-$  will show at least a single negative formal charge somewhere.

#### SYNTHESIS

Notice that whether we choose to view bonds as single or double to satisfy either the octet rule or the formal charge, it does not change our determination of molecular geometries or bond angles. How would perchlorate  $(\text{ClO}_4^-)$  look when satisfying the octet rule? How would we draw it to minimize the formal charge? What geometry do we predict for the ion in either event? It is clearly tetrahedral, regardless of how we choose to draw the bonds.



ASSESSING THE  
OBJECTIVE FOR  
SECTION 9-9

**EXERCISE 9-9(a) ANALYSIS:** In  $\text{HClO}$ , use formal charge to predict which is the central atom.

**EXERCISE 9-9(b) ANALYSIS:** In  $\text{COCl}_2$ , use formal charge to determine whether the necessary double bond is between the C and O or the C and a Cl.

**EXERCISE 9-9(c) SYNTHESIS:** Draw a Lewis structure of the molecule  $\text{SO}_2\text{Cl}_2$  (S is the central atom) that follows the octet rule and assign formal charges to the atoms. Write a second structure that does not follow the octet rule but has the best distribution of formal charge.

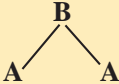
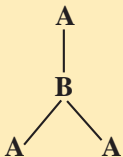
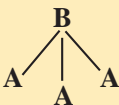
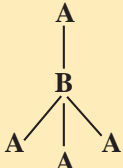
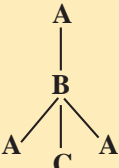
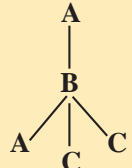
For additional practice, work chapter problems 9-69 and 9-75.

PART C  
SUMMARY

## KEY TERMS

- 9-6.1 Electronegativity** is a measure of the attraction of an atom for electrons in a bond. p. 272
- 9-6.2 Polar covalent bonds** (or simply **polar bonds**) have a **dipole** which indicates a separation of charge. p. 272
- 9-6.3 A nonpolar bond** has no charge separation. p. 273
- 9-7.1 VSEPR theory** describes the geometry around a central atom in a molecule. p. 275
- 9-7.1** The **electronic geometry** of a molecule includes both unshared pairs of electrons and electrons in bonds. p. 275
- 9-7.2** The **molecular geometry** of a specific molecule includes only the atoms involved. p. 276
- 9-8.1 A molecular dipole** is the resultant dipole of all of the bond dipoles. p. 279
- 9-9.1** Assignment of **formal charge** is useful in determining important resonance structures. p. 281

## SUMMARY CHART

| Molecular Polarity* |   |   |   |
|---------------------|---|---|---|
| Number of bonds     | Nonpolar Molecules  | Polar Molecules   |   |
| 1                   | A—A   | A—B   |   |
| 2                   | A—B—A   |  | A—B—C   |
| 3                   |  |  |   |
| 4                   |  |  |  |

\*A, B, and C represent hypothetical elements.

## CHAPTER SUMMARY

A simple observation followed by a hypothesis leads us to a solid understanding of why representative elements interact with each other as they do. The observation is that noble gas elements exist as solitary atoms, and the hypothesis is that they are that way because their electron configuration (an octet of electrons) is stable. From this we can rationalize why the representative elements adjust their electron configurations to follow the **octet rule**. For example, a metal and a nonmetal combine by an exchange of electrons, thereby achieving an octet for both.

The use of **Lewis dot symbols** of the elements aids us in focusing on the **valence electrons**. The ions formed by the electron exchange are arranged in a **lattice** held together by **ionic bonds**. Two nonmetals, on the other hand, follow the octet rule by electron sharing, forming a **covalent bond**. In certain cases, two atoms form **double bonds** or **triple bonds**. Covalent bonds also exist between the atoms comprising polyatomic ions.

| Elements          | Type of Bond | Comments   |
|-------------------|--------------|--|
| Metal–nonmetal    | Ionic        | Nonmetal can form $-1$ , $-2$ , or $-3$ ion. Metal can form $+1$ , $+2$ , or $+3$ ion. |
| Nonmetal–nonmetal | Covalent     | Single, double, or triple bonds are used to form an octet.                             |

By following certain rules, we can become proficient at writing **Lewis structures** of compounds. Not all molecules

follow these rules exactly, such as **free radicals**. Two or more equally correct Lewis structures can be written for a molecule such as ozone ( $O_3$ ), an *allotrope* of oxygen. These are known as **resonance structures**, and the actual structure is a **resonance hybrid** of all the Lewis structures.

Atoms of two different nonmetals do not share electrons equally. **Electronegativity** is a measure of the periodic property of the atoms of an element to attract the electrons in the bond. When electrons are not shared equally, the bond is **polar covalent**, or simply **polar**, and contains a **dipole**. Atoms of the same element share electrons equally, so the bond is **nonpolar**.

Whether or not a molecule is polar depends not only on the polarity of the bonds in the molecule but also on its **molecular geometry**. The **electronic geometry** and molecular geometry of simple molecules can be determined from their Lewis structures and the **VSEPR theory**. If equal polar bonds are in a geometric arrangement where their dipoles cancel each other, the compound has no **molecular dipole** and is nonpolar. If the bond dipoles are not the same in each direction or they do not cancel, the compound is polar.

Finally, the use of **formal charge** was introduced as an alternate way of representing the bonding involving sulfur and phosphorus. It also is an aid in answering questions regarding bonding that may not be obvious in writing Lewis structures.

## OBJECTIVES

| SECTION    | YOU SHOULD BE ABLE TO...   | EXAMPLES           | EXERCISES          | CHAPTER PROBLEMS               |
|------------|--|--------------------|--------------------|--------------------------------|
| <b>9-1</b> | Explain the significance of the octet rule.  |                    | 1c, 1d             | 4, 10, 12                      |
|            | Write the Lewis dot symbol of the atoms of any representative element.   |                    | 1a, 1b             | 1, 3, 11                       |
| <b>9-2</b> | Using the Lewis dot structure and the octet rule, predict the charges on the ions of representative elements and the formulas of binary ionic compounds. | 9-1                | 2a, 2b, 2c         | 7, 9, 15, 16, 20, 22           |
| <b>9-3</b> | Describe the covalent bond and how the octet rule determines the number of such bonds for simple compounds.  |                    | 3a, 3b, 3c         | 26, 27, 29                     |
| <b>9-4</b> | Draw Lewis structures of a number of molecular compounds and polyatomic ions.  | 9-2, 9-3, 9-4, 9-5 | 4a, 4b, 4c         | 32, 33, 34, 35, 36, 37, 38, 39 |
| <b>9-5</b> | Discuss the significance of resonance.   |                    | 5c                 | 43, 44                         |
|            | Write resonance structures of appropriate molecules or ions.   | 9-6                | 5a, 5b, 5c         | 40, 41                         |
| <b>9-6</b> | Classify a bond as being nonpolar, polar, or ionic.  | 9-7                | 6a, 6b, 6c, 6d     | 46, 47, 48, 49                 |
| <b>9-7</b> | Determine the bond angles and geometries present in simple molecules or ions from the Lewis structure.   | 9-8                | 7a, 7b, 7c, 7d, 7e | 53, 54, 55, 56, 57, 58         |
| <b>9-8</b> | Classify a molecule as polar or nonpolar based on geometry and electronegativity.  |                    | 8a, 8b, 8c         | 59, 60, 61, 64, 66, 68         |
| <b>9-9</b> | Determine the validity of a Lewis structure based on formal charge considerations.   | 9-9                | 9a, 9b, 9c         | 69, 70, 71, 72, 75             |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

9-1(a) (a) 3 (b) 6 (c) 8

9-1(b) (a)  $\text{Mg}\cdot$  (b)  $\cdot\dot{\text{N}}\cdot$  (c)  $\cdot\ddot{\text{I}}\cdot$

9-1(c) The eight electrons are the ones necessary to fill up the  $s(2)$  and the  $p(6)$  subshells in the valence shell of an atom.

9-1(d) The  $s(2)$ , the  $p(6)$ , and  $d(10)$  subshells hold a total 18 electrons.

9-2(a) Be, +2; As, -3.

9-2(b)  $\text{Be}_3\text{As}_2$

9-2(c) In the lattice structure of the compound, there is a 2:3 ratio of aluminum cations to oxide anions.

## PART B

## EXERCISES

9-3(a) (a) three (b) one (c) four

9-3(b) (a)  $\text{AsH}_3$  (b)  $\text{CCl}_4$  (a)  $\text{ClF}$

9-3(c) A quadruple bond actually exists in transition metals but not among the representative elements. There are various complex reasons, but, basically, the sharing of eight electrons would require too much energy.

9-4(a) (a)  $\ddot{\text{F}}-\ddot{\text{S}}-\ddot{\text{F}}:$  (b)  $\begin{array}{c} \ddot{\text{O}}-\text{N}=\ddot{\text{O}}: \\ | \\ \ddot{\text{C}}:\ddot{\text{I}}: \end{array}$

(c)  $\text{Mg}^{2+} 2[\ddot{\text{O}}-\ddot{\text{C}}\ddot{\text{I}}-\ddot{\text{O}}:]^{-}$

9-4(b) (a)  $\text{H}-\text{C}\equiv\text{N}$  (b)  $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$

(c)  $\left[ \begin{array}{c} \ddot{\text{O}}-\ddot{\text{P}}-\ddot{\text{O}}: \\ | \\ \ddot{\text{O}}: \end{array} \right]^{3-}$

9-4(c) Oxygen difluoride:  $\ddot{\text{F}}-\ddot{\text{O}}-\ddot{\text{F}}$ ; Dioxygen difluoride:

$\ddot{\text{F}}-\ddot{\text{O}}-\ddot{\text{O}}-\ddot{\text{F}}$ : Typically, the central atom (the least electronegative) is written first, and the outer atoms second.

Oxygen is second in electronegativity to fluorine, so only when it is bonded to fluorine is it the central atom.

9-5(a)  $\begin{array}{c} \ddot{\text{O}}: \\ \diagup \\ \text{O}=\ddot{\text{N}}-\text{N} \\ \diagdown \\ \ddot{\text{O}}: \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}}: \\ \diagdown \\ \text{O}=\ddot{\text{N}}-\text{N} \\ \diagup \\ \ddot{\text{O}}: \end{array}$   
 $\leftrightarrow \begin{array}{c} \ddot{\text{O}}: \\ \diagdown \\ \text{O}=\text{N}=\text{N} \\ \diagup \\ \ddot{\text{O}}: \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}}: \\ \diagup \\ \text{O}=\text{N}=\text{N} \\ \diagdown \\ \ddot{\text{O}}: \end{array}$

9-5(b) The molecule (b)  $\text{SO}_2$  and the ion (d)  $\text{OCN}^-$

9-5(c)  $\ddot{\text{O}}-\text{C}\equiv\text{O}:$  and  $:\text{O}\equiv\text{C}-\ddot{\text{O}}:$  These resonance structures imply either that the bonds are unequal (which they are not) or that they average out to two double bonds (which they do). Resonance structures are not necessary in this case since they lead to the same conclusion as the one structure with two double bonds.

## PART C

9-6(a) The most electronegative element is fluorine. The second most electronegative element is oxygen. In a covalent bond between unlike atoms, the more electronegative element has a partial negative charge. This type of bond is said to be a polar covalent bond. A large difference in electronegativity between two atoms leads to an ionic bond.

9-6(b) (a)  $\text{Al}\overset{\rightarrow}{-}\text{Se}$  (b)  $\text{As}\overset{\rightarrow}{-}\text{S}$  (c)  $\text{S}-\text{S}$  (d)  $\text{F}\overset{\leftarrow}{-}\text{Br}$   
 (e)  $\text{C}\overset{\leftarrow}{-}\text{H}$

9-6(c) (a) nonpolar (b) polar (nearly ionic) (c) polar (d) nonpolar

9-6(d) The larger the difference in electronegativity, the more likely the bond between two atoms is to be an ionic bond. Smaller difference leads to covalent bonds. Electronegativity is a periodic property, so the farther apart two atoms are on the periodic table, the more likely they are to form ionic bonds.

9-7(a) (a) two (b) three

9-7(b) a little less than  $109.5^\circ$

9-7(c) trigonal planar

9-7(d) bent or V-shaped

9-7(e) (a)  $180^\circ$ , linear, linear (b)  $120^\circ$ , trigonal planar, bent

9-8(a) (a) polar (b) polar (c) nonpolar (d) nonpolar

9-8(b)  $\text{CS}_2 < \text{SO}_2 < \text{CH}_2\text{O} < \text{HF}$

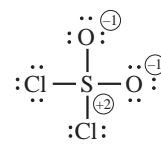
9-8(c)  $\text{CH}_2\text{F}_2$  is a polar molecule. (Making a model helps to visualize this.) If the molecule were square instead, there would be two possibilities. It would be nonpolar if the fluorines were opposite to each other, but polar if they were adjacent to each another.

9-9(a) The O is the central atom.  $\text{H}-\text{O}-\text{Cl}$  has no formal charge. The other possibility is  $\text{H}-\text{Cl}-\text{O}$ , which has formal charges.

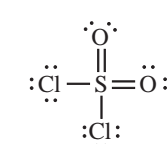
9-9(b) The double bond is between the C and the O.

9-9(c)

Lewis structure for octet rule:



Lewis structure for formal charge:



## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## Dot Symbols of Elements (SECTION 9-1)

9-1. Write Lewis dot symbols for

- (a) Ca                      (d) I                      (g) all Group VIA elements  
 (b) Sb                      (e) Ne  
 (c) Sn                      (f) Bi

9-2. Identify the representative element groups from the dot symbols.

- (a)  $\cdot\overset{\cdot}{M}\cdot$       (b)  $:\overset{\cdot\cdot}{X}\cdot$       (c)  $\overset{\cdot}{A}\cdot$

9-3. Identify the representative element groups from the dot symbols.

- (a) R $\cdot$       (b)  $:\overset{\cdot\cdot}{Q}\cdot$       (c)  $\cdot\overset{\cdot}{D}\cdot$

9-4. Why are only outer electrons represented in dot symbols?

9-5. Which of the following dot symbols are incorrect?

- (a) Pb $\cdot$                       (c)  $:\overset{\cdot\cdot}{H}e:$                       (e)  $\cdot\overset{\cdot\cdot}{T}e\cdot$   
 (b)  $\cdot\overset{\cdot}{Bi}\cdot$                       (d) Cs $\cdot$                       (f)  $\cdot\overset{\cdot}{Tl}\cdot$

## Binary Ionic Compounds (SECTION 9-2)

9-6. From the periodic table, predict which pairs of elements can combine to form ionic bonds.

- (a) H and Cl                      (c) H and K                      (e) B and Cl  
 (b) S and Sr                      (d) Al and F                      (f) Xe and F

9-7. From the periodic table, predict which pairs of elements can combine to form ionic bonds.

- (a) Ba and I                      (c) C and O                      (e) P and S  
 (b) Cs and Se                      (d) H and Se                      (f) Cs and P

9-8. Which ions would not have a noble gas electron configuration?

- (a) Sr<sup>2+</sup>                      (c) Cr<sup>2+</sup>                      (e) In<sup>+</sup>                      (g) Ba<sup>2+</sup>  
 (b) S<sup>-</sup>                      (d) Te<sup>2-</sup>                      (f) Pb<sup>2+</sup>                      (h) Tl<sup>3+</sup>

9-9. Which ions would not have a noble gas electron configuration?

- (a) Rb<sup>+</sup>                      (c) Sc<sup>2+</sup>                      (e) As<sup>2-</sup>  
 (b) Si<sup>4-</sup>                      (d) I<sup>2-</sup>                      (f) Se<sup>2-</sup>

9-10. The ions Li<sup>+</sup>, Be<sup>2+</sup>, and H<sup>-</sup> do not follow the octet rule. Why?

9-11. Write Lewis dot symbols for the following ions.

- (a) K<sup>+</sup>                      (c) I<sup>-</sup>                      (e) Ba<sup>+</sup>                      (g) Sc<sup>3+</sup>  
 (b) O<sup>-</sup>                      (d) P<sup>3-</sup>                      (f) Xe<sup>+</sup>

9-12. What is the origin of the octet rule? How does the octet rule relate to *s* and *p* subshells and to noble gases?

9-13. Which of the ions listed in problem 9-11 do not follow the octet rule?

9-14. For the following atoms, write the charge that would give the element a noble gas configuration.

- (a) Mg      (b) Ga      (c) Br      (d) S      (e) P

9-15. For the following atoms, write the charge that would give the element a noble gas configuration.

- (a) Rb      (b) Ba      (c) Te      (d) N

9-16. Write six ions that have the same electron configuration as Ne.

9-17. Write five ions that have the same electron configuration as Kr.

9-18. The Tl<sup>3+</sup> ion does not have the same electron configuration as Xe, even though it lost its three outermost electrons. Explain.

9-19. Complete the following table with formulas of the ionic compounds that form between the anions and cations shown.

| Cation/Anion     | Br <sup>-</sup> | S <sup>2-</sup> | N <sup>3-</sup> |
|------------------|-----------------|-----------------|-----------------|
| Cs <sup>+</sup>  | CsBr            | _____           | _____           |
| Ba <sup>2+</sup> | _____           | _____           | _____           |
| In <sup>3+</sup> | _____           | _____           | _____           |

9-20. Complete the following table with formulas of the ionic compounds that form between the anions and cations shown.

| Cation/Anion     | F <sup>-</sup> | Te <sup>2-</sup> | P <sup>3-</sup> |
|------------------|----------------|------------------|-----------------|
| Rb <sup>+</sup>  | _____          | _____            | _____           |
| Mg <sup>2+</sup> | _____          | _____            | _____           |
| Cr <sup>3+</sup> | _____          | _____            | _____           |

9-21. Write the formulas of the compounds formed between the following nonmetals and the metal calcium.

- (a) I      (b) O      (c) N      (d) Te      (e) F

9-22. Write the formulas of the compounds formed between the following metals and the nonmetal sulfur.

- (a) Be      (b) Cs      (c) Ga      (d) Sr

9-23. Most transition metal ions cannot be predicted by reference to the octet rule. Determine the charge on the metal cation from the charge on the anion for each of the following compounds.

- (a) Cr<sub>2</sub>O<sub>3</sub>                      (c) MnS                      (e) NiBr<sub>2</sub>  
 (b) FeF<sub>3</sub>                      (d) CoO                      (f) VN

9-24. Determine the charge on the metal cation from the charge on the anion for each of the following compounds.

- (a) IrO<sub>4</sub>                      (c) PtF<sub>6</sub>                      (e) Tc<sub>2</sub>O<sub>3</sub>  
 (b) ScN                      (d) CoCl<sub>3</sub>                      (f) Ag<sub>2</sub>Se

9-25. Why isn't a formula unit of BaCl<sub>2</sub> referred to as a molecule?

## Lewis Structures of Compounds

## (SECTIONS 9-3 AND 9-4)

**9-26.** From their Lewis dot symbols, predict the formula of the simplest compound formed by the combination of each pair of elements.

- (a) H and Se      (c) Cl and F      (e) N and Cl  
(b) H and Ge      (d) Cl and O      (f) C and Br

**9-27.** From their Lewis dot symbols, predict the formula of the simplest compound formed by the combination of each pair of elements.

- (a) H and I      (c) Si and Br  
(b) Se and Br      (d) H and As

**9-28.** From a consideration of the octet rule, which of the following compounds are impossible?

- (a) PH<sub>3</sub>      (c) SCl<sub>2</sub>      (e) H<sub>3</sub>O  
(b) Cl<sub>3</sub>      (d) NBr<sub>4</sub>

**9-29.** Which of the following binary compounds does not follow the octet rule?

- (a) NI<sub>3</sub>      (c) CH<sub>3</sub>      (e) FCl  
(b) F<sub>3</sub>O      (d) HSe      (f) SCl<sub>2</sub>

**9-30.** Determine the charge on each polyatomic anion from the charge on the cation.

- (a) K<sub>2</sub>SO<sub>4</sub>      (c) Al<sub>2</sub>(SeO<sub>4</sub>)<sub>3</sub>      (e) BaC<sub>2</sub>  
(b) Ca(IO<sub>3</sub>)<sub>2</sub>      (d) Ca(H<sub>2</sub>PO<sub>3</sub>)<sub>2</sub>

**9-31.** Determine the charge on each polyatomic anion from the charge on the cation.

- (a) NaBrO<sub>2</sub>      (c) AlAsO<sub>4</sub>  
(b) SrSeO<sub>3</sub>      (d) Mg(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>

**9-32.** Write Lewis structures for the following.

- (a) C<sub>2</sub>H<sub>6</sub>      (c) NF<sub>3</sub>  
(b) H<sub>2</sub>O<sub>2</sub>      (d) SCl<sub>2</sub>  
(e) C<sub>2</sub>H<sub>6</sub>O (There are two correct answers; both have the lone pairs on the oxygen.)

**9-33.** Write Lewis structures for the following.

- (a) N<sub>2</sub>H<sub>4</sub>      (c) C<sub>3</sub>H<sub>8</sub>  
(b) AsH<sub>3</sub>      (d) CH<sub>4</sub>O (All unshared electrons are on the O.)

**9-34.** Write Lewis structures for the following.

- (a) CO      (c) KCN  
(b) SO<sub>3</sub>      (d) H<sub>2</sub>SO<sub>3</sub> (H's are on different O's.)

**9-35.** In the following four ions, the C is the central atom. Write the Lewis structures.

- (a) CN<sub>2</sub><sup>2-</sup>      (c) HCO<sub>3</sub><sup>-</sup> (H on the O)  
(b) HCO<sub>2</sub><sup>-</sup> (H is on the C.)      (d) ClCO<sup>-</sup>

**9-36.** Write Lewis structures for the following.

- (a) N<sub>2</sub>O (N is the central atom.)      (d) H<sub>2</sub>S  
(b) Ca(NO<sub>2</sub>)<sub>2</sub>      (e) CH<sub>2</sub>Cl<sub>2</sub>  
(c) AsCl<sub>3</sub>      (f) NH<sub>4</sub><sup>+</sup>

**9-37.** Write Lewis structures for the following.

- (a) Cl<sub>2</sub>O      (c) C<sub>2</sub>H<sub>4</sub>      (e) BF<sub>3</sub>  
(b) SO<sub>3</sub><sup>2-</sup>      (d) H<sub>2</sub>CO      (f) NO<sup>+</sup>

**9-38.** Write Lewis structures for the following.

- (a) CO<sub>2</sub>      (c) BaCl<sub>2</sub>      (e) HOCN      (g) C<sub>2</sub>H<sub>2</sub>  
(b) H<sub>2</sub>NOH      (d) NO<sub>3</sub><sup>-</sup>      (f) SiCl<sub>4</sub>      (h) O<sub>3</sub>

**9-39.** Write Lewis structures for the following.

- (a) Cs<sub>2</sub>Se  
(b) CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> (All H's are on one C, and both O's are bonded to the other C.)  
(c) LiClO<sub>3</sub>      (d) N<sub>2</sub>O<sub>3</sub>      (e) PBr<sub>3</sub>

## Resonance Structures (SECTION 9-5)

**9-40.** Write all equivalent resonance structures (if any) for the following.

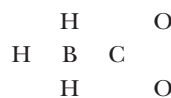
- (a) SO<sub>3</sub>      (b) NO<sub>2</sub><sup>-</sup>      (c) SO<sub>3</sub><sup>2-</sup>

**9-41.** Write all equivalent resonance structures (if any) for the following.

- (a) NO<sub>3</sub><sup>-</sup>  
(b) N<sub>2</sub>O<sub>4</sub> (skeletal geometry)



**9-42.** Write the equivalent resonance structures for the H<sub>3</sub>BCO<sub>2</sub><sup>2-</sup> anion. The skeletal structure for the ion is



**9-43.** What is meant by a resonance hybrid? What is implied about the nature of the C—O bonds from the resonance structures in problem 9-42?

**9-44.** Write any resonance structures possible for the ions in problem 9-35. What are the implications for any bonds where resonance structures exist?

## Electronegativity and Polarity (SECTION 9-6)

**9-45.** Rank the following elements in order of increasing electronegativity: B, Ba, Be, C, Cl, Cs, F, O.

**9-46.** For bonds between the following elements, indicate the positive end of the dipole by a δ<sup>+</sup> and the negative end by a δ<sup>-</sup>. Also indicate with a dipole arrow the direction of the dipole.

- (a) N—H      (d) F—O      (g) C—B  
(b) B—H      (e) O—Cl      (h) Cs—N  
(c) Li—H      (f) S—Se      (i) C—S

**9-47.** Rank the bonds in problem 9-46 in order of increasing polarity.

**9-48.** Which of the following bonds is ionic, which is polar covalent, and which is nonpolar?

- (a) C—F      (b) Al—F      (c) F—F

**9-49.** On the basis of difference in electronegativity, predict whether the following pairs of elements will form an ionic or a polar covalent bond.

- (a) Ga and Br      (c) B and Br  
(b) H and B      (d) Al and F



**9-50.** On the basis of difference in electronegativity, predict whether the following pairs of elements will form an ionic or a polar covalent bond.

- (a) Al and Cl                      (c) K and O  
(b) Ca and I                        (d) Sn and Te

**9-51.** Which of the following bonds is nonpolar or nearly nonpolar?

- (a) I—F                              (c) C—H                              (e) B—N  
(b) I—I                                (d) N—Br

**9-52.** On the following pairs of bonds, which is the more polar?

- (a) N—H or C—H                      (c) S—Cl or S—F  
(b) Si—O or Si—N                      (d) P—Cl or P—I

### Molecular Geometry (SECTION 9-7)

**9-53.** From the Lewis structure, determine the molecular geometry of the following molecules.

- (a) SF<sub>2</sub>                                  (b) CS<sub>2</sub>  
(c) CCl<sub>2</sub>F<sub>2</sub> (C is the central atom.)  
(d) NOCl (N is the central atom.)  
(e) Cl<sub>2</sub>O

**9-54.** From the Lewis structure, determine the molecular geometry of the following molecules or ions.

- (a) BF<sub>2</sub>Cl (B is the central atom.)  
(b) ClO<sub>3</sub><sup>-</sup>  
(c) N<sub>2</sub>O (N is the central atom.)  
(d) COCl<sub>2</sub> (C is the central atom.)  
(e) SO<sub>3</sub>

**9-55.** What are the approximate carbon–oxygen bond angles in the following?

- (a) CO                                  (b) CO<sub>2</sub>                                  (c) CO<sub>3</sub><sup>2-</sup>

**9-56.** Which of the following have bond angles of approximately 109°?

- (a) H<sub>2</sub>O                                  (c) NH<sub>4</sub><sup>+</sup>  
(b) HCO<sub>2</sub><sup>-</sup>                                  (d) HCN

**\*9-57.** When a molecule or ion has more than one central atom, the geometry is determined at each central atom site. What are the geometries around the two central atoms in the following?

- (a) H<sub>2</sub>NOH (N and O)  
(b) HOCN (O and C)  
(c) H<sub>3</sub>CCN (two C's)  
(d) H<sub>3</sub>BCO<sub>2</sub><sup>2-</sup> (B and C; see problem 9-42.)

**\*9-58.** When a molecule or ion has more than one central atom, the geometry is determined at each central atom site. What are the geometries around the two central atoms in the following?

- (a) H<sub>2</sub>CCH<sub>2</sub> (2 C's)                      (c) HClO<sub>2</sub> (Cl and O)  
(b) Cl<sub>2</sub>NNO (2 N's)                      (d) H<sub>3</sub>COCl (C and O)

### Molecular Polarity (SECTION 9-8)

**9-59.** How can a molecule be nonpolar if it contains polar bonds?

**9-60.** Discuss the molecular polarities of the molecules in problem 9-53.

**9-61.** Discuss the molecular polarities of the molecules in problem 9-54.

**9-62.** Write the Lewis structure of SO<sub>2</sub>Cl<sub>2</sub> (S is the central atom). Is the molecule polar?

**9-63.** Compare the expected molecular polarities of H<sub>2</sub>O and H<sub>2</sub>S. Assume that both molecules have the same angle.

**9-64.** Compare the expected molecular polarities of CH<sub>4</sub> and CH<sub>2</sub>F<sub>2</sub>.

**9-65.** Compare the expected molecular polarities of CHCl<sub>3</sub> and CHF<sub>3</sub>.

**9-66.** CO<sub>2</sub> is a nonpolar molecule, but CO is polar. Explain.

**9-67.** SO<sub>3</sub> is a nonpolar molecule, but SO<sub>2</sub> is polar. Explain.

**9-68.** Propene has the formula C<sub>3</sub>H<sub>6</sub> (H<sub>3</sub>CCHCH<sub>2</sub>). Write the Lewis structure and determine whether the molecule is polar.

### Formal Charge (SECTION 9-9)

**9-69.** Nitrogen dioxide is also a free radical. By means of formal charge, assign the unpaired electron as being on the N or O atom.

**9-70.** In hydrogen cyanide, the hydrogen is bonded to the carbon rather than the nitrogen. Write Lewis structures for both possibilities (i.e., HCN or HNC), assign formal charges, and rationalize the known sequence of atoms.

**9-71.** Assign formal charges to all the atoms in problem 9-34.

**9-72.** Assign formal charges to all the atoms in problem 9-35.

**9-73.** Assign formal charges that follow the octet rule to the atoms in the ClO<sub>3</sub><sup>-</sup> ion. Write a structure that does not follow the octet rule but has the best formal charge distribution.

**9-74.** Write the Lewis structure of SO<sub>3</sub> that has the best distribution of formal charge.

**9-75.** The correct structure of nitrous oxide (N<sub>2</sub>O) has an NNO sequence of atoms as opposed to the more symmetrical NON. Write the Lewis structures of both possibilities and rationalize the actual structure with formal charge.

### General Problems

**9-76.** Write the formulas of three binary ionic compounds that contain one cation and one anion. One compound should contain Rb, one Sr, and one N.

**9-77.** There is a noble gas compound formed by xenon, XeO<sub>3</sub>, that follows the octet rule. Write the Lewis structure of this compound. What is the geometry of the molecule? Is the XeO<sub>3</sub> molecule polar?

**9-78.** Which of the following compounds contains both ionic and covalent bonds?

- (a) H<sub>2</sub>SO<sub>3</sub>                              (c) K<sub>2</sub>S                                      (e) C<sub>2</sub>H<sub>6</sub>  
(b) K<sub>2</sub>SO<sub>4</sub>                              (d) H<sub>2</sub>S

**9-79.** Write the Lewis structure of  $\text{H}_3\text{BCO}$  (all H's on the B). Can any resonance structures be written? What is the geometry around the B? What is the geometry around the C?

**9-80.** Carbon suboxide has the formula  $\text{C}_3\text{O}_2$ . All the atoms in the molecule are arranged linearly with an oxygen at each end. Write the Lewis structure.

**9-81.** A molecule may exist that has the formula  $\text{N}_2\text{O}_2$ . The order of the bonds is  $\text{O}-\text{N}-\text{N}-\text{O}$ . Write a Lewis structure for the compound that has two  $\text{N}-\text{O}$  double bonds. Write any resonance structures.

**9-82.** Cyanogen has the formula  $\text{C}_2\text{N}_2$ . The order of the bonds is  $\text{N}-\text{C}-\text{C}-\text{N}$ . Write a Lewis structure for cyanogen involving a  $\text{C}-\text{C}$  single bond. What is the geometry around a C atom? Draw dipole arrows for the bonds. Is the molecule polar?

**9-83.** A certain species is composed of one As and four Cl's. It contains 32 valence electrons. Write the Lewis structure of the species. What is the geometry of the species and the approximate  $\text{Cl}-\text{As}-\text{Cl}$  bond angle?

**9-84.** A certain species is composed of P and three O's. It contains 26 valence electrons. Write the Lewis structure of the species. What is the geometry of the species and the approximate  $\text{O}-\text{P}-\text{O}$  bond angle?

**9-85.** A certain species contains one chlorine and two iodines. It has a total of 20 valence electrons. Write the Lewis structure of the species. What is the geometry of the species and the approximate  $\text{I}-\text{Cl}-\text{I}$  bond angle?

**9-86.** A certain species contains one B, three C's, and 9 H's. It has a total of 24 valence electrons. Write the Lewis structure if the B is bonded only to the three C's. What is the geometry around the B and the approximate  $\text{C}-\text{B}-\text{C}$  bond angle? What is the geometry around the C's and the approximate  $\text{H}-\text{C}-\text{H}$  bond angle? Is the species polar?

**\*9-87.** There are two compounds composed of potassium and nitrogen. Write the formula of the compound expected between potassium and nitrogen. Another compound ( $\text{KN}_3$ ) is named potassium azide. Write the Lewis structure for the azide ion plus any resonance structures. What is the geometry about the central N atom?

**\*9-88.** Write two resonance structures for hydrogen azide  $\text{HN}_3$  ( $\text{HNNN}$ ). What is the predicted  $\text{HNN}$  bond angle in each structure? The actual angle is about  $110^\circ$ . What does this indicate?

**9-89.** Write the Lewis structure for phosphoric acid (hydrogens bonded to oxygens). What is the geometry around the P? What is the geometry around the oxygen in the  $\text{H}-\text{O}-\text{P}$  bond? What is the negative end of the dipole in the  $\text{P}-\text{O}$  bond? Is the molecule polar?

**9-90.** Cyanic acid has the formula  $\text{HOCN}$  (atoms bonded in that order). The  $\text{H}-\text{O}-\text{C}$  bond angle is about  $105^\circ$ . Write the Lewis structure that demonstrates this fact. What is the geometry around the C?

**9-91.** Thiocyanic acid has the formula  $\text{HSCN}$  (atoms bonded in that order). The  $\text{H}-\text{S}-\text{C}$  bond angle is about  $116^\circ$ . Write the Lewis structure that demonstrates this fact. What is the geometry around the C?

**9-92.** A compound has the formula  $\text{N}_2\text{F}_2$ . Write a Lewis structure that contains an  $\text{N}=\text{N}$  bond.

**9-93.** A second compound of nitrogen and fluorine contains one nitrogen and the expected number of fluorines. A third has the formula  $\text{N}_2\text{F}_4$ . Write the Lewis structures of these two compounds. What is the geometry around the N in each compound? Are either or both compounds polar?

**\*9-94.** Two compounds of oxygen are named oxygen difluoride and dioxygen difluoride. Write the Lewis structures of these two compounds. The latter compound contains an  $\text{O}-\text{O}$  bond. Oxygen is usually written and named second in binary compounds. Why not here? Are either or both of these compounds polar?

**\*9-95.** A compound has the formula  $\text{Na}_2\text{C}_2\text{O}_4$ . Write a Lewis structure for the compound that contains a  $\text{C}-\text{C}$  bond. Write any resonance structures present.

**\*9-96.** If you have already covered Chapter 6, consider the following problem. A compound is 27.4% Na, 14.3% C, 57.1% O, and 1.19% H. What is the formula of the compound? Write the Lewis structure of the anion (H bonded to O). What is the geometry around the C? What is the approximate  $\text{O}-\text{C}-\text{O}$  bond angle? What is the geometry around the  $\text{H}-\text{O}-\text{C}$  bond and the approximate angle?

**\*9-97.** If you have already covered Chapter 6, consider the following problem. A compound is 21.7% Li, 75.0% C, and 3.16% H. What is the formula of the compound? Write the Lewis structure of the anion. What is the geometry around the central C and the approximate  $\text{H}-\text{C}-\text{C}$  bond angle?

**\*9-98.** If you have already covered Chapter 6, consider the following problem. A compound is 19.8% Ca, 1.00% H, 31.7% S, and 47.5% O. What is the formula of the compound? (*Hint:* The formula of the anion should be reduced to its empirical formula.) What is the name of the compound? (Refer to Table 4-2.) What is the geometry around the S in the anion? What is the approximate  $\text{H}-\text{O}-\text{S}$  bond angle?

**\*9-99.** Refer to problem 8-99 in the previous chapter. Use the periodic table from the planet Zerk to answer the following.

- What are the simplest formulas of compounds formed between the following (Example: between 7 and 7 is  $\text{Z}_2$ ).
 

|             |               |             |
|-------------|---------------|-------------|
| (a) 1 and 7 | (d) 7 and 9   | (g) 6 and 7 |
| (b) 1 and 3 | (e) 7 and 13  | (h) 3 and 6 |
| (c) 1 and 5 | (f) 10 and 13 |             |
- Write Lewis structures for all of the above. Indicate which are ionic. (Remember that on Zerk there will be something different from an octet rule.)

## VSEPR Theory

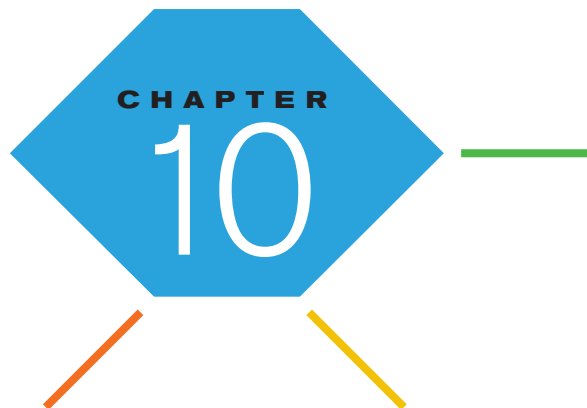
**Purpose:** To make models of several small molecules and ions, and to evaluate them using VSEPR theory. (Work in groups of three or four. Estimated time: 20 min.)

**Equipment:** molecular model kit

- As a group, draw out the Lewis structures of the following chemicals.



- Make the model using the kits provided.
- Determine bond angle, electronic geometry, and molecular geometry from VSEPR theory. Verify these with the model.
- Using this model, identify whether the molecule is polar or nonpolar.
- Indicate whether the chemical has resonance and/or formal charge.



# The Gaseous State

**O**ur atmosphere is a protective blanket of gases. The behavior of these gases can be predicted by gas laws, which are discussed in this chapter.

**PART A**  
**THE NATURE OF THE  
GASEOUS STATE AND THE  
EFFECTS OF CONDITIONS**

**10-1** The Nature of Gases and the  
Kinetic Molecular Theory



**MAKING IT REAL**

*Ozone—Friend and Foe*

**10-2** The Pressure of a Gas

**10-3** Charles's, Gay-Lussac's, and  
Avogadro's Laws

**PART B**  
**RELATIONSHIPS AMONG  
QUANTITIES OF GASES,  
CONDITIONS, AND  
CHEMICAL REACTIONS**

**10-4** The Ideal Gas Law

**10-5** Dalton's Law of Partial Pressures

**10-6** The Molar Volume and Density  
of a Gas



**MAKING IT REAL**

*Defying Gravity—Hot-Air Balloons*

**10-7** Stoichiometry Involving Gases

**SETTING THE STAGE** Our atmosphere of gases is like the combination of a warm blanket and a protective shield. It nurtures life on this planet in numerous ways. Oxygen supports the metabolism that gives energy to living things. Nitrogen becomes part of proteins and also dilutes the oxygen so that combustion does not occur explosively. Carbon dioxide and water vapor lock in the daytime heat so that the temperature does not become bitterly cold at night. Ozone high in the stratosphere absorbs the harmful portion of the sun's radiation. The thickness of the air burns up most incoming meteorites and other debris from space. Life as we know it requires the constant support and protection of this sea of gases.

Just over 200 years ago, there was little understanding of the nature of the gases that support our existence. It wasn't until the late eighteenth century that the experiments of Antoine Lavoisier in France and Joseph Priestley in England gave us some understanding about the gaseous mixture of the atmosphere. These scientists proved that air was not just one substance, as had been previously thought, but was mainly a mixture of two elements: nitrogen and oxygen. Their work also laid the foundation for the development of the law of conservation of mass. This was the beginning of modern quantitative chemistry.

With a few exceptions, gases are invisible. This makes the study of gases somewhat difficult. Except on a windy day, it is easy to forget that this form of matter surrounds us at all.

There is good news when we study the nature of gases, however. In many ways, they all behave similarly, which allows convenient generalizations, including the gas laws. Solids and liquids are less abstract than gases simply because they are visible. The downside of working with solids and liquids, however, is that few generalizations apply and each substance must be studied individually.

In Part A of this chapter, we will examine how conditions such as pressure and temperature affect the volume of a gas. In Part B, we will apply these relationships to how the volume of a gas relates to the amount present under various conditions. We can then expand the concept of stoichiometry to include gas volumes.

**PART A**  
**THE NATURE OF THE**  
**GASEOUS STATE AND THE**  
**EFFECTS OF CONDITIONS**

**SETTING A GOAL**

- You will learn how the molecular nature of gases leads to predictable behavior, known as the gas laws.

**OBJECTIVES**

- 10-1** List the general properties of gases based on the postulates of the kinetic molecular theory.
- 10-2 (a)** Define *pressure*. **(b)** Convert between units of pressure, and calculate how pressure affects the volume of a gas (Boyle's law).
- 10-3 (a)** Using the gas laws, perform calculations involving the relationships among volume, pressure, and temperature. **(b)** Define the conditions known as STP.

**OBJECTIVE FOR SECTION 10-1**

List the general properties of gases based on the postulates of the kinetic molecular theory.

**10-1 THE NATURE OF GASES AND THE KINETIC MOLECULAR THEORY**



**LOOKING AHEAD!** Living in a sea of gases, we tend to take the properties of the gaseous state for granted. In this section, we will not only examine their common properties but also provide the accepted theory that explains them. ■

**10-1.1 The Properties of Gases**

Four of the common properties of gases are described below.

**1. Gases are compressible.**

When a glass of water is full, we mean what we say—no more can be added. But when is an automobile tire full of air? Actually, never. We can always add more air (at least until the tire bursts). The nature of the gaseous state allows us to press a volume of gas into a smaller volume. Liquids and solids are not like that. They are essentially incompressible.

**2. Gases have low densities.**

The density of a typical liquid or solid is around 2 g/mL. The density of a typical gas is around 2 g/L. This means that the density of a solid or liquid is roughly 1000 times greater than that of a gas. This is a big difference.

**3. Gases mix thoroughly.**

Nothing compares with a good home-cooked meal. Perhaps the best part is the pleasurable fragrances that we detect as the meal is being prepared. It doesn't take long for those familiar odors to drift from the kitchen throughout the entire home. The vapors from cooking mix thoroughly and rapidly with the surrounding air. This is a property of gases that is unique to their state. In contrast, some liquids do not mix at all (e.g., oil and water). If they do mix (e.g., water and alcohol), the mixing process occurs quite slowly.

**4. A gas fills a container, uniformly exerting the equal pressure in all directions.**

When we blow air into a round balloon, the balloon becomes spherical and uniform. The air in the balloon obviously pushes out equally in all directions. If we were to fill the balloon with water instead (for scientific reasons only, of course), we would notice that the balloon sags. The water accumulates in the bottom of the balloon.



The balloon is spherical because a gas exerts equal pressure in all directions.



In a room full of air, it would seem that gases defy gravity. The pressure of the atmosphere is the same on the ceiling, walls, and floor.\* Liquid water is quite different, however. Scuba divers are well aware of the increase in pressure as the depth of the water increases.

### 10-1.2 The Kinetic Molecular Theory

Obviously, the gaseous state of matter is quite different from the other two physical states. Gases are composed of either individual atoms (in the case of noble gases) or molecules (for all other gaseous elements and compounds). This fact and others can be summarized in a set of assumptions collectively known as the **kinetic molecular theory**, or simply the **kinetic theory**. The kinetic theory was advanced in the late nineteenth century to explain the common properties of gases. The major points of this theory as applied to gases are as follows.

1. A gas is composed of very small particles called molecules, which are widely spaced and occupy negligible volume. A container of gas is thus mostly empty space.
2. The molecules of a gas are in rapid, random motion, colliding with each other and the sides of the container. Pressure is a result of these collisions with the sides of the container. (See Figure 10-1.)
3. All collisions involving gas molecules are elastic. (The total energy of two colliding molecules is conserved. A ball bouncing off the pavement undergoes inelastic collisions; it does not bounce as high each time.)
4. Gas molecules have negligible attractive (or repulsive) forces between them.
5. The temperature of a gas is related to the average kinetic energy of the gas molecules. Also, at the same temperature, different gases have the same average kinetic energy (K.E.).

The kinetic theory explains the properties described above as well as the gas laws that follow. For example, since gas molecules themselves have essentially no volume and a gas is mostly empty space, it has a low density and is easily compressed. The rapid motion explains why gases mix rapidly and thoroughly. Because gas molecules are not attracted to each other, they do not “clump together” as do the molecules in liquids and solids. Thus, the molecules in gases spread out and fill a container uniformly, exerting pressure equally in all directions.

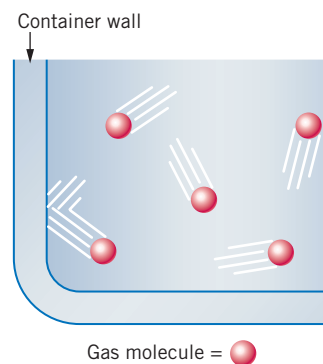
### 10-1.3 Graham's Law

Another consequence of the kinetic theory concerns the relative velocities of gas molecules at the same temperature. The kinetic energy of a gas is given by the equation

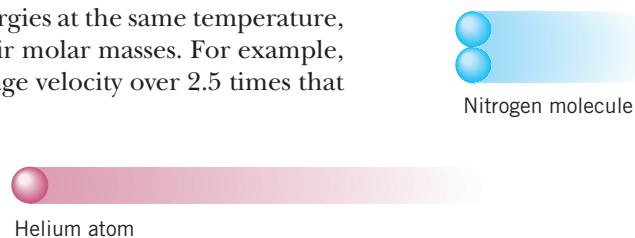
$$\text{K.E.} = \frac{1}{2}mv^2 \quad \text{where } m = \text{mass and } v = \text{velocity}$$

Since two different gases have the same kinetic energies at the same temperature, the relative velocities of their molecules relate to their molar masses. For example, at the same temperature, a helium atom has an average velocity over 2.5 times that of a nitrogen molecule. (See Figure 10-2.)

The average velocity of a gas molecule relates directly to two other aspects of molecular motion. These are the rates of **diffusion** (*mixing*) and **effusion** (*moving through an opening or hole*). The relationship between diffusion and molar mass was first proposed in 1832 by Thomas Graham. This was



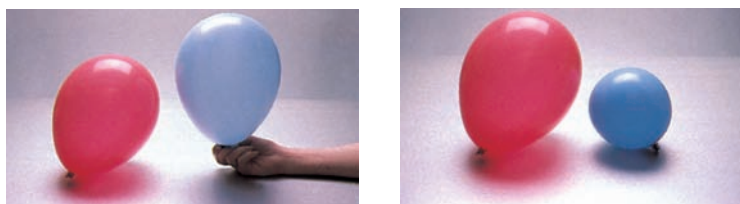
**FIGURE 10-1 Gases** Gas molecules are in rapid, random motion.



**FIGURE 10-2 Relative Velocities** At the same temperature, a helium atom travels almost three times faster than a nitrogen molecule.

\*In fact, gases do not really defy gravity, since our atmosphere gets thinner as the altitude increases. However, the thinning of the atmosphere occurs on a scale of several kilometers. It would not be noticed on the scale of a few meters in a room.

**FIGURE 10-3 Graham's Law and Helium Balloons** The balloon on the left is filled with air, and the one on the right is filled with helium. One day later, the helium balloon has shrunk because the small atoms of helium have effused out of the balloon.



actually some time before the acceptance of kinetic theory. **Graham's law** states that the rates of diffusion of gases at the same temperature are inversely proportional to the square roots of their molar masses. Although we will not do calculations involving Graham's law, gaseous effusion has important applications, such as the enrichment of the isotope of uranium ( $^{235}\text{U}$ ) used for nuclear power or as a nuclear weapon. In this case, we take advantage of the very slightly increased rate of effusion of gaseous  $^{235}\text{UF}_6$  compared to  $^{238}\text{UF}_6$ . This procedure is used to enrich the uranium from the naturally occurring 0.7%  $^{235}\text{U}$  to 2-3% for nuclear reactors and to around 90% for nuclear weapons.

You may have noticed Graham's law in action with a helium balloon. Since average helium atoms move over 2.6 times faster than nitrogen molecules, it effuses out of a balloon faster than nitrogen and oxygen in a balloon filled with air. As a result, the helium balloon decreases in size faster than one holding only air. (See Figure 10-3.)

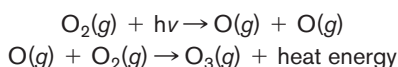


### Ozone—Friend and Foe



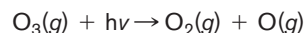
Ozone is associated with air pollution.

Oxygen is the element that made animal life possible. Billions of years ago, primitive forms of life on this planet began to use solar energy, carbon dioxide, and water to generate energy-rich compounds with oxygen as a by-product. As the oxygen became more concentrated in the atmosphere, new life-forms appeared that used this oxygen for metabolism. But this new life could not have survived on the surface of Earth if it were not for another role that oxygen plays in a region around 50 km above Earth's surface known as the stratosphere. There, solar radiation is powerful enough to break the bond in  $\text{O}_2$  to form oxygen atoms. (Chemical reactions that are initiated by light energy are known as *photochemical reactions*.) The atoms of oxygen combined in another form, or allotrope, of oxygen known as ozone. (The solar energy is represented as  $h\nu$  in the equation below.)



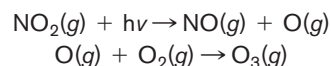
The solar radiation that breaks the  $\text{O}_2$  bond lies in the higher-energy ultraviolet region of the spectrum (around 240 nm). However, there are lower-energy wavelengths of

ultraviolet light (UVA and UVB from 240 nm to 310 nm) that would still come through to the surface if it were not for ozone. Ozone in the stratosphere effectively absorbs these damaging wavelengths of ultraviolet radiation. The equation is represented as



Without ozone in the stratosphere, most life on the surface of Earth would be roasted by ultraviolet radiation. Destruction of ozone by synthetic chemicals is a crucial area of concern and is being addressed. (See Section 15-2.)

On the other hand, in the lower atmosphere, where we live, ozone is a problem. Ozone is associated with what is called *photochemical smog*. Automobiles and daylight are the culprits.  $\text{NO}_2$  is formed in the atmosphere from NO that is produced in automobiles and other heat sources. In this case, oxygen atoms are produced from visible light from the sun acting on the  $\text{NO}_2$ .



Ozone is toxic and chemically reactive. It causes trouble for anyone with lung disorders or those exercising outdoors. It is considered a serious pollutant. So ozone is essentially our friend when it is high up in the stratosphere but a serious problem near the surface. "Everything in its place" is a saying that seems appropriate.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 10-1

**EXERCISE 10-1(a) KNOWLEDGE:** Fill in the blanks.

Unlike solids and liquids, a gas has a \_\_\_\_\_ density and fills a container \_\_\_\_\_. The reason for the unique behavior of gases can be explained by the \_\_\_\_\_ theory. In this theory, gas molecules are in \_\_\_\_\_, \_\_\_\_\_ motion, exerting pressure by \_\_\_\_\_ with the walls of the container. Another aspect of this theory is that the temperature relates to the average \_\_\_\_\_ energy of the gas. At the same temperature, the gas with the larger molar mass will have the \_\_\_\_\_ velocity. The velocity of a gas relates to the rates of \_\_\_\_\_ and \_\_\_\_\_ as expressed by Graham's law.

**EXERCISE 10-1(b) ANALYSIS:** How does the average velocity of an  $\text{SF}_6$  molecule compare to an  $\text{N}_2$  molecule at the same temperature?

**EXERCISE 10-1(c) SYNTHESIS:** It is dangerous to leave aerosol containers in the trunk of a car in the summer. Use the postulates of kinetic molecular theory to explain why.

*For additional practice, work chapter problems 10-5, 10-7, and 10-9.*

## 10-2 THE PRESSURE OF A GAS



**LOOKING AHEAD!** Since kinetic theory makes the nature of gases seem so simple and reasonable, it is sometimes difficult to appreciate the advances made by those who were not aware of the existence of atoms, molecules, or their motions. Before we look at how other conditions affect gases, we will take a closer look at the property known as pressure and how it affects the volume of a gas. ■

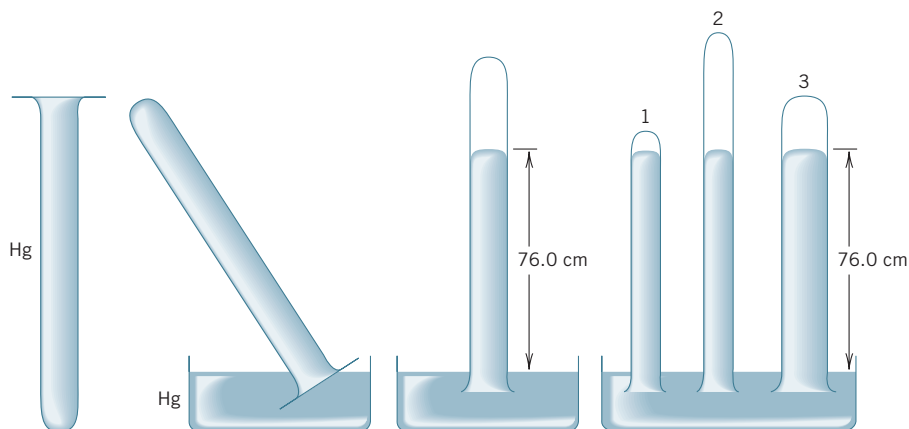
▶ OBJECTIVES FOR  
SECTION 10-2

(a) Define *pressure*. (b) Convert between units of pressure, and calculate how pressure affects the volume of a gas (Boyle's law).

## 10-2.1 The Barometer and Pressure

A newscast on TV would not be complete without the weather forecast. The weather data probably include the atmospheric pressure as read from a **barometer**. Rising pressure usually means improving weather, and a dropping barometer often means that a storm is approaching.

The barometer has been around for quite a while. It was invented by an Italian scientist, Evangelista Torricelli, in 1643. Torricelli filled a long glass tube with mercury, a dense liquid metal, and then inverted the tube into a bowl of mercury so that no air would enter the tube. Torricelli found that the mercury in the tube seemed to defy gravity by staying suspended to a height of about 76 cm no matter how long or wide the tube. (See Figure 10-4.)



**FIGURE 10-4 The Barometer** When a long tube is filled with mercury and inverted in a bowl of mercury, the atmosphere supports the column to a height of 76.0 cm.



The pressure of the atmosphere is measured by a barometer. The barometric pressure can be used to forecast weather.

At the time, many scientists thought that since “nature abhors a vacuum,” the vacuum created at the top of the tube suspended the mercury. Torricelli suggested instead that it is the weight of the air on the outside that pushes the mercury up. Otherwise, the greater vacuum present in tubes 2 and 3 in Figure 10-4 would support a higher level of mercury. Torricelli also suggested that the thinner atmosphere at higher levels in the mountains would support less mercury. He was correct. The higher the elevation, the lower the level of mercury in the barometer.

The weight of a quantity of matter pressing on a surface exerts a *force*. **Pressure** is defined as the *force applied per unit area*. This can be expressed mathematically as

$$P(\text{pressure}) = \frac{F(\text{force})}{A(\text{area})}$$

In a barometer, the pressure exerted by the atmosphere on the outside is balanced by the pressure exerted by the weight of the column of mercury on the inside.

If, at times, it seems like you are under a lot of “pressure,” it is not necessarily from the atmosphere. However, you are under a lot of “force” from the atmosphere—over 20,000 lb of it. Fortunately, this force is spread out over your entire body surface (about 1500 in.<sup>2</sup>, with much individual variation). When we divide the actual force on any one person by that person’s body area, the resulting pressure comes out the same for everyone—a reasonable 15 lb/in.<sup>2</sup>

**One atmosphere** (1 atm) is defined as the average pressure of the atmosphere at sea level and is the standard of pressure. As we have seen, this is equivalent to the pressure exerted by a column of mercury 76.0 cm (760 mm) high.

$$1.00 \text{ atm} = 76.0 \text{ cm Hg} = 760 \text{ mm Hg} = 760 \text{ torr}$$

The unit of mm of Hg is also known as the *torr* in honor of Torricelli. In addition to the torr, there are several other units of pressure (e.g., lb/in.<sup>2</sup>) that have special uses. The relationships of the units to 1 atm and their applications are listed in Table 10-1. An example of a conversion between units is shown in Example 10-1.

**TABLE 10-1** One Atmosphere

| UNIT OF PRESSURE               | SPECIAL USE   |
|--------------------------------|---|
| 760 mm Hg or 760 torr          | most chemistry laboratory measurements for pressures in the neighborhood of one atmosphere                |
| 14.7 lb/in. <sup>2</sup> (psi) | U.S. pressure gauges  |
| 29.9 in. Hg                    | U.S. weather reports  |
| 101.325 kPa (kilopascals)      | the metric unit of pressure [1 N (newton)/m <sup>2</sup> ]  |
| 1.013 bars                     | used in physics and astronomy mainly for very low pressures (millibars) or very high pressures (kilobars) |

### EXAMPLE 10-1

#### Converting Between Units of Pressure

What is 485 torr expressed in atmospheres?

#### PROCEDURE

The conversion factors between atm and torr are

$$\frac{760 \text{ torr}}{\text{atm}} \quad \text{and} \quad \frac{1 \text{ atm}}{760 \text{ torr}}$$

#### SOLUTION

$$485 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = \underline{\underline{0.638 \text{ atm}}}$$

#### ANALYSIS

This is a good simple example to review the use of the factor-label method to solve mathematical problems. While pressure readings come from a number of different sources, and therefore in a number of different units, you’ll find it most convenient to convert all pressure units into atmospheres for purposes of comparison and canceling.

## SYNTHESIS

Generally we fill our tires up to around 35 psi (lbs/in.<sup>2</sup>), according to our tire pressure gauge. At 14.7 psi/atm, this means that the gauge is reading greater than 2 atm. Does that mean that there is more than 2 atm of pressure in the tire? What if your gauge reads zero? Does that mean that there is *no* pressure inside the tire? No. It means that there is *equal* pressure inside as out. The gauge reads the *difference* in pressure between the inside of a tire and the outside. *Gauge pressure* is always 1 atm (or whatever the external pressure) less than the actual pressure inside a container. When you get a chance, check your tire pressure gauge for units. Chances are that along with psi, there's also a listing for kPa and perhaps bars as well.

## 10-2.2 Boyle's Law

Every breath we take illustrates the interaction between the volume and the pressure of a gas. When the diaphragm under our rib cage relaxes, it moves up, squeezing our lungs and decreasing their volume. The decreased volume increases the air pressure inside the lungs relative to the outside atmosphere, and we expel air. When the diaphragm contracts, it moves down, increasing the volume of the lungs and, as a result, decreasing the pressure. Air rushes in from the atmosphere until the pressures are equal.

The relationship between the volume and pressure of a sample of gas under constant-temperature conditions was first described in 1660 by the English scientist Robert Boyle. In an apparatus similar to that shown in Figure 10-5, Boyle found that the decrease in volume can be predicted by the amount of pressure increase. This observation is now expressed as **Boyle's law**, which states that *there is an inverse relationship between the pressure exerted on a quantity of gas and its volume if the temperature is held constant.*

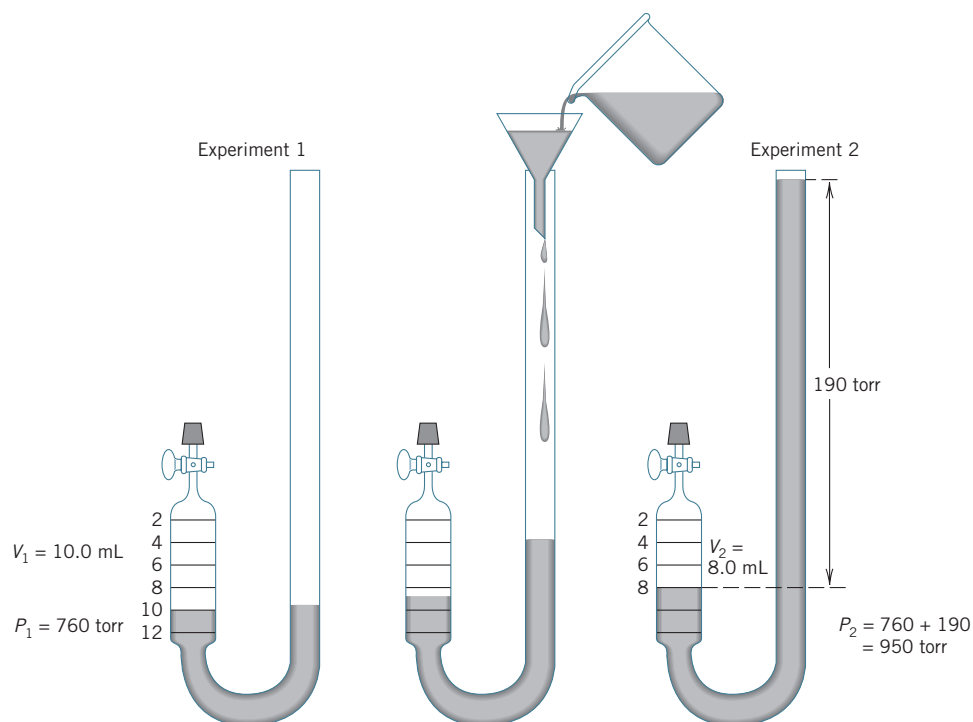
The inverse relationship suggested by Boyle is represented as

$$V \propto \frac{1}{P}$$

or as an equality with  $k$  the constant of proportionality:

$$V = \frac{k}{P} \quad \text{or} \quad PV = k$$

Boyle's law can be illustrated with the apparatus shown in Figure 10-5. In experiment 1, a certain quantity of gas ( $V_1 = 10.0$  mL) is trapped in a U-shaped tube by



**FIGURE 10-5 Boyle's Law Apparatus** Addition of mercury in the apparatus causes an increase in pressure on the trapped gas. This leads to a reduction in the volume.





At higher altitudes, or in an airplane where the external pressure is lower, the bag of potato chips expands.

some mercury. Since the level of mercury is the same in both sides of the tube and the right side is open to the atmosphere, the pressure on the trapped gas is the same as the atmospheric pressure ( $P_1 = 760$  torr). In this experiment,

$$P_1 V_1 = 760 \text{ torr} \times 10.0 \text{ mL} = 7600 \text{ torr} \cdot \text{mL} = k$$

When mercury is added to the tube, the pressure on the trapped gas is increased to 950 torr (760 torr originally plus 190 torr from the added mercury). Note in experiment 2 that the increase in pressure has caused a decrease in volume to 8.0 mL. Applying Boyle's law to this experiment, we have

$$P_2 V_2 = 950 \text{ torr} \times 8.0 \text{ mL} = 7600 \text{ torr} \cdot \text{mL} = k$$

As predicted by Boyle's law,  $PV$  equals the same value in both experiments. Therefore, for a quantity of gas under two sets of conditions at the same temperature,

$$P_1 V_1 = P_2 V_2 = k$$

We can use this equation to calculate how a volume of gas changes when the pressure changes. For example, if  $V_2$  is the new volume that we are to find at a given new pressure,  $P_2$ , the equation becomes

$$V_2 = V_1 \times \frac{P_1}{P_2}$$

If a series of measurements are made of volume and pressure, the results can be graphed. The construction of such a graph illustrating Boyle's law is found in Appendix D.

### EXAMPLE 10-2

#### Applying Boyle's Law

Inside a certain automobile engine, the volume of a cylinder is 475 mL when the pressure is 1.05 atm. When the gas is compressed, the pressure increases to 5.65 atm at the same temperature. What is the volume of the compressed gas?

#### PROCEDURE

First, identify and list the initial and final conditions. Make sure the units of pressure are the same in the initial and final conditions.

#### SOLUTION

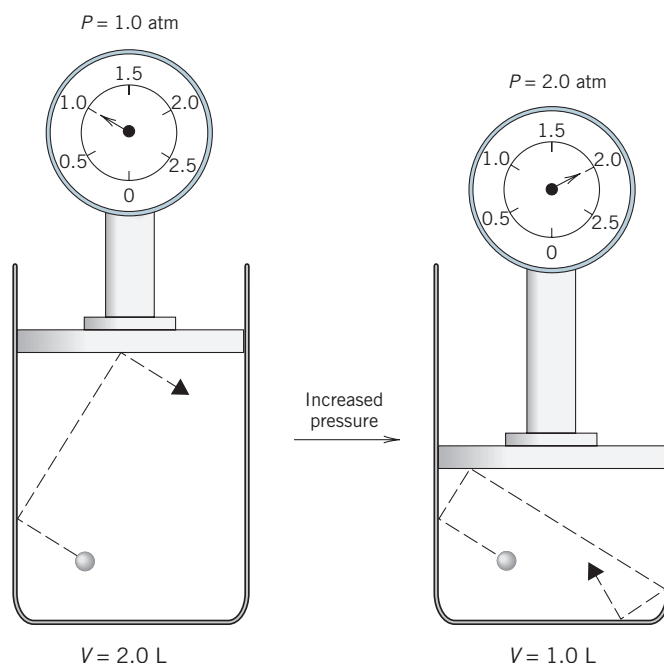
| <i>Initial Conditions</i>   | <i>Final Conditions</i>  |
|---|--------------------------|
| $V_1 = 475 \text{ mL}$  | $V_2 = ?$                |
| $P_1 = 1.05 \text{ atm}$  | $P_2 = 5.65 \text{ atm}$ |
| $V_2 = V_1 \times \frac{P_1}{P_2}$  |                          |
| $V_2 = 475 \text{ mL} \times \frac{1.05 \text{ atm}}{5.65 \text{ atm}} = \underline{\underline{88.3 \text{ mL}}}$ |                          |

#### ANALYSIS

Problems of this sort go by the descriptive name among students of "plug and chug." The equation for the relationship has four variables, and the problem identifies three of them. Simply rearrange the equation for the target variable, plug in the given values in the problem, and mathematically chug through the calculation for the answer. Gas law problems can also be worked by logic, since we know qualitatively how a gas should react to a change of conditions. In this example, we should predict that an increase in pressure ( $P_2 > P_1$ ) would lead to a decrease in volume ( $V_2 < V_1$ ). We therefore choose a pressure ratio that will do the job. This requires the use of a proper fraction (a fraction less than 1) with the lower pressure in the numerator.

Although it wasn't known in the 1660s, Boyle's law is a natural consequence of the kinetic theory of gases. In order to focus on how a change in volume affects the pressure, we will assume that there is an average molecule of a gas at a given temperature. In Figure 10-6, the path of this one average molecule is traced. The pressure exerted by this molecule is a result of collisions with the sides of the container. The distance





**FIGURE 10-6** Boyle's Law and Kinetic Molecular Theory When the volume decreases, the pressure increases because of more frequent collisions with the walls of the container.

traveled in a given unit of time is represented by the length of the path. Since this is an average molecule, it travels the same distance per unit time in both the high-volume situation (on the left) and the low-volume situation (on the right). Note that, on the right, the lower volume leads to an increased number of collisions with the sides of the container. More frequent collisions mean higher pressure.

**ASSESSING THE OBJECTIVES FOR SECTION 10-2**

**EXERCISE 10-2(a) KNOWLEDGE:** Fill in the blanks.

Atmospheric pressure is read from a device called a \_\_\_\_\_. Pressure is defined as \_\_\_\_\_ per unit \_\_\_\_\_. One atmosphere of pressure is equivalent to \_\_\_\_\_ torr. An increase in pressure on a volume of gas causes the volume to \_\_\_\_\_,

**EXERCISE 10-2(b) ANALYSIS:** What is 0.650 atm expressed in (a) torr, (b) kPa, and (c) lb/in.<sup>2</sup>?

**EXERCISE 10-2(c) ANALYSIS:** The volume of 0.0388 mol of gas is 870 mL at a pressure of 1.00 atm and a temperature of 0°C. What is the volume at 1.32 atm and 0°C?

**EXERCISE 10-2(d) SYNTHESIS:** How does the kinetic molecular theory explain Boyle's law?

*For additional practice, work chapter problems 10-10, 10-12, 10-16, and 10-19.*

## 10-3 CHARLES'S, GAY-LUSSAC'S, AND AVOGADRO'S LAWS



**LOOKING AHEAD!** We probably sense that all matter expands when it is heated. Only gases expand by the same amount, however, regardless of the identity of the gas. One hundred years after Boyle's relationship was advanced, the quantitative relationship between volume and temperature was studied. Other relationships discussed in this section involve temperature, pressure, and the amount of gas present. ■

**OBJECTIVES FOR SECTION 10-3**

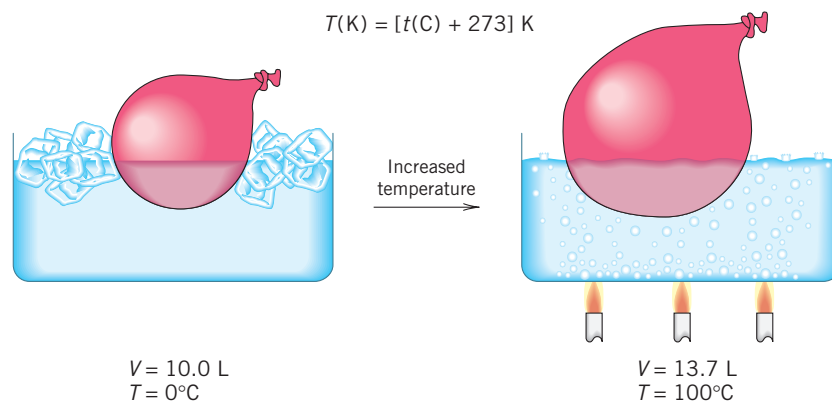
(a) Using the gas laws, perform calculations involving the relationships among volume, pressure, and temperature. (b) Define the conditions known as STP.



Hot-air balloons are practical applications of Charles's law.

### 10-3.1 Charles's Law

Very few sights appear more tranquil than brightly colored hot-air balloons drifting across a blue summer sky. Except for the occasional “swoosh” of gas burners, they cruise by in majestic silence. With heating, air expands. As it expands, it becomes less dense than the surrounding cooler air and thus rises. When the hot, expanded air is trapped, the balloon and attached gondola become “lighter than air” and lift into the sky. The quantitative effect of temperature on the volume of a sample of gas at constant pressure was first advanced by a French scientist, Jacques Charles, in 1787. Charles showed that any gas expands by a definite fraction as the temperature rises. He found that the volume increases by a fraction of  $1/273$  for each  $1^\circ\text{C}$  rise in the temperature. (See Figure 10-7.)

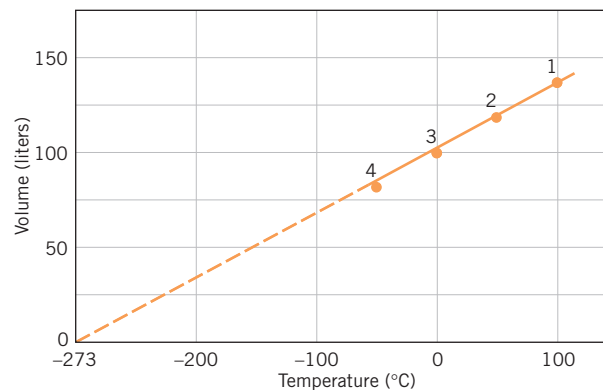


**FIGURE 10-7** Effect of Temperature on Volume When the temperature increases, the volume of the balloon increases.

Let's assume that we have made four measurements of the volume of a gas at four temperatures at constant pressure. The results of these experiments are listed in the table on the left in Figure 10-8. The four points are also plotted in a graph on the right. When the four points in the graph are connected, we have a straight line. The relationship between volume and temperature is known as a *linear relationship*. (Refer to Appendix D on graphs.) In the graph, the straight line has been extended to what the volume would be at temperatures lower than those in the experiment. (The procedure of extending data beyond experimental results is known as *extrapolation*.) If extended all the way to where the gas would theoretically have zero volume, the line would intersect the temperature axis at  $-273.15^\circ\text{C}$ . Certainly, matter could never have zero volume, and it is impossible to cool gases indefinitely. At some point, all gases condense to become liquids or solids, so gas laws no longer apply. However, this temperature does have significance, because it is the lowest temperature possible. As noted in kinetic molecular theory, the average kinetic energy or velocity of molecules is related to the temperature. *The lowest possible temperature, known as absolute zero, is the temperature at which translational motion (motion from point to point) ceases. The Kelvin scale starts at absolute zero.*

**FIGURE 10-8** Volume and Temperature The volume of a gas increases by a definite amount as the temperature increases.

| Experiment | $T(^{\circ}\text{C})$ | $V(\text{L})$ |
|------------|-----------------------|---------------|
| 1          | 100                   | 136.7         |
| 2          | 50                    | 118.3         |
| 3          | 0                     | 100.0         |
| 4          | -50                   | 81.7          |



Thus, there are no negative values on the Kelvin scale, just as there are no negative values on any pressure scale and no such thing as a negative volume. Since the magnitudes of Celsius and Kelvin degrees are the same, we have the following simple relationship between scales, where  $T(\text{K})$  is the temperature in kelvins and  $T(^{\circ}\text{C})$  represents the Celsius temperature. In our calculations, we will use the value of the lowest temperature expressed to three significant figures (i.e.,  $-273^{\circ}\text{C}$ ).

$$T(\text{K}) = T(^{\circ}\text{C}) + 273$$

The relationship between volume and temperature noted by Charles can now be restated in terms of the Kelvin scale. **Charles's law** states that the volume of a gas is directly proportional to the Kelvin temperature ( $T$ ) at constant pressure. (From this point on,  $T$  will represent the Kelvin temperature exclusively.) This can be expressed mathematically as a proportion or as an equality, with  $k$  again serving as the symbol for the constant of proportionality.

$$V \propto T \quad V = kT \quad \text{or} \quad \frac{V}{T} = k$$

For a quantity of gas at two temperatures at the same pressure,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This equation can be used to calculate how the volume of gas changes when the temperature changes. For example, if  $V_2$  is a new volume that we are to find at a given new temperature  $T_2$ , the equation becomes

$$V_2 = V_1 \times \frac{T_2}{T_1}$$

### EXAMPLE 10-3

#### Applying Charles's Law

A given quantity of gas in a balloon has a volume of 185 mL at a temperature of  $52^{\circ}\text{C}$ . What is the volume of the balloon if the temperature is lowered to  $-17^{\circ}\text{C}$ ? Assume that the pressure remains constant.

#### PROCEDURE

As before, identify the initial and final conditions. Remember we must use the Kelvin temperature scale in all gas law calculations.

#### SOLUTION

*Initial Conditions*

$$V_1 = 185 \text{ mL}$$

$$T_1 = (52 + 273) = 325 \text{ K}$$

$$V_2 = V_1 \times \frac{T_2}{T_1}$$

$$V_2 = 185 \text{ mL} \times \frac{256 \text{ K}}{325 \text{ K}} = \underline{\underline{146 \text{ mL}}}$$

*Final Conditions*

$$V_2 = ?$$

$$T_2 = (-17 + 273) = 256 \text{ K}$$

#### ANALYSIS

Rather than just substituting numbers, we can also set this problem up with logic. Note that since the temperature decreases, the volume decreases. The temperature factor must therefore be less than 1, which means the factor must again be a proper fraction.

Qualitatively, is our answer reasonable? The volume has decreased about 40 mL, or close to 1/5 of its volume. This must be due to an accompanying 1/5 decrease in the temperature. Looking at the Celsius temperatures,  $52^{\circ}\text{C}$  down to  $-17^{\circ}\text{C}$ , it's hard to say if that's our 1/5 decrease. But looking at the Kelvin temperatures, 325 down to 256, we see a drop of about  $70^{\circ}$ , or close to 1/5 of the total initial temperature. The decreases in volume and temperature are proportional, and the answer is reasonable. This is why temperature must be expressed in the Kelvin scale. Also, a Celsius reading with two significant figures (e.g.,  $-17^{\circ}\text{C}$ ) becomes a Kelvin reading with three significant figures (e.g., 256 K).

## SYNTHESIS

The existence of a lowest possible temperature (absolute zero) was first conceived as a result of the relationships found in Charles's law. While there are half a dozen ways of calculating the value of absolute zero, historically it was the concept of extrapolation down to zero volume and notation of the corresponding temperature that gave us the earliest reported value. Prior to observations based on Charles's law, there was no real concept that matter couldn't just keep getting colder but was instead limited. The same result was achieved years later with more accuracy by employing the relationship expressed in Gay-Lussac's law, as discussed in the next section.



Heat increases the pressure of gas in a confined volume. If heated enough, the can will explode.

## 10-3.2 Gay-Lussac's Law

We have now expressed as laws how the volume of a gas is affected by a change in pressure and a change in temperature. Now imagine that we have a confined or constant volume of gas that is subjected to a change in temperature. If the volume cannot change, what about the pressure? The answer is implied on any pressurized can such as hairspray or deodorant: DO NOT INCINERATE OR STORE NEAR HEAT. This practical warning hints at what will happen. When a confined quantity of gas is heated, the pressure increases. Eventually, the seals on the can break and an explosion follows. The relationship between temperature and pressure was proposed in 1802 by Joseph Louis Gay-Lussac. **Gay-Lussac's law** states that the pressure is directly proportional to the Kelvin temperature at constant volume. The law can be expressed mathematically as follows.

$$P \propto T \quad P = kT$$

For a sample of gas under two sets of conditions at the same volume,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad P_2 = P_1 \times \frac{T_2}{T_1}$$

## EXAMPLE 10-4

## Applying Gay-Lussac's Law

A quantity of gas in a steel container has a pressure of 760 torr at 25°C. What is the pressure in the container if the temperature is increased to 50°C?

## PROCEDURE

Identify the initial and final conditions and substitute. Again, the temperature must be expressed in kelvins in the calculation.

## SOLUTION

*Initial Conditions*

$$P_1 = 760 \text{ torr}$$

$$T_1 = (25 + 273) = 298 \text{ K}$$

*Final Conditions*

$$P_2 = ?$$

$$T_2 = (50 + 273) = 323 \text{ K}$$

$$P_2 = P_1 \times \frac{T_2}{T_1}$$

$$P_2 = 760 \text{ torr} \times \frac{323 \text{ K}}{298 \text{ K}} = \underline{\underline{824 \text{ torr}}}$$

## ANALYSIS

We can again apply logic to this problem. Since the temperature increases, the pressure increases. The temperature correction factor must therefore be greater than 1. This is known as an improper fraction.

Again, we can do a quick estimation regarding the size of our answer. The initial analysis leads us to believe that the answer should be greater than the starting pressure, and it is. Is the size of the increase appropriate? We're increasing from 25°C to 50°C. But we also know that it's the Kelvin temperatures that matter, so the appropriate increase is from 298 K to 323 K, less than a 10% rise. The pressure increases from 760 torr to 824 torr, also less than a 10% rise. Our answer appears to be correct in both the direction and magnitude of the change.

## SYNTHESIS

When one variable affects another, it can do so in a number of ways. Two of the most common are *inversely* and *directly*. With variables that are related directly, *when the value of one increases, the other also increases proportionately*. Temperature and pressure are directly related. For variables that are inversely related, *when the value of one increases, the second decreases*. Pressure and volume are inversely related. Can you come up with examples of other variables that are related directly and inversely?

Both Charles's law and Gay-Lussac's law follow naturally from kinetic theory. In Figure 10-9, we again focus on one average molecule of gas moving in a container. In the center, we have the situation before any changes are made. To the left, we have raised the temperature at constant pressure. The molecule travels faster on average at the higher temperature, as shown by its longer path. It also collides with more force on the walls of the container. In order for the pressure to remain constant, the volume must expand correspondingly, which confirms Charles's law. To the right, we have again raised the temperature but this time at constant volume. The more frequent and more forceful collisions mean that the pressure is now higher, which explains Gay-Lussac's law.

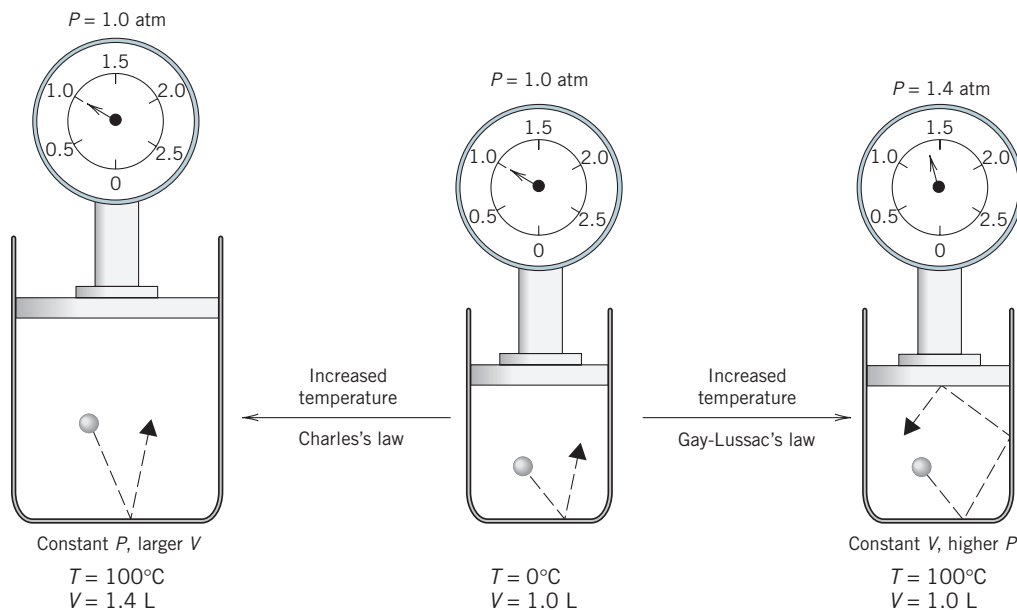
## 10-3.3 The Combined Gas Law

What if we have a quantity of gas where both temperature and pressure change? Of course, we could calculate the new volume of the gas by first correcting for the pressure change (Boyle's law) and then correcting for the temperature change (Charles's law). Or we could construct a new relationship that includes both laws and even Gay-Lussac's law as well. This is known, logically, as the **combined gas law** and is expressed as follows, first as a proportionality and second for a quantity of gas under two sets of conditions. This is not actually a new gas law but a combination of Boyle's, Charles's, and Gay-Lussac's laws.

$$\frac{PV}{T} = k \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

We can now work problems involving simultaneous changes of two conditions. Notice in the following problems that the calculations require that the units of temperature must be Kelvin. The units of pressure and volume can vary but must be the same on both sides in the calculations (i.e., mL or L for volume, torr or atm for pressure).

Obviously, a major property of a gas is that its volume is very dependent on temperature and pressure. Yet gas is sold by the local gas utility in volume units of cubic feet.



**FIGURE 10-9**  
**Charles's Law and Gay-Lussac's Law** When temperature increases, molecules travel faster. If the pressure is constant, the volume increases in order to permit the frequency of collisions to remain the same. If the volume is constant, the pressure increases as a result of the more frequent and more forceful collisions.

Does that mean we get more or less gas in the warm summer than in the cold winter? Actually, we get the same amount because the volume of the gas is measured under certain universally accepted conditions known as **standard temperature and pressure (STP)**.

*Standard temperature:* 0°C or 273 K

*Standard pressure:* 760 torr or 1 atm

Example 10-6 illustrates the use of STP in the combined gas law.

### EXAMPLE 10-5

#### Applying the Combined Gas Law

A 25.8-L quantity of gas has a pressure of 690 torr and a temperature of 17°C. What is the volume if the pressure is changed to 1.85 atm and the temperature to 345 K?

#### PROCEDURE

Identify the two sets of conditions as initial or final. Make sure the units of pressure are the same and temperature is expressed in kelvins.

| <i>Initial Conditions</i>  | <i>Final Conditions</i>  |
|--|--------------------------|
| $V_1 = 25.8 \text{ L}$   | $V_2 = ?$                |
| $P_1 = 690 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.908 \text{ atm}$ | $P_2 = 1.85 \text{ atm}$ |
| $T_1 = (17 + 273) \text{ K} = 290 \text{ K}$   | $T_2 = 345 \text{ K}$    |

#### SOLUTION

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$V_2 = 25.8 \text{ L} \times \frac{0.908 \text{ atm}}{1.85 \text{ atm}} \times \frac{345 \text{ K}}{290 \text{ K}} = \underline{\underline{15.1 \text{ L}}}$$

#### ANALYSIS

$$\text{final volume} = \text{initial volume} \times \begin{matrix} \text{pressure} \\ \text{factor} \end{matrix} \times \begin{matrix} \text{temperature} \\ \text{correction} \\ \text{factor} \end{matrix}$$

Notice that pressure increases, so its correction factor should be less than 1, but the temperature increases, so its correction factor should be greater than 1. In this case, whether the final answer is larger or smaller than the original depends on the relative changes of each. Notice that the pressure nearly doubled. The temperature had a modest increase of less than 20%. The pressure effect should be greater, and it is. The volume decreases.

#### SYNTHESIS

What would have to happen to the pressure and temperature of a gas to produce an increase in volume? What would have to happen to have a decrease in volume? For the gas to expand, the pressure would have to fall and/or the temperature rise. For the gas to contract, just the opposite would have to occur. If both the temperature and pressure rose or fell, then we have the situation as in this example. Which effect is more pronounced? That will be the one having the greater effect on gas volume. It is hard to predict without actually doing the calculation.

### EXAMPLE 10-6

#### Applying the Combined Gas Law and STP

A 5850-ft<sup>3</sup> quantity of natural gas measured at STP was purchased from the gas company. Only 5625 ft<sup>3</sup> was received at the house. Assuming that all the gas was delivered, what was the temperature at the house if the delivery pressure was 1.10 atm?



**PROCEDURE**

Notice that the initial conditions are STP and the final conditions are different. List the conditions and substitute into the combined gas law.

| <i>Initial Conditions</i> | <i>Final Conditions</i>   |
|---------------------------|---------------------------|
| $V_1 = 5850 \text{ ft}^3$ | $V_2 = 5625 \text{ ft}^3$ |
| $P_1 = 1.00 \text{ atm}$  | $P_2 = 1.10 \text{ atm}$  |
| $T_1 = 273 \text{ K}$     | $T_2 = ?$                 |

**SOLUTION**

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad T_2 = T_1 \times \frac{P_2}{P_1} \times \frac{V_2}{V_1}$$

$$T_2 = 273 \text{ K} \times \frac{1.10 \text{ atm}}{1.00 \text{ atm}} \times \frac{5625 \text{ ft}^3}{5850 \text{ ft}^3} = 289 \text{ K}$$

$$T(^{\circ}\text{C}) = 289 \text{ K} - 273 = \underline{\underline{16^{\circ}\text{C}}}$$

**ANALYSIS**

In this case, the final temperature is corrected by a pressure factor and a volume factor. Since the final pressure is higher, the pressure factor must be greater than 1 to increase the temperature. The final volume is lower, so the volume factor must be less than 1 to decrease the temperature.

**SYNTHESIS**

In the course of studying chemistry, it should be a goal of the student to attempt to memorize as little as possible but instead learn applicable concepts that work in the widest number of cases. If you are going to memorize a gas law, make it the combined gas law.

$$\frac{PV}{T} = k \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Notice, then, that if temperature is not part of the problem (or is being held constant), it's no longer part of the equation, and the result is Boyle's law. Similarly, if pressure is no longer a variable, this reduces to Charles's law; if volume is constant, it disappears, and Gay-Lussac's law is the result. You can know four gas laws by knowing just one!

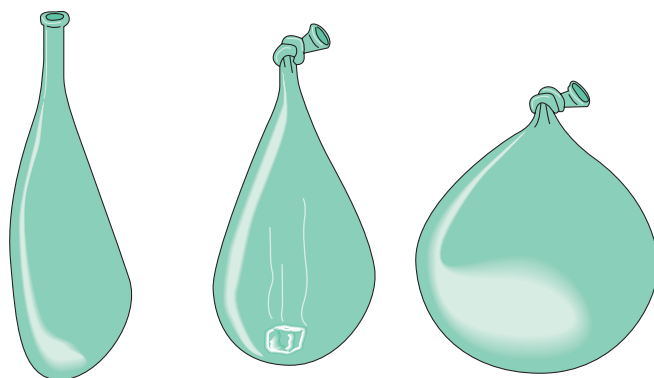
**10-3.4 Avogadro's Law**

The more air we blow into a balloon, the larger it gets. This very obvious statement is the basis of still another gas law.

**Avogadro's law** states that equal volumes of gases at the same pressure and temperature contain equal numbers of molecules. Another way of stating this law is that the volume of a gas is proportional to the number of molecules (moles) of gas present at constant pressure and temperature. Mathematically, this can be stated in three ways, where  $n$  represents the number of moles of gas.

$$V \propto n \quad V = kn \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

In Figure 10-10, the expansion of a balloon by adding carbon dioxide is illustrated. The following example illustrates the use of Avogadro's law in a sample calculation.



**FIGURE 10-10 Avogadro's Law** The addition of carbon dioxide to the balloon increases the number of gas molecules, which increases the volume.

**EXAMPLE 10-7****Applying Avogadro's Law**

A balloon that is not inflated but is full of air has a volume of 275 mL and contains 0.0120 mol of air. As shown in Figure 10-10, a piece of dry ice (solid  $\text{CO}_2$ ) weighing 1.00 g is placed in the balloon and the neck is tied. What is the volume of the balloon after the dry ice has vaporized? (Assume constant  $T$  and  $P$ .)

**PROCEDURE**

Identify the initial and final conditions. The mass of carbon dioxide must be converted to moles and added to the original number of moles present to find the final number of moles of gas.

*Initial Conditions*

$$V_1 = 275 \text{ mL}$$

$$n_1 = 0.0120 \text{ mol}$$

*Final Conditions*

$$V_2 = ?$$

$$n_2 = \text{mol air} + \text{mol CO}_2$$

$$= 0.0120 + \left( 1.00 \text{ g CO}_2 \times \frac{1 \text{ mol}}{44.01 \text{ g CO}_2} \right)$$

$$= 0.0120 + 0.0227 = 0.0347 \text{ mol}$$

**SOLUTION**

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$V_2 = V_1 \times \frac{n_2}{n_1} = 275 \text{ mL} \times \frac{0.0347 \text{ mol}}{0.0120 \text{ mol}}$$

$$V_2 = \underline{795 \text{ mL}}$$

**ANALYSIS**

Notice that the final condition of moles is the original amount plus the added amount. Since more gas has been added, the volume should increase and the mole factor is greater than 1.

**SYNTHESIS**

An interesting consequence of Avogadro's law is that it tells us that *all* gases behave identically. Notice that the volume of a gas at a given temperature and pressure is dependent only on the number of moles. It doesn't matter if the gas particles themselves are big or small. So one mole of very tiny H<sub>2</sub> molecules and one mole of gigantic (relatively speaking) CO<sub>2</sub> molecules occupy exactly the same amount of space. This is counterintuitive at first, until we remember from kinetic molecular theory that gas particles are widely spaced apart and that gases themselves are mostly empty space. So when 1 L of oxygen gas reacts with 2 L of hydrogen gas, it is this nature of gases that allows us to say that the resulting water must have a formula of H<sub>2</sub>O.

**ASSESSING THE OBJECTIVES FOR SECTION 10-3****EXERCISE 10-3(a) KNOWLEDGE:** Fill in the blanks.

An increase in the pressure of a gas causes the volume to \_\_\_\_\_, whereas an increase in temperature causes the same volume to \_\_\_\_\_. Gay-Lussac's law tells us that if the temperature of a confined volume of gas increases, the pressure \_\_\_\_\_. To calculate the effect of two changes in conditions, the \_\_\_\_\_ \_\_\_\_\_ is used. Increasing the number of moles of gas present will \_\_\_\_\_ the volume if other conditions are constant.

**EXERCISE 10-3(b) ANALYSIS:** The volume of 0.0227 mol of gas is 550 mL at a pressure of 1.25 atm and a temperature of 22°C.

- What is the volume at 1.25 atm and 44°C?
- What is the volume if 0.0115 mol of gas is added at the same *T* and *P*?
- What is the pressure at 122°C if the volume remains 550 mL?
- What is the pressure at 22°C if the volume expands to 825 mL?
- What is the volume when you convert to STP conditions?

**EXERCISE 10-3(c) KNOWLEDGE:** Name the law used in each of the calculations in Exercise 10-3(b).

**EXERCISE 10-3(d) SYNTHESIS:** Decide which law predicts the behavior of gas in each of the following conditions.

- a balloon in the winter being moved from indoors to outdoors
- a car tire pressure fluctuating over the course of a year

- (c) dry ice being used in a fog machine to cover a stage with mist  
 (d) piston movement in an internal combustion engine

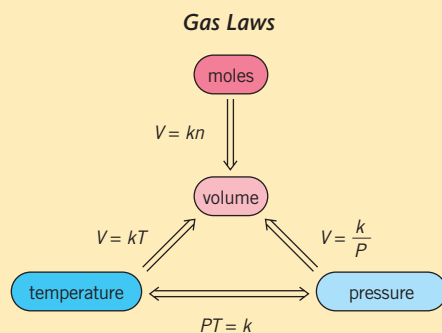
For additional practice, work chapter problems 10-24, 10-25, 10-31, 10-33, 10-40, 10-43, 10-51, and 10-54.

## PART A SUMMARY

### KEY TERMS

- 10-1.2** The properties of gases are explained by the assumptions of the **kinetic molecular theory**, or simply the **kinetic theory**. p. 295
- 10-1.3** **Graham's law** follows from kinetic theory and relates the rates of **diffusion** and **effusion** of a gas to its molar mass. pp. 295–296
- 10-2.1** The **barometer** was the first instrument to measure atmospheric pressure. p. 297
- 10-2.1** **Pressure** is defined as force per unit area. p. 297
- 10-2.1** The pressure of **one atmosphere** equals 760 mm Hg or 760 torr. p. 298
- 10-2.2** **Boyle's law** relates to the effect of pressure on the volume of a gas. p. 299
- 10-3.1** **Charles's law** relates the volume of a gas to the **Kelvin** scale, which begins at **absolute zero**. pp. 302–303
- 10-3.2** **Gay-Lussac's law** relates the pressure of a gas to the temperature. p. 304
- 10-3.3** The **combined gas law** combines Boyle's, Charles's, and Gay-Lussac's laws. p. 305
- 10-3.3** **Standard temperature and pressure (STP)** defines specific conditions for a gas. p. 306
- 10-3.4** **Avogadro's law** relates the volume to the moles of gas present. p. 307

### SUMMARY CHART



## PART B RELATIONSHIPS AMONG QUANTITIES OF GASES, CONDITIONS, AND CHEMICAL REACTIONS

### SETTING A GOAL

- You will learn to apply a generalized gas law to a variety of quantitative gas problems.

### OBJECTIVES

- 10-4** Using the ideal gas law, calculate one condition of a gas given the other stated conditions.
- 10-5** Using Dalton's law, calculate the partial pressure of a gas.
- 10-6 (a)** Using the molar volume, convert volume to moles and mass. **(b)** Calculate the density of a gas at STP.
- 10-7** Perform stoichiometric calculations involving gas volumes.

▶ **OBJECTIVE FOR SECTION 10-4**

Using the ideal gas law, calculate one condition of a gas given the other stated conditions.

## 10-4 THE IDEAL GAS LAW



**LOOKING AHEAD!** In this section, we will find that we can arrive at the ultimate general gas law by putting the information in the last two sections together in the form of one equation. This very important equation leads us to other general properties of gases. ■

### 10-4.1 Derivation of the Ideal Gas Law

How can we make a small balloon larger? In fact, we have discussed three ways. First, we could take it up a mountain to a higher elevation. The lower atmospheric pressure would allow it to expand (Boyle's law). Second, we could raise the temperature. If we placed the balloon in boiling water, it would certainly expand (Charles's law). And finally, we could just blow more gas in it (Avogadro's law). We can summarize these three relationships as follows.

$$V \propto \frac{1}{P} \quad V \propto T \quad V \propto n$$

We can put all three individual relationships into one general relationship as follows.

$$V \propto \frac{nT}{P}$$

This relationship is an extended version of the combined gas law that now includes Avogadro's law. As before, we can change a proportionality to an equality by introducing a constant of proportionality. The constant used in this case is designated  $R$  and is called the **gas constant**. Since we are now examining *all* the variables that can affect a gas, this constant will not change under any condition. Traditionally, the constant is placed between the  $n$  and  $T$  in the equation.

$$V = \frac{nRT}{P} \quad \text{or} \quad PV = nRT$$

This relationship is known as the **ideal gas law**. In fact, all of the laws previously discussed (except for Graham's law) can be derived from this one relationship. For example, consider a confined quantity of gas that is subject to a change of pressure when the temperature is constant. Before the change (conditions designated by the subscript 1) we have  $P_1V_1 = n_1RT_1$ . After the change (conditions designated by the subscript 2), we have  $P_2V_2 = n_2RT_2$ . By solving both equations for the constant  $R$  and setting them equal to each other we have

$$R = \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

If we have a confined quantity of gas (i.e.,  $n_1 = n_2$ ) and the temperature does not change (i.e.,  $T_1 = T_2$ ), we can substitute  $n_1$  for  $n_2$  and  $T_1$  for  $T_2$ . Notice then that  $n$  and  $T$  both cancel and we have Boyle's law.

$$\frac{P_1V_1}{\cancel{n_1T_1}} = \frac{P_2V_2}{\cancel{n_2T_2}} = \frac{P_2V_2}{\cancel{n_1T_1}} \quad P_1V_1 = P_2V_2$$

Similar exercises lead to Charles's, Gay-Lussac's, and the combined gas laws. However, the ideal gas law has a more important application than the exercises we have covered so far, where the effect of changing conditions is calculated. With this law we can calculate one condition (e.g., the volume) of a gas if the other three are known (i.e.,  $n$ ,  $P$ , and  $T$ ). For these calculations, however, we need the value of the gas constant, which is

$$0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

For the calculations used in this text, we will use the value of  $R$  expressed to three significant figures (e.g., 0.0821). Note that the units of  $R$  are a result of specific units of  $P$ ,  $V$ , and  $T$ . Thus, in all calculations that follow, the pressure must be expressed in *atmospheres*, the temperature in *Kelvin*, and the volume in *liters*. The following three examples illustrate the use of the ideal gas law with a missing variable under one set of conditions.

### 10-4.2 The Meaning of an Ideal Gas

This law is called “ideal” because it follows from the assumptions of the kinetic theory, which describes an ideal gas. The molecules of an ideal gas have negligible volume and no attraction or repulsion for each other. The molecules of a “real” gas obviously do have a volume, and there is some interaction between molecules, especially at high pressures (i.e., the molecules are pressed close together) and low temperatures (i.e., the molecules move more slowly).

Fortunately, at normal temperatures and pressures found on the surface of Earth, gases have close to ideal behavior. That is, they are far enough apart so that the gas molecules themselves essentially take up no space and they move past one another so fast that interactions between molecules can be ignored. The latter situation is like a young man and young woman rapidly passing each other in jet airliners, unaware of each other’s presence. In contrast, assume they pass while walking in the park, where they may very likely slow down as they exchange glances indicating attraction (or, conversely, speed up if they are repelled). Therefore, the use of the ideal gas law is justified. On the other hand, regions of the atmosphere of the planet Jupiter are composed of cold gases under very high pressures. Under these conditions, the ideal gas law would not provide acceptable values for a variable (i.e.,  $PV$  does not exactly equal  $nRT$ ). Other, more complex equations would have to be used that take into account the volume of the molecules and the interactions between molecules.

#### EXAMPLE 10-8

##### Calculating Pressure Using the Ideal Gas Law

What is the pressure of a 1.45-mol sample of a gas if the volume is 20.0 L and the temperature is 25°C?

##### PROCEDURE

Write down conditions, making sure the units correspond to those in  $R$ . Solve the ideal gas law for  $P$  by dividing both sides of the equation by  $V$ .

$$P = ? \quad V = 20.0 \text{ L} \quad n = 1.45 \text{ mol} \quad T = (25 + 273)\text{K} = 298\text{K}$$

$$PV = nRT \quad P = \frac{nRT}{V}$$

##### SOLUTION

$$P = \frac{nRT}{V} = \frac{1.45 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}}{20.0 \text{ L}}$$

$$= \underline{\underline{1.77 \text{ atm}}}$$

#### EXAMPLE 10-9

##### Calculating Volume Using the Ideal Gas Law

What is the volume of 1.00 mol of gas at STP?

##### PROCEDURE

List the variables given and solve for  $V$  in the ideal gas law.

$$P = 1.00 \text{ atm} \quad V = ? \quad T = 273 \text{ K} \quad n = 1.00 \text{ mol}$$

**SOLUTION**

$$\begin{aligned}
 PV &= nRT \\
 V &= \frac{nRT}{P} \\
 V &= \frac{1.00 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 273 \text{ K}}{1.00 \text{ atm}} = \underline{\underline{22.4 \text{ L}}}
 \end{aligned}$$

**EXAMPLE 10-10****Calculating Temperature Using the Ideal Gas Law**

What is the Celsius temperature of a 1.10-g quantity of oxygen in a 4210-mL container at a pressure of 495 torr?

**PROCEDURE**

Convert mass of oxygen to moles, mL to L, and torr to atm to be consistent with the units expressed for  $R$ . Solve for  $T$  by dividing both sides of the ideal gas equation by  $nR$ . Substitute variables in the equation and solve for  $T$  (i.e.,  $T = PV/nR$ ). Finally, convert  $T$  to  $T(^{\circ}\text{C})$ .

**SOLUTION**

$$\begin{aligned}
 n &= 1.10 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} = 0.0344 \text{ mol O}_2 \\
 P &= \frac{495 \text{ torr}}{760 \text{ torr/atm}} = 0.224 \text{ atm} \quad V = 4210 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} = 4.21 \text{ L} \\
 T &= \frac{PV}{nR} = \frac{0.224 \text{ atm} \times 4.21 \text{ L}}{(0.0344 \text{ mol}) \times \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)} = 334 \text{ K} \\
 ^{\circ}\text{C} &= 334 - 273 = \underline{\underline{61^{\circ}\text{C}}}
 \end{aligned}$$

**ANALYSIS**

In all the previous cases of applications of gas laws, we were merely converting gas conditions from one set of variables to another. The reason is that we were always missing two of the four variables (volume, pressure, temperature, and moles). But in these last three problems, three of the four variables are given. With the knowledge of the proportionality constant,  $R$ , we are in a position to calculate specifics of a particular example, rather than just comparing how a sample might change.

**SYNTHESIS**

There might be initial confusion when faced with a typical gas law problem. Which of the several possible laws is the one to use? A careful accounting of the specific variables mentioned in the problem shows the right path. A problem providing two volumes and a pressure while asking for a second pressure requires which law to solve? Boyle's law. A problem giving a volume, pressure, and number of moles (or some value, like grams, easily converted to moles) while asking for a temperature? The ideal gas law.

**ASSESSING THE OBJECTIVE FOR SECTION 10-4**

**EXERCISE 10-4(a) ANALYSIS:** What is the Celsius temperature of  $2.46 \times 10^{-4}$  g of  $\text{N}_2\text{O}$  if it is present in a 2.35-mL container at a pressure of 0.0468 atm?

**EXERCISE 10-4(b) ANALYSIS:** How many particles of gaseous air molecules are found in a 500.0-mL flask at STP?

**EXERCISE 10-4(c) SYNTHESIS:** If you were writing your own gas law, and exploring the relationship between moles and pressure at constant volume and temperature, what would the law look like?

*For additional practice, work chapter problems 10-55, 10-57, and 10-59.*



## 10-5 DALTON'S LAW OF PARTIAL PRESSURES

### OBJECTIVE FOR SECTION 10-5

Using Dalton's law, calculate the partial pressure of a gas.



**LOOKING AHEAD!** Kinetic theory tells us that gas molecules behave independently. This property has several consequences. Avogadro's law illustrates that equal volumes of gases contain equal numbers of molecules regardless of their masses or nature. In this section, we will see that pressures are also independent of the identity of the gases involved. ■

About 78% of the atmosphere is composed of nitrogen, 21% is oxygen, and a little less than 1% is argon. This means that 21% of the molecules as well as 21% of the pressure we feel from the atmosphere are due to oxygen. Only in terms of the mass of the atmosphere does oxygen not represent 21%, because of the different molar masses of the components. The fact that pressure, like volume, does not depend on the identity of the gas was first suggested by John Dalton, author of modern atomic theory. Another gas law resulted. **Dalton's law** states that the total pressure of a gas in a system is the sum of the partial pressures of each component gas. The partial pressure of a specific gaseous element or compound is defined as the pressure due to that substance alone. Mathematically, this can be stated as  $P_{\text{tot}} = P_1 + P_2 + P_3 + \dots$  ( $P_1$  is the pressure due to gas 1, etc.).

### EXAMPLE 10-11

#### Calculating the Total Pressure of a Mixture of Gases

Three gases, Ar, N<sub>2</sub>, and H<sub>2</sub>, are mixed in a 5.00-L container. Ar has a pressure of 255 torr, N<sub>2</sub> has a pressure of 228 torr, and H<sub>2</sub> has a pressure of 752 torr. What is the total pressure in the container?

#### PROCEDURE

According to Dalton's law, the total pressure is the sum of the partial pressures of each gas. Add the three partial pressures together.

#### SOLUTION

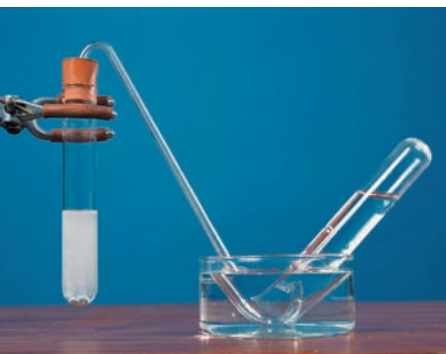
$$\begin{aligned} P_{\text{Ar}} &= 255 \text{ torr} & P_{\text{N}_2} &= 228 \text{ torr} & P_{\text{H}_2} &= 752 \text{ torr} \\ P_{\text{tot}} &= P_{\text{Ar}} + P_{\text{N}_2} + P_{\text{H}_2} = 255 \text{ torr} + 228 \text{ torr} + 752 \text{ torr} \\ &= \underline{\underline{1235 \text{ torr}}} \end{aligned}$$

#### ANALYSIS

While the pressures of each of the gases are different, the volume of each is 5.00 L. Each gas must also necessarily be at the same temperature, 25°C. By using the ideal gas law, we can calculate the number of moles of each. Doing so, we realize that in a sample of gas that is a mixture, the number of moles is directly proportional to each gas's partial pressure. So, for our sample above, there are close to the same number of moles of argon and nitrogen, and three times as many moles of hydrogen as either of the others.

#### SYNTHESIS

One of the important applications of Dalton's law occurs is when we collect gas samples. How can we fill a container full of gas? The process is called "collecting over water." Fill the container with water first, and then allow the gas to bubble into the inverted container, placed in a sink. The gas displaces the water. This process, though, results in two gases actually being in the container—the gas we're collecting and water vapor. By Dalton's law, we have to subtract the vapor pressure of water from the total pressure if we are to know the pressure of the gas we were hoping to isolate. (See the photo on the next page)



Gases collected over water are actually a mixture of the gas and water vapor.

We can now apply Dalton's law to the composition of our atmosphere. Since 21% of the molecules of the atmosphere are oxygen, 21% of the pressure of the atmosphere is due to oxygen. The partial pressure of oxygen can be calculated by multiplying the percent in decimal form by the total pressure.

$$P_{\text{O}_2} = 0.21 \times 760 \text{ torr} = 160 \text{ torr}$$

Most of us function best breathing this partial pressure of oxygen. When we live at higher elevations, the partial pressure of oxygen is lower and our bodies adjust by producing more red blood cells, which transport oxygen. On top of the highest mountain, Mt. Everest, the total atmospheric pressure is 270 torr, so the partial pressure of oxygen is only 57 torr, or about one-third of normal. A human cannot survive for long at such a low pressure of oxygen. At that altitude, even conditioned climbers must use an oxygen tank and mask, which give an increased partial pressure of oxygen to the lungs.

### EXAMPLE 10-12

#### Calculating the Partial Pressure of a Gas

On a humid summer day, the partial pressure of water in the atmosphere is 18 torr. If the barometric pressure on this day is a high 766 torr, what are the partial pressures of nitrogen and of oxygen if 78.0% of the dry atmosphere is composed of nitrogen molecules and 21.0% is oxygen? (1% of the dry atmosphere is composed of all other gases.)

#### PROCEDURE

1. Find the pressure of the dry atmosphere by subtracting the pressure of water from the total. This is an application of Dalton's law (i.e.,  $P_{\text{tot}} = P_{\text{N}_2} + P_{\text{O}_2} + P_{\text{H}_2\text{O}} + P_{\text{other}}$ ).
2. Find the partial pressures of  $\text{N}_2$  and of  $\text{O}_2$  from the total pressure of the dry atmosphere and the percents.

#### SOLUTION

1.  $P$  (dry atmosphere) =  $P_{\text{tot}} - P_{\text{H}_2\text{O}} = 766 - 18 = 748 \text{ torr}$
2.  $P_{\text{N}_2} = 0.780 \times 748 \text{ torr} = \underline{583 \text{ torr}}$   
 $P_{\text{O}_2} = 0.210 \times 748 \text{ torr} = \underline{157 \text{ torr}}$

#### ANALYSIS

The percentages we are supplying for the gases in the atmosphere are *mole* percentages as opposed to *mass* percentages. The percent composition of a mixture could be presented in either fashion, depending on which amount (mass or number of particles) is more important. For applications involving gas theory and specifically Dalton's law, mole percentages (or *mole fractions*) are the necessary values. They are calculated like any other percentage; that is, the number of moles of the component is divided by the total number of moles present.

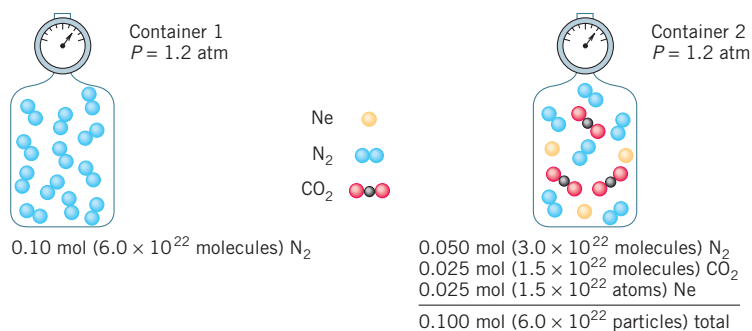
#### SYNTHESIS

Water vapor is a variable component of the atmosphere and can range from almost 0% in dry climates to as much as 4% in humid areas. We don't typically include it in our discussion of atmospheric gases, which are reported under dry conditions. The amount of water vapor in the air is also limited by the temperature. The warmer it is, the more water vapor the atmosphere can hold. What time of year do your lips chafe the worst? Why? Typically it's in the winter, which, despite snow and ice, has very low amounts of water vapor in the air; therefore, your lips dry out. We will discuss this in more detail in the next chapter.

The total pressure of a mixture of gases can be extended to the ideal gas law. For example, for three gases in one container,

$$P_{\text{tot}} = P_1 + P_2 + P_3 = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} = \frac{n_{\text{tot}}RT}{V}$$

We see that, at a given temperature, the pressures of gases depend only on the total number of moles present. This is illustrated in Figure 10-11 and Example 10-13.



**FIGURE 10-11**  
**Pressures of a Pure Gas and a Mixture of Gases** Pressure depends only on the number of molecules at a certain temperature, not on their identity.

### EXAMPLE 10-13

#### Calculating the Total Pressure of a Mixture of Gases

What is the pressure (in atmospheres) exerted by a mixture of 12.0 g of  $\text{N}_2$  and 12.0 g of  $\text{O}_2$  in a 2.50-L container at  $25^\circ\text{C}$ ?

#### PROCEDURE

1. Find the number of moles of  $\text{N}_2$  and  $\text{O}_2$  present.
2. Use the total number of moles, temperature, and volume in the ideal gas law.

#### SOLUTION

$$1. \quad n_{\text{O}_2} = 12.0 \text{ g-O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g-O}_2} = 0.375 \text{ mol O}_2$$

$$n_{\text{N}_2} = 12.0 \text{ g-N}_2 \times \frac{1 \text{ mol N}_2}{28.02 \text{ g-N}_2} = 0.428 \text{ mol N}_2$$

$$n_{\text{tot}} = 0.375 \text{ mol} + 0.428 \text{ mol} = 0.803 \text{ mol of gas}$$

$$V = 2.50 \text{ L} \quad T = (25 + 273) = 298 \text{ K} \quad R = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

$$2. \quad PV = nRT$$

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

$$P = \frac{0.803 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}}{2.50 \text{ L}} = \underline{\underline{7.86 \text{ atm}}}$$

#### ANALYSIS

Notice that the volume of each gas is taken to be the volume of the container (2.50 L), reinforcing the notion that each gas acts independently when mixed, expanding to fill the container completely. Furthermore, all gases act the same way, so we can add the moles of two different gases together and treat them as one.

#### SYNTHESIS

This example has applications during pressure-changing events like scuba diving, ballooning, or mountain climbing. It also explains why airlines pressurize cabins before flights. The percent of each component of a gas will remain constant, even as the pressure changes. This leads to a lower partial pressure of oxygen when ascending in the atmosphere or a higher partial pressure when descending (while scuba diving, for instance). If we are to get the necessary amount of oxygen into our system during these various events, sometimes extra precautions are needed, such as tanks of pure  $\text{O}_2$  to supplement the lack of  $\text{O}_2$  in the air or, on the other end of the spectrum, diving tables that instruct us how to limit the amount of pressurized  $\text{N}_2$  that we're exposed to during submersion.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 10-5

**EXERCISE 10-5(a) ANALYSIS:** For a gas collected over water at a total pressure of 750 torr, if the vapor pressure of the water is 35 torr, what's the pressure of the gas?

**EXERCISE 10-5(b) ANALYSIS:** What is the partial pressure of  $O_2$  if 0.0450 mol of  $O_2$  is mixed with 0.0328 mol of  $N_2$  and the total pressure in the container is 596 torr?

**EXERCISE 10-5(c) SYNTHESIS:** If you had equal masses of helium, methane ( $CH_4$ ), and carbon dioxide, which would exert the highest pressure?

*For additional practice, work chapter problems 10-64, 10-66, and 10-68.*

▶ OBJECTIVES FOR  
SECTION 10-6

(a) Using the molar volume, convert volume to moles and mass. (b) Calculate the density of a gas at STP.

## 10-6 THE MOLAR VOLUME AND DENSITY OF A GAS



**LOOKING AHEAD!** In previous chapters, we found that one mole of a compound represents a set number of molecules and a specific mass. If the compound also happens to be a gas, we find that one mole also represents a set volume under specified conditions. We explore this next. ■

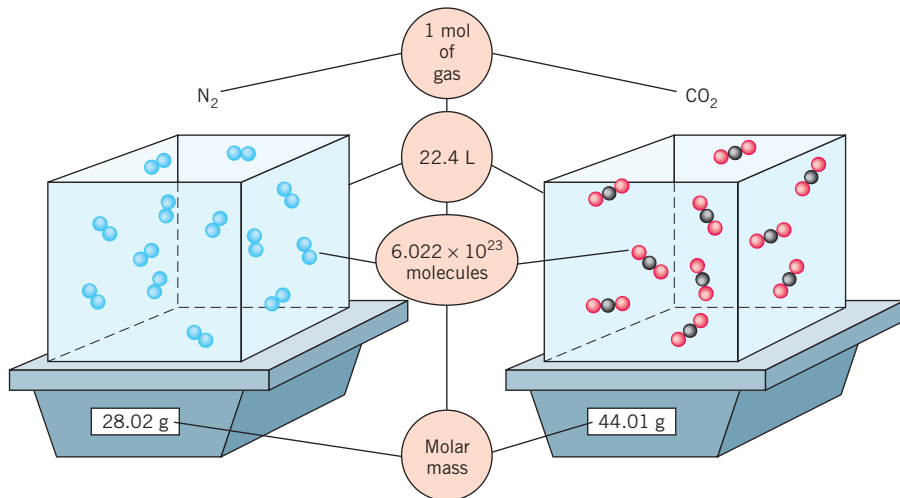
## 10-6.1 The Molar Volume

In Example 10-9, we calculated the volume of one mole of a gas at standard temperature and pressure. This result represents the volume of one mole of *any* gas, or

even one mole of a mixture of gases, at STP. This phenomenon is certainly not true of equal volumes of liquids and solids. *The volume of one mole of gas at STP, 22.4 L, is known as the molar volume.* This corresponds to about 6 gallons. We can now expand on the significance of the mole that was described in Chapter 6. One mole of a gas refers to three quantities: (1) the molar volume (22.4 L/mol, or 22.414 L/mol to be more precise) and (2) Avogadro's number ( $6.022 \times 10^{23}$  molecules/mol), both of which are independent of the identity of the gas, and (3) the molar mass (g/mol), which depends on the identity of the gaseous compound or element.

(See Figure 10-12.) By using the molar volume relationship, scientists were able to calculate the relative masses of various gaseous compounds. This occurred well before they even knew about the existence of the protons and neutrons that provide the actual masses.

Moles of a gas relate directly to volume at STP using the molar volume relationship. At any other conditions, moles relate to the volume using the ideal gas law.



**FIGURE 10-12 Moles of Two Different Gases** At STP, one mole of any gas has the same volume, the same number of molecules, but different masses.

**EXAMPLE 10-14****Calculating Mass from Volume at STP**

What is the mass of 4.55 L of O<sub>2</sub> measured at STP?

**PROCEDURE**

- Convert volume to moles using the molar volume relationship. The two possible conversion factors for converting volume to moles are

$$\frac{1 \text{ mol}}{22.4 \text{ L}} \quad \text{and} \quad \frac{22.4 \text{ L}}{\text{mol}}$$

- Convert moles to mass of O<sub>2</sub> using the molar mass of O<sub>2</sub>. The complete unit map is

**SOLUTION**

$$4.55 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}} \times \frac{32.00 \text{ g}}{\text{mol}} = \underline{\underline{6.50 \text{ g}}}$$

**EXAMPLE 10-15****Calculating Molar Mass from Volume at STP**

A sample of gas has a mass of 3.20 g and occupies 2.00 L at 17°C and 380 torr. What is the molar mass of the gas?

**PROCEDURE**

- Convert the given volume to the corresponding volume at STP using the combined gas law.

| <i>Initial Conditions</i>                    | <i>Final Conditions</i>  |
|--|--------------------------|
| $V_1 = 2.00 \text{ L}$                       | $V_2 = ?$                |
| $P_1 = 380 \text{ torr}$                     | $P_2 = 760 \text{ torr}$ |
| $T_1 = (17 + 273) \text{ K} = 290 \text{ K}$ | $T_2 = 273 \text{ K}$    |

- Convert volume at STP to moles of gas using the molar volume relationship.
- Convert moles and mass to molar mass (represented in equations as MM) as follows.

$$n = \frac{\text{mass}}{\text{MM}} \quad \text{MM} = \frac{\text{mass}}{n}$$

**SOLUTION**

$$1. \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$V_2 = 2.00 \text{ L} \times \frac{380 \text{ torr}}{760 \text{ torr}} \times \frac{273 \text{ K}}{290 \text{ K}} = \underline{\underline{0.941 \text{ L (STP)}}}$$

$$2. \quad 0.941 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 0.0420 \text{ mol of gas}$$

$$3. \quad \text{molar mass} = \frac{\text{mass}}{n} = \frac{3.20 \text{ g}}{0.0420 \text{ mol}} = \underline{\underline{76.2 \text{ g/mol}}}$$

**ANALYSIS**

There is actually a more direct way of solving this problem using the ideal gas law. First, use the ideal gas law to find the number of moles of gas at the given conditions. Then use the relationship for molar mass (i.e.,  $n = \text{mass}/\text{MM}$ ) to find the molar mass of the gas.

$$PV = nRT \quad n = PV/RT \quad T = 17 + 273 = 290 \text{ K}$$

$$P = \frac{380 \text{ torr}}{760 \text{ torr/atm}} = 0.500 \text{ atm}$$

$$n = \frac{0.500 \text{ atm} \times 2.00 \text{ L}}{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 290 \text{ K}} = 0.0420 \text{ mol}$$

$$n = \frac{\text{mass}}{\text{MM}} \quad \text{MM} = \frac{\text{mass}}{n} = \frac{3.20 \text{ g}}{0.0420 \text{ mol}} = \underline{\underline{76.2 \text{ g/mol}}}$$

**SYNTHESIS**

This problem illustrates how much gas can be compressed into a container as a liquid. Whether in a butane lighter, a carbon dioxide fire extinguisher, or a propane tank for a gas grill, one mole of the liquid will expand to a volume of 22.4 L at STP. Since we usually use these gases at temperatures higher than 0°C, the volume of one mole is even higher—closer to 25 L per mole. That's a dramatic increase in volume and why caution should be exercised every time you use gases under compressed conditions. The possibility of a rapid expansion (or explosion) is very real if the regulators on these tanks fail.

**10-6.2 Density of a Gas at STP**

In Chapter 3, the densities of solids and liquids were given in units of g/mL. Since gases are much less dense, units in this case are usually given in g/L (STP). The density of a gas at STP can be calculated by dividing the molar mass by the molar volume.

$$\text{CO}_2: 44.01 \text{ g/mol} = 22.4 \text{ L/mol}$$

$$\frac{44.01 \text{ g/mol}}{22.4 \text{ L/mol}} = 1.96 \text{ g/L (STP)}$$

The densities of several gases are given in Table 10-2. According to kinetic molecular theory, two different gases under identical conditions with the same volume contain the same number of particles. But if one gas has a higher molar mass, then it has a higher mass per unit volume, or density. The density of air (a mixture) is 1.29 g/L. Gases such as He and H<sub>2</sub> have low molar masses and are thus less dense than air. Gases less dense than air rise in the air, just as solids or liquids less dense than water float on water. Helium is used as the gas in blimps to make the whole craft “lighter than air.” (See chapter problem 10-62.)

**TABLE 10-2****Densities of Some Gases**

| GAS                             | DENSITY<br>[g/L (STP)] |
|---------------------------------|------------------------|
| H <sub>2</sub>                  | 0.090                  |
| He                              | 0.179                  |
| N <sub>2</sub>                  | 1.25                   |
| Air (average)                   | 1.29                   |
| O <sub>2</sub>                  | 1.43                   |
| CO <sub>2</sub>                 | 1.96                   |
| CF <sub>2</sub> Cl <sub>2</sub> | 5.40                   |
| SF <sub>6</sub>                 | 6.52                   |

**ASSESSING THE OBJECTIVES FOR SECTION 10-6**

**EXERCISE 10-6(a) KNOWLEDGE:** Fill in the blanks.

One mole of any gas occupies \_\_\_\_\_ L at STP; this is known as the \_\_\_\_\_. The density of a gas at STP is obtained by dividing the \_\_\_\_\_ by the molar volume.

**EXERCISE 10-6(b) ANALYSIS:** What is the volume occupied by 142 g of SF<sub>4</sub> at STP?

**EXERCISE 10-6(c) ANALYSIS:** What is the density of SF<sub>4</sub> at STP?

**EXERCISE 10-6(d) SYNTHESIS:** It is well known that breathing helium makes your voice higher. This is due to the lighter, less dense atoms of helium causing your vocal cords to vibrate faster and at a higher pitch. Which other gases on the periodic table would have the same effect. What gases on the table would lower the pitch of your voice? (This is certainly not an experiment that one would actually try.)

*For additional practice, work chapter problems 10-75, 10-78, 10-80, and 10-83.*



MAKING

IT

REAL

## Defying Gravity—Hot-Air Balloons



Hot air is less dense than cool air.

In July 2002, Steve Fossett became the first person to fly solo around the globe in a hot-air balloon. However, hot-air balloons have a long history. Ancient peoples probably realized that hot air rose by observing the ascending embers of a campfire. The first creatures to go aloft in a hot-air balloon were a duck, a chicken, and a sheep on September 19, 1783. The inventors of this device were the Montgolfier brothers in France. Convinced that the apparatus worked, two men made the first

ascent into space by humans later that year. Since the 1960s, hot-air ballooning has become increasingly popular with the use of newer, lightweight materials. Now we have the magnificent displays of balloons of all shapes and sizes floating with the wind over the countryside.

How do they work? They are actually an application of Charles's law, which states that the hotter a gas becomes, the more volume it requires at the same pressure. The expansion of a gas lowers its density, so it becomes buoyant in the surrounding air. Thus, it rises, just like a cork floats in water because it is less dense. The normal density

of air at 25°C is about 1.18 g/L. (It is 1.29 g/L at STP.) If the air is heated to 125°C, the expansion causes the density to decrease to 0.88 g/L. The difference is the lifting power of the balloon. Thus a 1-L balloon containing the hot gas could lift 0.30 g. In order to lift the balloon, a gondola, a burner, and a couple of people, the balloon must lift about 1000 lb. That would take a volume of over  $1.5 \times 10^6$  L (about 53,000 ft<sup>3</sup>). A larger balloon or hotter air could lift more weight or go higher.

The other way to have a gas less dense than the surroundings is to use a gas with a low molar mass such as helium (4 g/mol) or hydrogen (2 g/mol). For 1 L of gas at 25°C, this means that He can lift 1.0 g and hydrogen, 1.1 g. Helium is preferred since it is noncombustible. Hydrogen was used until the 1930s disaster at Lakehurst, New Jersey, when the German airship *Hindenburg* caught fire. (Recent evidence, though, suggests that it was, in fact, the skeletal structure of the airship, not the hydrogen, that initially ignited.)

In fact, Fossett's lighter-than-air ship used a combination of hot air and helium. It ascended as high as 35,000 feet to the altitude of jet airliners. It was a marvelous feat that he accomplished on the sixth try. It only took 219 years after the first two men left the bounds of Earth.

## 10-7 STOICHIOMETRY INVOLVING GASES

### OBJECTIVE FOR SECTION 10-7

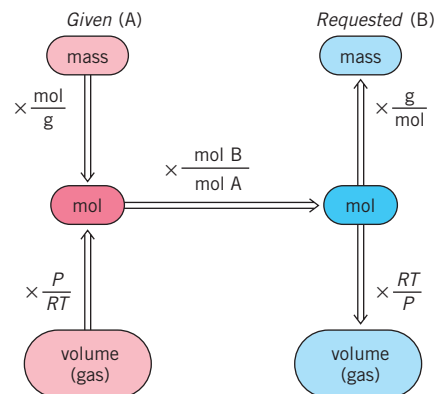
Perform stoichiometric calculations involving gas volumes.



**LOOKING AHEAD!** Gases are formed or consumed in many chemical reactions. Since the volumes of gases relate directly to the number of moles, we can use volume as we did mass or number of molecules in previous stoichiometric calculations discussed in Chapter 7. ■

Recall that gas volumes relate to moles using the ideal gas law. At standard conditions, it is more convenient to use the molar volume relationship [i.e.,  $n = V(\text{STP})/22.4 \text{ L/mol}$ ]. We can now add gas volumes to mass and number of molecules (see Figure 7-1) to the procedure for solving stoichiometry problems. (See Figure 10-13.) We have omitted number of molecules from this scheme because problems involving actual numbers of molecules are rarely encountered.

The following two examples illustrate the relationship of the gas laws to stoichiometry.

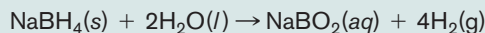


**FIGURE 10-13** General Procedure for Stoichiometric Problems

Gas volumes relate directly to moles, so they are included in stoichiometric calculations.

**EXAMPLE 10-16****Calculating Mass of a Reactant from the Volume of a Product**

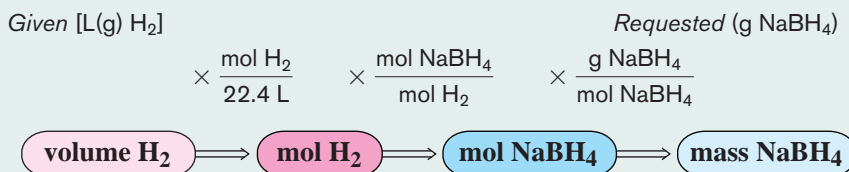
Automobiles in the future may likely run on hydrogen gas in a fuel cell. Storing the hydrogen and providing it conveniently remain problems, however. One possibility is the addition of water to a solid compound such as sodium borohydride. The balanced equation illustrating the generation of hydrogen by this reaction is



What mass of  $\text{NaBH}_4$  is needed to produce 50.0 L of  $\text{H}_2$  measured at STP?

**PROCEDURE**

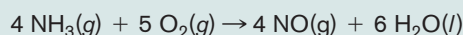
The general procedure is shown below. Since the conditions of this case are at STP, it is easier to use the molar volume as a conversion factor between volume and moles. The complete unit map for this problem is illustrated below.

**SOLUTION**

$$50.0 \text{ L (STP)} \times \frac{1 \text{ mol H}_2}{22.4 \text{ L (STP)}} \times \frac{1 \text{ mol NaBH}_4}{4 \text{ mol H}_2} \times \frac{37.83 \text{ g NaBH}_4}{\text{mol NaBH}_4} = \underline{\underline{21.1 \text{ g NaBH}_4}}$$

**EXAMPLE 10-17****Calculating Volume of a Product from Mass of a Reactant**

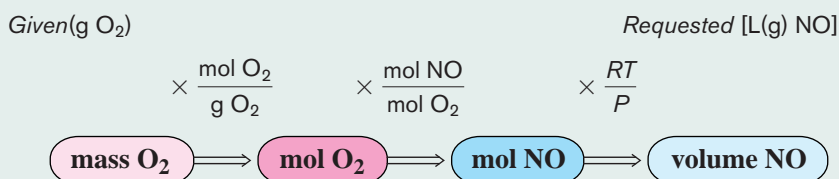
Given the balanced equation



what volume of NO gas measured at 0.724 atm and 25°C will be produced from 19.5 g of  $\text{O}_2$ ?

**PROCEDURE**

Convert mass of  $\text{O}_2$  to moles of  $\text{O}_2$ , then moles of  $\text{O}_2$  to moles of NO, and finally to volume of NO at the stated conditions. The complete unit map for this problem is illustrated below.

**SOLUTION**

$$19.5 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{4 \text{ mol NO}}{5 \text{ mol O}_2} = 0.488 \text{ mol NO}$$

Using the ideal gas law

$$V = \frac{nRT}{P} = \frac{0.488 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}}{0.724 \text{ atm}} = \underline{\underline{16.5 \text{ L}}}$$

**ANALYSIS**

An alternate path is to (1) convert the moles of NO to the volume at STP then (2) convert from STP to the stated conditions using the combined gas law.

$$1. \quad 0.488 \text{ mol} \times 22.4 \text{ L/mol} = 10.9 \text{ L (STP)}$$

$$2. V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

Initial Conditions

$$\begin{aligned} V_1 &= 10.9 \text{ L} \\ P_1 &= 760 \text{ torr} \\ T_1 &= 273 \text{ K} \end{aligned}$$

Final Conditions

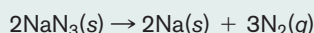
$$\begin{aligned} V_2 &= ? \\ P_2 &= 550 \text{ torr} \\ T_2 &= (25 + 273) \text{ K} = 298 \text{ K} \end{aligned}$$

$$V_2 = 10.9 \text{ L} \times \frac{760 \text{ torr}}{550 \text{ torr}} \times \frac{298 \text{ K}}{273 \text{ K}} = \underline{\underline{16.4 \text{ L}}}$$

(The slight difference in the two values is due to rounding off.)

### SYNTHESIS

Gas stoichiometry has real-world significance if you have been unfortunate enough to have been in an automobile when the airbag deployed. The bag fills with nitrogen gas ( $\text{N}_2$ ) produced from the decomposition of solid sodium azide ( $\text{NaN}_3$ ). The decomposition of sodium azide is illustrated by the equation



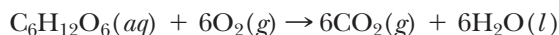
Can you estimate how much  $\text{NaN}_3$  it would take to prime an airbag? Let's assume an airbag of 50 L. Under conditions close to STP, that's about 2 mol of gas. It takes 2 mol of  $\text{NaN}_3$  to produce 3 mol of  $\text{N}_2$ , or about  $1\frac{1}{3}$  mol of  $\text{NaN}_3$  to make 2 mol of  $\text{N}_2$ . The molar mass of  $\text{NaN}_3$  is 65 grams per mole, so it will take between 80 and 90 g of  $\text{NaN}_3$  to inflate the bag.

### ASSESSING THE OBJECTIVE FOR SECTION 10-7

**EXERCISE 10-7(a) KNOWLEDGE:** Fill in the blanks.

In stoichiometry calculations, the volume of a gas can be converted to number of moles by use of the \_\_\_\_\_ if the volume is measured at STP. If other conditions are present, the volume is related to the number of moles by the \_\_\_\_\_.

**EXERCISE 10-7(b) ANALYSIS:** Humans obtain energy from the combustion of blood sugar (glucose) according to the equation



- What volume of  $\text{O}_2$  measured at STP is required to react with 0.122 mol of glucose?
- What volume of  $\text{CO}_2$  measured at  $25^\circ\text{C}$  and 1.10 atm pressure is released from the combustion of 228 g of glucose?
- What mass of glucose is required to react with 2.48 L of oxygen measured at  $22^\circ\text{C}$  and 655 torr?

**EXERCISE 10-7(c) SYNTHESIS:**  $\text{NO}$  reacts with  $\text{O}_2$  to form  $\text{NO}_2$ . What happens to the volume if you begin with 2 L of  $\text{NO}$  and add 1 L of  $\text{O}_2$  at the same temperature and pressure?

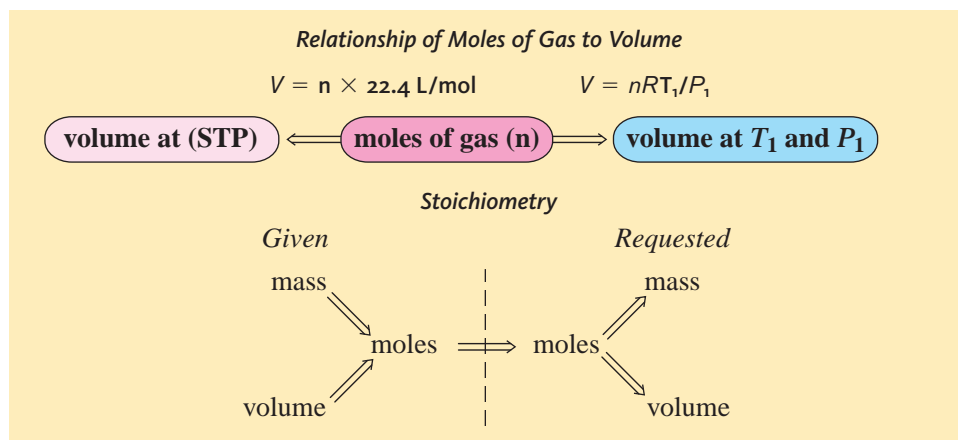
For additional practice, work chapter problems 10-75, 10-78, 10-80, and 10-83.

### PART B SUMMARY

#### KEY TERMS

- 10-4.1** The **ideal gas law** includes all the variables that affect a volume of gas. p. 310
- 10-4.1** The **gas constant,  $R$** , uses specific units for temperature, volume, and pressure. p. 310
- 10-5** **Dalton's law** tells us that gas partial pressures are additive. p. 313
- 10-6.1** The **molar volume** of a gas is 22.4 L under STP conditions. p. 316

## SUMMARY CHARTS



## CHAPTER SUMMARY

Our modern theories about matter depended on some basic understanding about the most abstract state of matter—gases. Beginning in the 1600s, the quantitative laws that we know as the gas laws began to be advanced. These laws and other observations of the nature of gases led to the accepted model of behavior known as the **kinetic molecular theory**. One important result of **kinetic theory** is the relationship between temperature and the average kinetic energy of molecules. The velocity of the molecules, rate of **effusion**, and rate of **diffusion** all relate to the molar mass of the gas and are described by **Graham's law**.

An understanding of the gaseous state began in the mid-1600s with Torricelli. His studies of the **barometer** led to a description of **pressure** as a force per unit area

exerted by gases of the atmosphere. The principal unit of gas pressure is the **atmosphere** (atm) which is usually expressed in torr. The gas laws now seem quite reasonable and predictable from kinetic theory. Except for average velocity and density, which depend on the mass of the molecules, the other gas laws are independent of the identity of the gas. Avogadro advanced the observation that equal volumes of gases contain equal numbers of molecules under the same conditions, and Dalton observed that pressures depended on the total amount of gas present.

The gas laws require the use of the **Kelvin scale**, which begins at **absolute zero**. The volumes of gases are often described under **standard temperature and pressure (STP)** conditions.

| Gas Law      | Relationship                       | Meaning   | Constant Conditions | Application  |
|--------------|------------------------------------|---|---------------------|--|
| Graham's     | $v \propto \frac{1}{\sqrt{MM}}$    | $v \uparrow MM \downarrow$                        | $T$                 | Relates MM and $v$ of two different gases at a specific $T$              |
| Boyle's      | $V \propto \frac{1}{P}$            | $V \uparrow P \downarrow$                         | $T, n$              | Relates $V$ and $P$ of a gas under two different sets of conditions      |
| Charles's    | $V \propto T$                      | $V \uparrow T \uparrow$                           | $P, n$              | Relates $V$ and $T$ of a gas under two different sets of conditions      |
| Gay-Lussac's | $P \propto T$                      | $P \uparrow T \uparrow$                           | $V, n$              | Relates $P$ and $T$ of a gas under two different sets of conditions      |
| Combined     | $PV \propto T$                     | $PV \uparrow T \uparrow$                          | $n$                 | Relates $P, V$ , and $T$ of a gas under two different sets of conditions |
| Avogadro's   | $V \propto n_{\text{tot}}$         | $V \uparrow n_{\text{tot}} \uparrow$              | $P, T$              | Relates $V$ and $n$ of gas under two different sets of conditions        |
| Ideal        | $PV \propto n_{\text{tot}}T$       | $PV \uparrow n_{\text{tot}}T \uparrow$            | —                   | Relates $P, V, T$ , or $n$ to the other three variables                  |
| Dalton's     | $P_{\text{tot}} = P_1 + P_2$ , etc | $P_{\text{tot}} \uparrow n_{\text{tot}} \uparrow$ | $T, V$              | Relates $P_{\text{tot}}$ to partial pressures of component gases         |

$V$  = volume  
 $T$  = Kelvin temperature  
 $P$  = pressure

$P_{\text{tot}}$  = total pressure  
 $n$  = moles  
 $n_{\text{tot}}$  = total moles  
 $MM$  = molar mass

$v$  = average velocity  
 $\uparrow$  = quantity increases  
 $\downarrow$  = quantity decreases

At STP, the volume of one mole of a gas is 22.4 L and is known as the **molar volume**. The molar volume can be used to calculate the density of a gas at STP, or it can be used directly as a conversion factor between moles and volume at STP. To convert between moles and

volume under other conditions, the use of the ideal gas law is convenient. In the **ideal gas law** ( $PV = nRT$ ),  $R$  is known as the **gas constant**.

In the final section, we related the volume of a gas to stoichiometry as summarized in Figure 10-13.

| SECTION | YOU SHOULD BE ABLE TO...   | EXAMPLES               | OBJECTIVES     |  |
|---------|--|------------------------|----------------|--|
|         |  |                        | EXERCISES      | CHAPTER PROBLEMS                               |
| 10-1    | List the general properties of gases based on the postulates of the kinetic molecular theory.                |                        | 1a, 1b, 1c, 2d | 1, 3, 7, 9, 20, 27, 36                         |
| 10-2    | Define <i>pressure</i> .   | 10-1                   | 2a, 2b         | 10, 12, 15                                     |
|         | Convert between units of pressure and calculate how pressure affects the volume of a gas (Boyle's law).      | 10-2                   | 2c, 2d         | 17, 18, 19, 21                                 |
| 10-3    | Using the gas laws, perform calculations involving the relationships among volume, pressure, and temperature | 10-3, 10-4, 10-5, 10-7 | 3a, 3b, 3c, 3d | 24, 25, 28, 31, 33, 35, 41, 43, 44, 50, 52, 54 |
|         | Define the conditions known as STP.  | 10-6                   | 3b             | 39, 46   |
| 10-4    | Using the ideal gas law, calculate one condition of a gas given the other stated conditions.                 | 10-8, 10-9, 10-10      | 4a, 4b, 4c     | 55, 56, 58, 59, 61, 63                         |
| 10-5    | Using Dalton's law, calculate the partial pressure of a gas.   | 10-11, 10-12, 10-13    | 5a, 5b, 5c     | 65, 66, 67, 68, 69, 71, 74                     |
| 10-6    | Using the molar volume, convert volume to moles and mass.  | 10-14                  | 6a, 6b         | 75, 76, 78                                     |
|         | Calculate the density of a gas at STP.   | 10-15                  | 6a, 6c, 6d     | 81, 83, 86                                     |
| 10-7    | Perform stoichiometric calculations involving gas volumes.   | 10-16, 10-17           | 7a, 7b, 7c     | 87, 89, 90, 91, 92                             |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**10-1(a)** Unlike solids and liquids, a gas has a low density and fills a container completely. The reason for the unique behavior of gases can be explained by the kinetic molecular theory. In this theory, gas molecules are in constant, random motion, exerting pressure by collisions with the walls of the container. Another aspect of this theory is that the temperature relates to the average kinetic energy of the gas. At the same temperature, the gas with the larger molar mass will have the lower velocity. The velocity of a gas relates to the rates of effusion and diffusion as expressed by Graham's law.

**10-1(b)** Since the molar mass of the SF<sub>6</sub> (146 g/mol) is larger, it must have a lower velocity than the N<sub>2</sub> (28.0 g/mol).

**10-1(c)** The trunk of a car can heat up rapidly. At the higher temperatures, the gas particles are moving faster, colliding with the walls of the cylinder more frequently and with more energy, thereby increasing the pressure. Ultimately the can will explode.

**10-2(a)** Atmospheric pressure is read from a device called a barometer. Pressure is defined as force per unit area. One

atmosphere of pressure is equivalent to 760 torr. An increase in pressure on a volume of gas causes the volume to decrease.

**10-2(b)** (a) 494 torr (b) 65.8 kPa (c) 9.56 lb/in<sup>2</sup>

**10-2(c)** 659 mL

**10-2(d)** By decreasing the volume, you decrease the average distance between the particles of gas and the walls of the container. Since the temperature doesn't change, the particles are moving at the same speed and will therefore strike the walls of the container more frequently, leading to an increase in pressure.

**10-3(a)** An increase in the pressure of a gas causes the volume to decrease, whereas an increase in temperature causes the same volume to increase. Gay-Lussac's law tells us that if the temperature of a confined volume of gas increases, the pressure increases. To calculate the effect of two changes in conditions, the combined gas law is used. Increasing the number of moles of gas present will increase the volume if other conditions are constant.

**10-3(b)** (a) 591 mL (b) 829 mL (c) 1.67 atm  
(d) 0.833 atm (e) 636 mL

**10-3(c)** (a) Charles's law (b) Avogadro's law (c) Gay-Lussac's law (d) Boyle's law (e) combined gas law

**10-3(d)** (a) Volume is affected by temperature: Charles's law. (b) Tire pressure is affected by temperature: Gay-Lussac's law. (c) Volume is determined by the number of moles at constant  $T$  and  $P$ : Avogadro's law. (d) The piston moves from an increase in temperature and internal pressure: combined gas law.

## PART B

## EXERCISES

**10-4(a)**  $-33^{\circ}\text{C}$

**10-4(b)**  $1.34 \times 10^{22}$  particles

**10-4(c)**  $P/n = k$  or  $P_1/n_1 = P_2/n_2$

**10-5(a)** 715 torr

**10-5(b)** 344 torr

**10-5(c)** Helium has the highest number of particles (moles) per mass unit. So in order of decreasing pressure,  $\text{He} > \text{CH}_4 > \text{CO}_2$ .

**10-6(a)** One mole of any gas occupies  $22.4$  L at STP; this is known as the molar volume. The density of a gas at STP is obtained by dividing the molar mass by the molar volume.

**10-6(b)** 29.4 L

**10-6(c)** 4.83 g/L

**10-6(d)** raising the pitch:  $\text{H}_2$ , He,  $\text{N}_2$  (barely), Ne; lowering the pitch:  $\text{O}_2$  (barely),  $\text{F}_2$  (barely, and includes death),  $\text{Cl}_2$  (more death), Ar, Kr, Xe, and Rn (radiation poisoning)

**10-7(a)** In stoichiometry calculations, the volume of a gas can be converted to number of moles by use of the molar volume if the volume is measured at STP. If other conditions are present, the volume is related to the number of moles by the ideal gas law.

**10-7(b)** (a) 16.4 L (b) 169 L (c) 2.65 g

**10-7(c)** The total volume decreases constant. In gas stoichiometry, for gases under the same conditions, volumes react according to their mole ratios. In the balanced equation,  $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ . Three total moles of gas reactant become two total moles of gas product, or 3 total liters of reactants become 2 total liters of product. So if you start with 2 liters of NO and add 1 liter of  $\text{O}_2$ , you'll end up with 2 liters of  $\text{NO}_2$ .

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## The Kinetic Theory of Gases (SECTION 10-1)

**10-1.** It is harder to move your arms in water than in air. Explain on the basis of kinetic molecular theory.

**10-2.** A balloon filled with water is pear-shaped, but a balloon filled with air is spherical. Explain.

**10-3.** When a gasoline tank is filled, no more gasoline can be added. When a tire is "filled," however, more air can be added. Explain.

**10-4.** The pressure inside an auto tire is the same regardless of the location of the nozzle (i.e., up, down, or to the side). Explain.

**10-5.** A sunbeam forms when light is reflected from dust suspended in the air. Even if the air is still, the dust particles can be seen to bounce around randomly. Explain.

**\*10-6.** A bowling ball weighs 6.00 kg and a bullet weighs 1.50 g. If the bowling ball is rolled down an alley at 20.0 mi/hr, what is the velocity of a bullet having the same kinetic energy?

**10-7.** Arrange the following gases in order of increasing average speed (rate of effusion) at the same temperature.

(a)  $\text{CO}_2$  (c)  $\text{N}_2$  (e)  $\text{N}_2\text{O}$   
(b)  $\text{SO}_2$  (d)  $\text{SF}_6$  (f)  $\text{H}_2$

**10-8.** Arrange the following gaseous elements or compounds in order of increasing rates of diffusion at the same temperature

(a) argon (d) methane  
(b) carbon monoxide (e) chlorine dioxide  
(c) chlorine (f) neon

**\*10-9.** The kinetic theory assumes that the volume of molecules and their interactions are negligible for gases. Explain why these assumptions may not be true when the pressure is very high and the temperature is very low.

## Units of Pressure and Boyle's Law (SECTION 10-2)

**10-10.** Make the following conversions.

(a) 1650 torr to atm (d) 5.65 kPa to atm  
(b)  $3.50 \times 10^{-5}$  atm to torr (e) 190 torr to  $\text{lb}/\text{in.}^2$   
(c) 185  $\text{lb}/\text{in.}^2$  to torr (f) 85 torr to kPa

**10-11.** Make the following conversions.

(a) 30.2 in. of Hg to torr (c) 57.9 kPa to  $\text{lb}/\text{in.}^2$   
(b) 25.7 kilobars to atm (d) 0.025 atm to torr

**10-12.** Complete the following table.

| torr  | $\text{lb}/\text{in.}^2$ | in. Hg | kPa   | atm    |
|-------|--------------------------|--------|-------|--------|
| 455   | _____                    | _____  | _____ | _____  |
| _____ | 2.45                     | _____  | _____ | _____  |
| _____ | _____                    | 117    | _____ | _____  |
| _____ | _____                    | _____  | 783   | _____  |
| _____ | _____                    | _____  | _____ | 0.0768 |

**10-13.** The atmospheric pressure on the planet Mars is 10.3 millibars. What is this pressure in Earth atmospheres?

**10-14.** The atmospheric pressure on the planet Venus is 0.0920 kilobar. What is this pressure in Earth atmospheres?

**10-15.** The density of water is 1.00 g/mL. If water is substituted for mercury in the barometer, how high (in feet) would a column of water be supported by 1 atm? A water well is 40 ft deep. Can suction be used to raise the water to ground level?

**10-16.** A gas has a volume of 6.85 L at a pressure of 0.650 atm. What is the volume of the gas if the pressure is decreased to 0.435 atm?

**10-17.** If a gas has a volume of 1560 mL at a pressure of 81.2 kPa, what is its volume if the pressure is increased to 2.50 atm?



**10-18.** At sea level, a balloon has a volume of 785 mL. What is its volume if it is taken to a place in Colorado where the atmospheric pressure is 610 torr?

**10-19.** A gas has a volume of 125 mL at a pressure of 62.5 torr. What is the pressure if the volume is decreased to 115 mL?

**10-20.** How does the kinetic molecular theory explain Boyle's law?

**10-21.** A few miles above the surface of Earth, the pressure drops to  $1.00 \times 10^{-5}$  atm. What would be the volume of a 1.00-L sample of gas at sea-level pressure (1.00 atm) if it were taken to that altitude? (Assume constant temperature.)

**\*10-22.** A gas in a piston engine is compressed by a ratio of 15:1. If the pressure before compression is 0.950 atm, what pressure is required to compress the gas? (Assume constant temperature.)

**\*10-23.** The volume of a gas is measured as the pressure is varied. The four measurements are reported as follows.

| Experiment | Volume (mL) | Pressure (torr) |
|------------|-------------|-----------------|
| 1          | 125         | 450             |
| 2          | 145         | 385             |
| 3          | 175         | 323             |
| 4          | 220         | 253             |

Make a graph using volume on the  $x$ -axis and pressure on the  $y$ -axis.

### Charles's Law (SECTION 10-3)

**10-24.** A balloon has a volume of 1.55 L at 25°C. What would be the volume if the balloon is heated to 100°C? (Assume constant  $P$ .)

**10-25.** A sample of gas has a volume of 677 mL at 63°C. What is the volume of the gas if the temperature is decreased to 46°C?

**10-26.** A balloon has a volume of 325 mL at 17°C. What is the temperature if the volume increases to 392 mL?

**10-27.** How does the kinetic molecular theory explain Charles's law?

**10-28.** A quantity of gas has a volume of  $3.66 \times 10^4$  L. What will be the volume if the temperature is changed from 455 K to 50°C?

**\*10-29.** The temperature of a sample of gas is 0°C. When the temperature is increased, the volume increases by a factor of 1.25 (i.e.,  $V_2 = 1.25V_1$ .) What is the final temperature in degrees Celsius?

**\*10-30.** The volume of a gas is measured as the temperature is varied. The four measurements are reported as follows.

| Experiment | Volume (L) | Temperature (°C) |
|------------|------------|------------------|
| 1          | 1.54       | 20               |
| 2          | 1.65       | 40               |
| 3          | 1.95       | 100              |
| 4          | 2.07       | 120              |

Make a graph of the volume on the  $x$ -axis and the Kelvin temperature on the  $y$ -axis. What is the average value of the constant of proportionality,  $k$ ?

### Gay-Lussac's Law (SECTION 10-3)

**10-31.** A confined quantity of gas is at a pressure of 2.50 atm and a temperature of  $-22^\circ\text{C}$ . What is the pressure if the temperature increases to  $22^\circ\text{C}$ ?

**10-32.** A quantity of gas has a volume of 3560 mL at a temperature of  $55^\circ\text{C}$  and a pressure of 850 torr. What is the temperature if the volume remains unchanged but the pressure is decreased to 0.652 atm?

**10-33.** A metal cylinder contains a quantity of gas at a pressure of 558 torr at  $25^\circ\text{C}$ . At what temperature does the pressure inside the cylinder equal 1 atm pressure?

**10-34.** An aerosol spray can has gas under pressure of 1.25 atm at  $25^\circ\text{C}$ . The can explodes when the pressure reaches 2.50 atm. At what temperature will this happen? (Do not throw these cans into a fire!)

**10-35.** The pressure in an automobile tire is 28.0 lb/in.<sup>2</sup> on a chilly morning of  $17^\circ\text{C}$ . After it is driven a while, the temperature of the tire rises to  $40^\circ\text{C}$ . What is the pressure in the tire if the volume remains constant?

**10-36.** How does the kinetic molecular theory explain Gay-Lussac's law?

**\*10-37.** The pressure of a confined volume of gas is measured as the temperature is raised. The four measurements are reported as follows:

| Experiment | Pressure (torr) | Temperature (K) |
|------------|-----------------|-----------------|
| 1          | 550             | 295             |
| 2          | 685             | 372             |
| 3          | 745             | 400             |
| 4          | 822             | 445             |

Make a graph of the pressure on the  $x$ -axis and the temperature on the  $y$ -axis. What is the average value of the constant of proportionality,  $k$ ?

### The Combined Gas Law (SECTION 10-3)

**10-38.** Which of the following are legitimate expressions of the combined gas law?

- (a)  $PV = kT$                       (d)  $\frac{P}{T} \propto \frac{1}{V}$   
 (b)  $PT \propto V$                       (e)  $VT \propto P$   
 (c)  $\frac{P_1 T_1}{V_1} = \frac{P_2 T_2}{V_2}$

**10-39.** Which of the following are not STP conditions?

- (a)  $T = 273$  K                      (e)  $T^\circ(\text{C}) = 273^\circ\text{C}$   
 (b)  $P = 760$  atm                      (f)  $P = 760$  torr  
 (c)  $T = 0$  K                          (g)  $T^\circ(\text{C}) = 0^\circ\text{C}$   
 (d)  $P = 1$  atm

**10-40.** In the following table, indicate whether the pressure, volume, or temperature increases or decreases.

| Experiment | $P$       | $V$       | $T$       |
|------------|-----------|-----------|-----------|
| 1          | increases | constant  | _____     |
| 2          | constant  | _____     | decreases |
| 3          | _____     | decreases | constant  |
| 4          | increases | increases | _____     |

**10-41.** In the following table, indicate whether the pressure, volume, or temperature increases or decreases.

| Experiment | $P$   | $V$       | $T$   |
|------------|---|-----------|---|
| 1          | decreases   | _____     | constant  |
| 2          | constant  | _____     | $T(\text{initial}) = 350 \text{ K}$<br>$T(\text{final}) = 40^\circ\text{C}$ |
| 3          | $P(\text{initial}) = 1.75 \text{ atm}$<br>$P(\text{final}) = 2200 \text{ torr}$ | constant  | _____   |
| 4          | _____   | increases | decreases   |

**10-42.** A 5.50-L volume of gas has a pressure of 0.950 atm at  $0^\circ\text{C}$ . What is the pressure if the volume decreases to 4.75 L and the temperature increases to  $35^\circ\text{C}$ ?

**10-43.** A quantity of gas has a volume of 17.5 L at a pressure of 6.00 atm and temperature of  $100^\circ\text{C}$ . What is its volume at STP?

**10-44.** A quantity of gas has a volume of 88.7 mL at STP. What is its volume at 0.845 atm and  $35^\circ\text{C}$ ?

**10-45.** A quantity of gas has a volume of  $4.78 \times 10^{-4}$  mL at a temperature of  $-50^\circ\text{C}$  and a pressure of 78.0 torr. If the volume changes to  $9.55 \times 10^{-5}$  mL and the pressure to 155 torr, what is the temperature?

**10-46.** A gas has a volume of 64.2 L at STP. What is the temperature if the volume decreases to 58.5 L and the pressure increases to 834 torr?

**10-47.** A quantity of gas has a volume of  $6.55 \times 10^{-5}$  L at  $7^\circ\text{C}$  and 0.882 atm. What is the pressure if the volume changes to  $4.90 \times 10^{-3}$  L and the temperature to 273 K?

**10-48.** A balloon has a volume of 1.55 L at  $25^\circ\text{C}$  and 1.05 atm pressure. If it is cooled in the freezer, the volume shrinks to 1.38 L and the pressure drops to 1.02 atm. What is the temperature in the freezer?

**10-49.** A bubble from a deep-sea diver in the ocean starts with a volume of 35.0 mL at a temperature of  $17^\circ\text{C}$  and a pressure of 11.5 atm. What is the volume of the bubble when it reaches the surface? Assume that the pressure at the surface is 1 atm and the temperature is  $22^\circ\text{C}$ .

### Avogadro's Law (SECTION 10-3)

**10-50.** A 0.112-mol quantity of gas has a volume of 2.54 L at a certain temperature and pressure. What is the volume of 0.0750 mol of gas under the same conditions?

**10-51.** A balloon has a volume of 188 L and contains 8.40 mol of gas. How many moles of gas would be needed to expand the balloon to 275 L? Assume the same temperature and pressure in the balloon.

**10-52.** A balloon has a volume of 275 mL and contains 0.0212 mol of  $\text{CO}_2$ . What mass of  $\text{N}_2$  must be added to expand the balloon to 400 mL?

**10-53.** A balloon has a volume of 75.0 mL and contains  $2.50 \times 10^{-3}$  mol of gas. What mass of  $\text{N}_2$  must be added to the balloon for the volume to increase to 164 mL at the same temperature and pressure?

**10-54.** A 48.0-g quantity of  $\text{O}_2$  in a balloon has a volume of 30.0 L. What is the volume if 48.0 g of  $\text{SO}_2$  is substituted for  $\text{O}_2$  in the same balloon?

### The Ideal Gas Law (SECTION 10-4)

**10-55.** What is the temperature (in degrees Celsius) of 4.50 L of a 0.332-mol quantity of gas under a pressure of 2.25 atm?

**10-56.** A quantity of gas has a volume of 16.5 L at  $32^\circ\text{C}$  and a pressure of 850 torr. How many moles of gas are present?

**10-57.** What mass of  $\text{NH}_3$  gas has a volume of 16,400 mL, a pressure of 0.955 atm, and a temperature of  $-23^\circ\text{C}$ ?

**10-58.** What is the pressure (in torr) exerted by 0.250 g of  $\text{O}_2$  in a 250-mL container at  $29^\circ\text{C}$ ?

**10-59.** A container of  $\text{Cl}_2$  gas has a volume of 750 mL and is at a temperature of  $19^\circ\text{C}$ . If there is 7.88 g of  $\text{Cl}_2$  in the container, what is the pressure in atmospheres?

**10-60.** What mass of Ne is contained in a large neon light if the volume is 3.50 L, the pressure 1.15 atm, and the temperature  $23^\circ\text{C}$ ?

**10-61.** A sample of  $\text{H}_2$  is collected in a bottle over water. The volume of the sample is 185 mL at a temperature of  $25^\circ\text{C}$ . The pressure of  $\text{H}_2$  in the bottle is 736 torr. What is the mass of  $\text{H}_2$  in the bottle?

**\*10-62.** A blimp has a volume of about  $2.5 \times 10^7$  L. What is the mass of He (in lb) in the blimp at  $27^\circ\text{C}$  and 780 torr? The average molar mass of air is 29.0 g/mol. What mass of air (in lb) would the blimp contain? The difference between these two values is the lifting power of the blimp. What mass could the blimp lift? If  $\text{H}_2$  is substituted for He, what is the lifting power? Why isn't  $\text{H}_2$  used?

**\*10-63.** A good vacuum pump on Earth can produce a vacuum with a pressure as low as  $1.00 \times 10^{-8}$  torr. How many molecules are present in each milliliter at a temperature of  $27.0^\circ\text{C}$ ?

### Dalton's Law (SECTION 10-5)

**10-64.** Three gases are mixed in a 1.00-L container. The partial pressure of  $\text{CO}_2$  is 250 torr, that of  $\text{N}_2$  is 375 torr, and that of He 137 is torr. What is the pressure of the mixture of gases?

**10-65.** The total pressure in a cylinder containing a mixture of two gases is 1.46 atm. If the partial pressure of one gas is 750 torr, what is the partial pressure of the other gas?

**10-66.** Air is about 0.90% Ar. If the barometric pressure is 756 torr, what is the partial pressure of Ar?

**10-67.** A sample of oxygen is collected in a bottle over water. The pressure inside the bottle is made equal to the barometric pressure, which is 752 torr. When collected over water, the gas is a mixture of oxygen and water vapor. The partial pressure of water (known as the vapor pressure) at that temperature is 24 torr. What is the pressure of the pure oxygen?

**10-68.** A container holds two gases, A and B. Gas A has a partial pressure of 325 torr and gas B has a partial pressure of 488 torr. What percent of the molecules in the mixture is gas A?

**10-69.** A volume of gas is composed of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{SO}_2$ . If the total pressure is 1050 torr, what is the partial pressure of each gas if the gas is 72.0%  $\text{N}_2$  and 8.00%  $\text{O}_2$ ?

**\*10-70.** A mixture of two gases is composed of CO<sub>2</sub> and O<sub>2</sub>. The partial pressure of O<sub>2</sub> is 256 torr, and it represents 35.0% of the molecules of the mixture. What is the total pressure of the mixture?

**\*10-71.** A volume of gas has a total pressure of 2.75 atm. If the gas is composed of 0.250 mol of N<sub>2</sub> and 0.427 mol of CO<sub>2</sub>, what is the partial pressure of each gas?

**\*10-72.** The following gases are all combined into a 2.00-L container: a 2.00-L volume of N<sub>2</sub> at 300 torr, a 4.00-L volume of O<sub>2</sub> at 85 torr, and a 1.00-L volume of CO<sub>2</sub> at 450 torr. What is the total pressure?

**\*10-73.** The total pressure of a mixture of two gases is 0.850 atm in a 4.00-L container. Before mixing, gas A was in a 2.50-L container and had a pressure of 0.880 atm. What is the partial pressure of gas B in the 4.00-L container?

**\*10-74.** What is the pressure (in atm) in a 825-mL container at 33°C if it contains 6.25 g of N<sub>2</sub> and 12.6 g of CO<sub>2</sub>?

### Molar Volume and Density (SECTION 10-6)

**10-75.** What is the volume of 15.0 g of CO<sub>2</sub> measured at STP?

**10-76.** What is the mass (in kilograms) of 850 L of CO measured at STP?

**10-77.** What is the volume of  $3.01 \times 10^{24}$  molecules of N<sub>2</sub> measured at STP?

**10-78.** A 6.50-L quantity of a gas measured at STP has a mass of 39.8 g. What is the molar mass of the compound?

**10-79.** What is the mass of  $6.78 \times 10^{-4}$  L of NO<sub>2</sub> measured at STP?

**10-80.** What is the density in g/L (STP) of B<sub>2</sub>H<sub>6</sub>?

**10-81.** What is the density in g/L (STP) of BF<sub>3</sub>?

**10-82.** A gas has a density of 1.52 g/L (STP). What is the molar mass of the gas?

**10-83.** A gas has a density of 6.14 g/L (STP). What is the molar mass of the gas?

**\*10-84.** A gas has a density of 3.60 g/L at a temperature of 25°C and a pressure of 1.20 atm. What is its density at STP?

**\*10-85.** What is the density (in g/L) of N<sub>2</sub> measured at 500 torr and 22°C?

**\*10-86.** What is the density (in g/L) of SF<sub>6</sub> measured at 0.370 atm and 37°C?

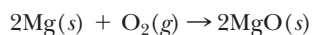
### Stoichiometry Involving Gases (SECTION 10-6)

**10-87.** Limestone is dissolved by CO<sub>2</sub> and water according to the equation



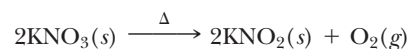
What volume of CO<sub>2</sub> measured at STP would dissolve 115 g of CaCO<sub>3</sub>?

**10-88.** Magnesium once used in flashbulbs, burns according to the equation



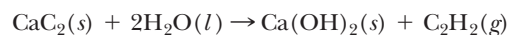
What mass of Mg combines with 5.80 L of O<sub>2</sub> measured at STP?

**10-89.** Oxygen gas can be prepared in the laboratory by decomposition of potassium nitrate according to the equation



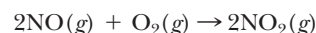
What mass of KNO<sub>2</sub> forms along with 14.5 L of O<sub>2</sub> measured at 1 atm and 25°C?

**10-90.** Acetylene (C<sub>2</sub>H<sub>2</sub>) is produced from calcium carbide as shown by the reaction



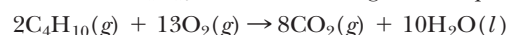
What volume of acetylene measured at 25°C and 745 torr would be produced from 5.00 g of H<sub>2</sub>O?

**10-91.** Nitrogen dioxide is an air pollutant. It is produced from NO (from car exhaust) as follows.



What volume of NO measured at STP is required to react with 5.00 L of O<sub>2</sub> measured at 1.25 atm and 17°C?

**10-92.** Butane (C<sub>4</sub>H<sub>10</sub>) burns according to the equation

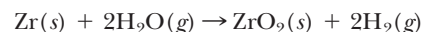


(a) What volume of CO<sub>2</sub> measured at STP would be produced by 85.0 g of C<sub>4</sub>H<sub>10</sub>?

(b) What volume of O<sub>2</sub> measured at 3.25 atm and 127°C would be required to react with 85.0 g of C<sub>4</sub>H<sub>10</sub>?

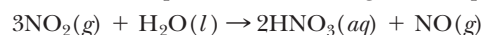
(c) What volume of CO<sub>2</sub> measured at STP would be produced from 45.0 L of C<sub>4</sub>H<sub>10</sub> measured at 25°C and 0.750 atm?

**10-93.** In March 1979, a nuclear reactor overheated, producing a dangerous hydrogen bubble at the top of the reactor core. The following reaction occurring at the high temperature (about 1500°C) accounted for the hydrogen. (Zr alloys hold the uranium pellets in long rods.)



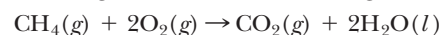
If the bubble had a volume of about 28,000 L at 250°C and 70.0 atm, what mass (in kg and tons) of Zr had reacted?

**10-94.** Nitric acid is produced according to the equation



What volume of NO<sub>2</sub> measured at -73°C and  $1.56 \times 10^{-2}$  atm would be needed to produce  $4.55 \times 10^{-3}$  mol of HNO<sub>3</sub>?

**\*10-95.** Natural gas (CH<sub>4</sub>) burns according to the equation



What volume of CO<sub>2</sub> measured at 27°C and 1.50 atm is produced from 27.5 L of O<sub>2</sub> measured at -23°C and 825 torr?

### General Problems

**10-96.** A column of mercury (density 13.6 g/mL) is 15.0 cm high. A cross-section of the column has an area of 12.0 cm<sup>2</sup>. What is the force (weight) of the mercury at the bottom of the tube? What is the pressure in grams per square centimeter and in atmospheres?

**10-97.** A tube containing an alcohol (density 0.890 g/mL) is 1.00 m high and has a cross-section of 15.0 cm<sup>2</sup>. What is the total force at the bottom of the tube? What is the pressure? Assuming the same cross-section, how high would an equivalent amount of mercury be?

**10-98.** A 1.00-L volume of a gas weighs 8.37 g. The gas volume is measured at 1.45 atm pressure and 35°C. What is the molar mass of the gas?

**10-99.** A gaseous compound is 85.7% C and 14.3% H. A 6.58-g quantity of this gas occupies 4500 mL at 77.0°C and a pressure of 1.00 atm. What is the molar mass of the compound? What is its molecular formula?

**10-100.** What is the volume at STP of a mixture of 10.0 g each of Ar, Cl<sub>2</sub>, and N<sub>2</sub>? What is the partial pressure of each gas?

**10-101.** What is the volume occupied by a mixture of 0.265 mol of O<sub>2</sub>, 9.88 g of N<sub>2</sub>, and  $9.65 \times 10^{22}$  molecules of CO<sub>2</sub> at a temperature of 37°C and a pressure of 2.86 atm? What is the partial pressure of each gas?

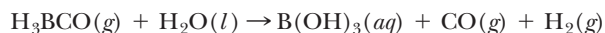
**10-102.** Molecular clouds in space contain 30,000 molecules/mL at a temperature of 10 K. What is the pressure in atmospheres?

**\*10-103.** What is the molar volume (i.e., volume of one mole) at 25°C and 1.25 atm? What is the density of CO<sub>2</sub> under these conditions?

**\*10-104.** A hot-air balloon rises because the heated air trapped in the balloon is less dense than the surrounding air. What is the density of air (assume an average molar mass of 29.0 g/mol) at 400°C and 1 atm pressure? (*Hint:* Calculate the volume of one mole of gas under these conditions.) Compare this to the density of air at STP.

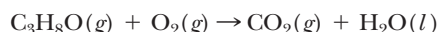
**10-105.** A compound is 80.0% carbon and 20.0% hydrogen. Its density at STP is 1.34 g/L. What is its molecular formula?

**10-106.** Given the following *unbalanced* equation



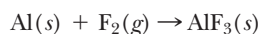
A 425-mL quantity of H<sub>3</sub>BCO measured at 565 torr and 100°C was allowed to react with excess H<sub>2</sub>O. What volume of gas was produced measured at 25°C and 0.900 atm?

**10-107.** Given the following *unbalanced* equation



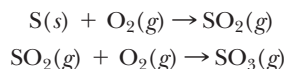
What mass of water forms if 6.50 L of C<sub>3</sub>H<sub>8</sub>O measured at STP is allowed to react with 42.0 L of O<sub>2</sub> measured at 27°C and 1.68 atm pressure? Assume that this is the only reaction that occurs.

**10-108.** Given the following *unbalanced* equation



An 8.23-L quantity of F<sub>2</sub> measured at 35°C and 725 torr was allowed to react with some Al. At the end of the reaction, 3.50 g of F<sub>2</sub> remained. What mass of AlF<sub>3</sub> formed?

**10-109.** Sulfuric acid is made from SO<sub>3</sub>, which is obtained from the combustion of sulfur according to the following *unbalanced* equations.



What volume of SO<sub>3</sub> measured at 2.75 atm and 400°C is prepared from 50.0 kg of sulfur?

**10-110.** Liquid N<sub>2</sub>O<sub>3</sub> decomposes according to the equation



What is the total volume of gas measured at 1.58 atm and 35°C produced by the decomposition of  $2.54 \times 10^{24}$  molecules of N<sub>2</sub>O<sub>3</sub>?

**\*10-111.** Calcium bicarbonate is formed according to the following equation.



If 80.0 g of CaO is mixed with  $7.85 \times 10^{23}$  molecules of H<sub>2</sub>O and 30.0 L of CO<sub>2</sub> measured at 25°C and 820 torr, what mass of calcium bicarbonate is formed?

**10-112.** What volume of water vapor (gas) measured at 22.0 torr and 25°C contains the same number of molecules as 15.0 mL of ice if the density of ice is 0.917 g/mL?

**10-113.** The following equation represents what happens in swimming pools when ammonia (from people) reacts with sodium hypochlorite (used as a disinfectant). The N<sub>2</sub>H<sub>4</sub> formed has a seriously bad odor.

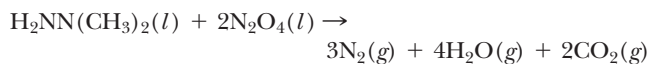


What volume of N<sub>2</sub>H<sub>4</sub> (in mL) measured at STP is produced if 20.0 mL of NH<sub>3</sub> gas measured at 1.20 atm and 25°C is dissolved in water?

**\*10-114.** A 1.000-g sample of a gaseous compound composed of only nitrogen and fluorine contains 0.269 g of nitrogen. The gas has a density of 4.25 g/L measured at room temperature (25°C) and standard pressure. What is the formula of the gas?

**\*10-115.** A liquid compound composed of only nitrogen and oxygen is 69.6% oxygen. Decomposition of 0.0220 mole of this compound produces 2.03 g of a single gas that has a volume of 1.05 L measured at standard temperature and 715 torr. What is the formula of the original compound?

**10-116.** Steering on space vehicles is provided by a propulsion system that produces gaseous products when two liquids are mixed. It can produce short bursts of gases. The reaction is



What volume of gas measured at 1.75 atm and 120°C is produced if 125 g of each of the two reactants are mixed?

**10-117.** Magnesium and lithium both react with elemental nitrogen to form their respective nitrides. Write the balanced equations illustrating these reactions and determine what mass of each metal would react with 256 L of nitrogen measured at 985 torr and 373 K.

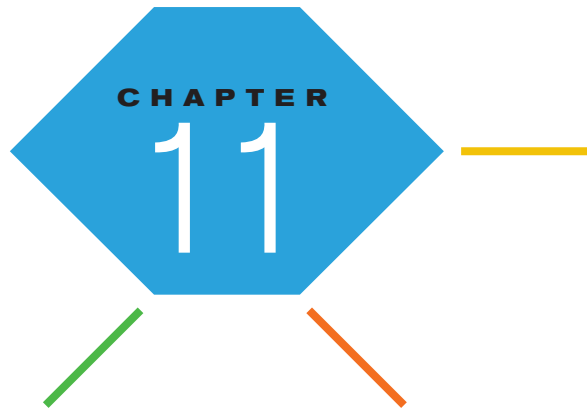
## Gas Properties

**Purpose:** To apply the laws governing the behavior of gases to some simple demonstrations. (Work in groups of three or four. Estimated time: Predictions—10 min.; Activities—30 min.)

Read the following activities. Based on the concepts of this chapter, predict what should happen. If time and space permit, perform the activities in your group. Were your predictions accurate?

1. Candle, matches, beaker,  $\text{NaHCO}_3$ , dilute HCl:
  - Light the candle.
  - In the beaker, mix a spatula full of solid  $\text{NaHCO}_3$  with 10 mL of HCl.
  - Hold the beaker at an angle over the flame.
2. Balloon, string, ruler:
  - Take a deep breath and blow once into a balloon.
  - Pinch the end and wrap the string around the balloon.
  - Measure the length of the string with a ruler.
  - Without releasing any air, repeat four more times.
  - Plot the number of breaths against the length of string squared.
3. Soda bottle, balloon, beaker, ice:
  - Fill the bottle with hot water.
  - Fill the beaker with ice water.
  - After one minute, empty the bottle and stretch the balloon over the mouth.
  - Place the bottle into the ice water.





# The Solid and Liquid States



Life can flourish on this planet because all three physical states of water can exist. Ice and snow form from the condensation of the vapor or the freezing of the liquid. The solid and liquid states of water are featured in this chapter.



**PART A**  
**THE PROPERTIES OF  
CONDENSED STATES AND  
THE FORCES INVOLVED**

**11-1** Properties of the Solid and Liquid States

**11-2** Intermolecular Forces and Physical State

**11-3** The Solid State: Melting Point



**MAKING IT REAL**

*The Melting Point of Iron and the World Trade Center*

**PART B**  
**THE LIQUID STATE AND  
CHANGES IN STATE**

**11-4** The Liquid State: Surface Tension, Viscosity, and Boiling Point



**MAKING IT REAL**

*The Oceans of Mars*

**11-5** Energy and Changes in State

**11-6** Heating Curve of Water

**SETTING THE STAGE** Ice cubes floating in a glass of water—what could be more familiar? What we may not appreciate in this common sight is that it represents very unusual behavior for a compound. Usually the solid state of a substance is denser than the liquid state, so the solid sinks to the bottom rather than floating on top. Life on Earth could not exist as we know it if water and ice behaved as do most other liquids and their solid forms. If the ice were to sink as it forms, lakes would freeze solid in winter. The hot summer sun would thaw only the top layer of a lake, so very little life could survive. Heat could not be distributed from warm to cold climates by ocean currents. Nothing would be the same on this planet. We wouldn't be here if water were not a very unusual compound. In addition to this property, the presence of water in the liquid state under conditions found on this planet is another key to our very existence. Scientists speculate that liquid water was the necessary medium allowing the complex chemical reactions connected with life processes to occur. In the next chapter, we will emphasize the properties of water as a solvent in which chemical reactions take place. Life on this planet is also dependent on the energy released or absorbed by water as it changes between its three physical states.

Water is certainly our most familiar liquid. Water and other liquids and their solid forms are, in a way, easier to study than the gaseous state. These forms of matter are more concrete—we can see them, feel them, and conveniently isolate and measure them. On the other hand, there is a disadvantage in our work with solids and liquids compared to gases. By their very nature, the condensed phases of matter do not lend themselves to such simplifying generalizations as the gas laws.

In Part A in this chapter, we will examine the general properties of solids and liquids, with emphasis on the solid state. In Part B, we will consider properties of the liquid state and the energies involved in phase transitions.

**PART A**  
**THE PROPERTIES OF**  
**CONDENSED STATES AND**  
**THE FORCES INVOLVED**

**SETTING A GOAL**

- You will become familiar with the various forces between molecules and ions and how these forces affect the condensed states of matter.

**OBJECTIVES**

- 11-1** List the physical properties of solids and liquids that distinguish them from gases.
- 11-2** Describe the types of intermolecular forces that can occur between two molecules and their relative strengths.
- 11-3 (a)** Classify a solid as ionic, molecular, network, or metallic. **(b)** Order solids by melting point.

**▶ OBJECTIVE FOR SECTION 11-1**

List the physical properties of solids and liquids that distinguish them from gases.

**11-1 PROPERTIES OF THE SOLID AND LIQUID STATES**



**LOOKING AHEAD!** Our first question concerns the difference between the liquid or solid states and the gaseous state at the molecular level. In this section, we will see where the kinetic theory, introduced in the previous chapter, does and does not apply to liquids and solids. ■

**11-1.1 Properties of the Condensed States**

Most of the properties of the solid and liquid states are obvious to us. Still, it is worthwhile to note these common properties in order to visualize the actions and interactions of the ions or molecules that comprise these states.

**1. They have high density.**

Solids and liquids are about 1000 times denser than a typical gas.

**2. They are essentially incompressible.**

A tall building can be supported by bricks and other solids because they don't compress as would a gas. Likewise, a hydraulic jack uses a liquid to support weights such as that of a huge truck. Unlike the behavior of a gas, an increase in pressure on a solid or liquid does not result in a significant decrease in volume.

**3. They undergo little thermal expansion.**

When a bridge is constructed, a small space must be left between sections for expansion on a hot day. Still, this space amounts to only a few centimeters for a bridge span many meters long. In addition, the degree of expansion varies for different solids and liquids. Gases, on the other hand, expand significantly as the temperature rises, and all gases expand by the same factor.

**4. They have a fixed volume.**

The volume of a gas is that of the container. Also, the volume is the same for the same number of particles under the same conditions. There is no such convenient relationship for solids and liquids. The same volumes of different solids or liquids have no relationship to the number of molecules present.

In addition to these common characteristics, solids and liquids differ with regard to shape. Solids are rigid and thus have a definite shape. Liquids flow and thus do not have a definite shape. (It is determined by the shape of the container.)

**11-1.2 The Condensed States and Kinetic Theory**

The characteristics of gases are adequately explained by the kinetic molecular theory. Two of the basic assumptions of the kinetic theory are also applicable to the

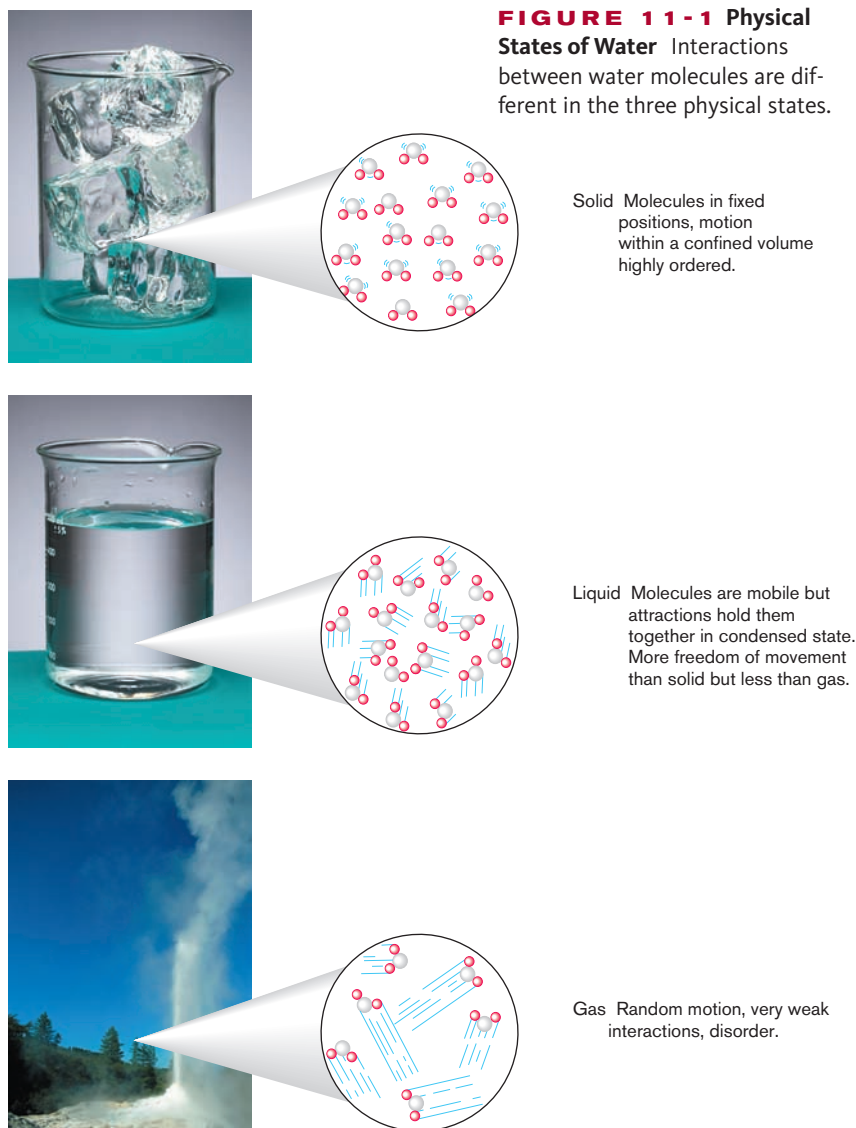
other states. That is, solids and liquids are composed of basic particles that have kinetic energy. The average kinetic energy of the particles is related to the temperature. However, to explain the characteristics of the other two states, there are obviously some assumptions related to gases that no longer apply. In the solid and liquid states the following circumstances exist.

1. The basic particles (molecules or ions) have significant attractions for each other and so are held close together.
2. Since the basic particles are close together, the particles occupy a significant portion of the volume of the substance.
3. The basic particles are not in random motion; their motion is restricted by interactions with other, neighboring particles.

The properties of the solid and liquid states are understandable on the basis of these assumptions. Because they are already close together, the basic particles cannot be pressed together easily, so the substances are incompressible and have high densities. In fact, both solids and liquids are referred to as *condensed states*. The attraction of the particles for each other holds them together and essentially counteracts the tendency of kinetic energy to move them apart. Thus, solids and liquids undergo little thermal expansion.

In Figure 11-1, we illustrate the fundamental differences in the behavior of molecules in the three states of matter. We use the water molecule as an example. This simple but amazing compound exists in all three physical states on Earth: vapor (the gaseous state of a substance normally in the liquid or solid state is sometimes referred to as vapor), liquid, and solid (ice). In fact, in a thermos of ice water, all three states exist at once, although the presence of some  $\text{H}_2\text{O}$  molecules in the gaseous state above the ice may not be obvious.

First, let's consider ice, the solid state of water. In this case, the forces of attraction between molecules hold them in fixed positions relatively close together. In any physical state, the molecules have kinetic energy, meaning that they have motion. But in the solid state the motion is restricted to various types of vibrations about a fixed point. This is much like a view of a crowded dance floor, with all the dancers shaking and vibrating but not moving around the dance floor. In the liquid state, the water molecules are also held close together by forces of attraction, but the molecules are not confined to fixed positions and thus have more freedom of motion than in the solid state. That is, individual molecules or groups of molecules have translational motion as well as vibrational motion. This is like viewing the same crowded dance floor as above but noticing the dancers now moving about the floor as well as shaking and vibrating. Since the molecules can move past one another, liquids can flow and take the shape of the bottom of the container. Finally, we are



already familiar with the behavior of water molecules in the gaseous state, as discussed in the preceding chapter. In this case, the molecules have so much translational motion that they move freely throughout the whole container and are unaffected by the attractions to other molecules. Their motion and collisions scatter them as far apart as possible. In the dance floor analogy, it's like the dance floor has greatly expanded. The dancers can now move around freely, eventually taking up all the added space.

**ASSESSING THE  
OBJECTIVE FOR  
SECTION 11-1**

**EXERCISE 11-1(a) KNOWLEDGE:** Fill in the blanks.

Compared to gases, liquids and solids have a \_\_\_\_\_ density and occupy a \_\_\_\_\_ volume. The molecules of the condensed states have appreciable \_\_\_\_\_ for each other.

**EXERCISE 11-1(b) SYNTHESIS:** Review the densities of the solids listed in Table 3-1 in Section 3-2.1. In general, which have higher densities, solids or liquids? Why is this so? What does this say about the forces between individual molecules of solids versus liquids?

*For additional practice, work chapter problems 11-1, 11-2, and 11-3.*

**▶ OBJECTIVE FOR  
SECTION 11-2**

Describe the types of intermolecular forces that can occur between two molecules and their relative strengths.

## 11-2 INTERMOLECULAR FORCES AND PHYSICAL STATE



**LOOKING AHEAD!** The ions and molecules in the condensed states obviously “stick together.” In this section, we will explore the attractive forces at work in molecular compounds and free elements that cause the molecules to stick together. The magnitude of these forces determines whether a compound is a gas, liquid, or solid at a particular temperature. ■

At room temperature methane is a gas, water is a liquid, and table sugar is a solid. Yet all three are molecular compounds. The physical state of molecular compounds at a specific temperature depends on how strongly the molecules are attracted to each other. These interactions are known as **intermolecular forces**.

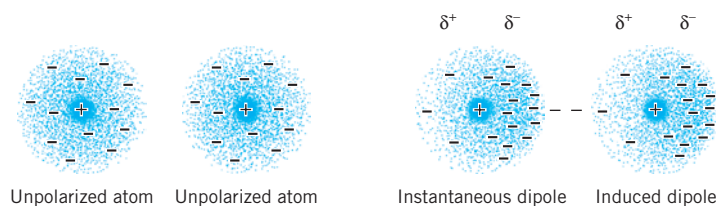
Molecular compounds are held together by attractions called London forces. Some molecules may have additional forces, called dipole–dipole or hydrogen-bonding forces, that may add to the basic London force. First, consider London forces.

### 11-2.1 London Forces

Since atoms and molecules are surrounded by negatively charged electrons, it may seem reasonable that one molecule would *repel* another because of repulsions of like charges. In fact, it is just the opposite. There are electrostatic forces of attraction between molecules. These forces are known as *London dispersion forces* or simply **London forces**. London forces also have the rather imposing name of *instantaneous dipole–induced dipole forces*. Let's see if we can make some sense of all this. In a molecule, positively charged nuclei do exist within negatively charged electron clouds. However, the electrons in these

clouds have probabilities of being in various locations. Because of this, a molecule may have an imbalance of electron charge on one side of the atom or molecule at a given instant. For that instant, the molecule becomes polar (i.e., forms a dipole with a negative side and an opposite positive side). In other words, the molecule achieves an *instantaneous dipole*. If another molecule happens to be nearby, it is influenced by this instantaneous dipole, and that molecule also becomes *polarized*. That is, a dipole is *induced* in the second molecule. Now there can form a force of attraction between the negative side of the instantaneous dipole on one molecule and the positive side of the induced dipole on another. Recall from Section 9-8 that  $\delta^+$  and  $\delta^-$  represent partial positive and negative charges respectively. (See Figure 11-2.)

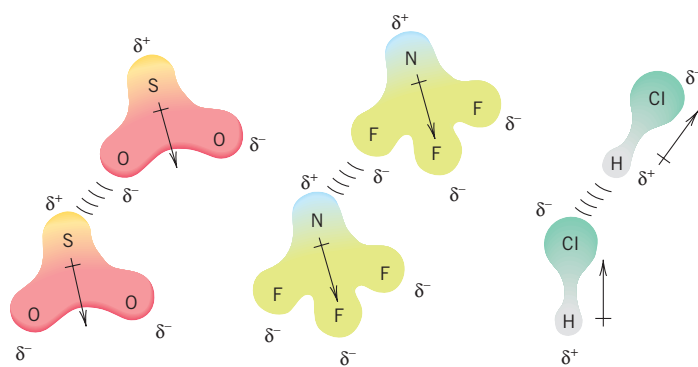
In larger molecules with more electrons, instantaneous dipoles become more common and stronger, so London forces become more significant. Also, larger molecules are generally more *polarizable* than smaller ones because they are surrounded by larger, more diffuse electron clouds. *Since molar mass usually indicates a larger molecule, we can state that the heavier the molecule, the greater the London forces and the more likely we are to find it in the liquid or solid state at a given temperature.* For example, at room temperature, natural gas [ $\text{CH}_4$  (molar mass = 16 g/mol)] is, of course, a gas. A major component of gasoline, called octane [ $\text{C}_8\text{H}_{18}$  (molar mass = 114 g/mol)], is a liquid, and paraffin [ $\text{C}_{24}\text{H}_{50}$  (molar mass = 338 g/mol)] is a solid. The trend of gas  $\rightarrow$  liquid  $\rightarrow$  solid corresponds to the magnitude of the London forces for the three molecules (i.e.,  $\text{CH}_4 < \text{C}_8\text{H}_{18} < \text{C}_{24}\text{H}_{50}$ ). All molecules are attracted by London forces, but in nonpolar molecules, London forces act exclusively.



**FIGURE 11-2** London Forces An instantaneous dipole in one atom or molecule creates an induced dipole in a neighbor.

### 11-2.2 Dipole–Dipole Attractions

Covalent bonds between unlike atoms in a molecule are all polar, at least to some extent, but the molecule itself may not be polar. This apparent contradiction was discussed in Chapter 9. In that discussion, with the help of the Lewis structures and VSEPR theory, we were able to predict that certain molecules may be linear (e.g.,  $\text{CO}_2$ ), trigonal planar (e.g.,  $\text{BF}_3$ ), or tetrahedral (e.g.,  $\text{CH}_4$ ). In these highly symmetrical structures, the equal bond dipoles cancel, and the molecule as a whole is nonpolar. Consider the case of  $\text{CO}_2$ . Since the two polar carbon–oxygen bonds lie at a  $180^\circ$  angle, the individual bond dipoles cancel and the molecule is nonpolar. On the other hand, carbonyl sulfide ( $\text{OCS}$ ) is also linear, like  $\text{CO}_2$ , but since the bond dipoles are unequal, they do not cancel and the molecule is polar. The  $\text{SO}_2$  molecule is also polar. In this case, the Lewis structure shows a pair of electrons on the sulfur, so the geometry is V-shaped rather than linear. Thus, the two equal bond dipoles are at an angle and do not cancel. The  $\text{OCS}$  and  $\text{SO}_2$  molecules each have a permanent dipole, meaning that they have locations with permanent partially negative and partially positive charges. (See Section 9-8.2.) *Molecules with a permanent dipole can align themselves so that the negative end of one molecule is attracted to the positive end of another.* (See Figure 11-3.) *These intermolecular interactions are known as dipole–dipole attractions and add to the effect of the London forces. Thus, if we have two compounds of similar molar mass (meaning similar London forces) but one is composed of polar molecules and one of nonpolar molecules, the compound with polar molecules is more likely to be in a condensed state at a given temperature.* Having additional dipole–dipole forces of attraction for molecules is like getting 5



**FIGURE 11-3** Dipole–Dipole Attractions  $\text{SO}_2$ ,  $\text{NF}_3$ , and  $\text{HCl}$  are polar molecules and have dipole–dipole attractions. The negative end ( $\delta^-$ ) of one molecule is attracted to the positive end ( $\delta^+$ ) of another.

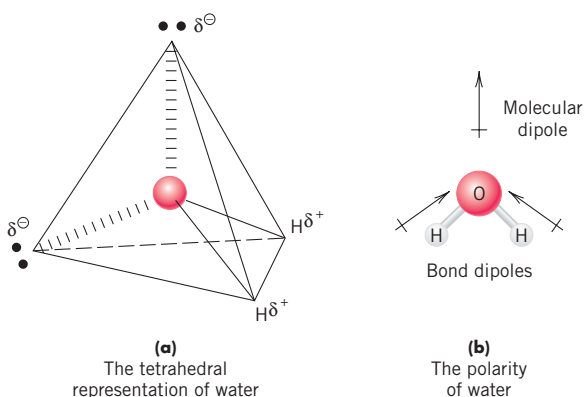


extra-credit points on a 100-point test. It may not change anything, but it may be just enough to get one a higher grade. In the case of compounds, the added attractions may be just enough to hold the molecules together in a condensed state. For example, at room temperature,  $\text{CO}_2$  (44 g/mol), a compound with nonpolar molecules, is a gas, whereas  $\text{CH}_3\text{CN}$  (41 g/mol), a compound with polar molecules, is a liquid. It is difficult to compare heavy nonpolar molecules with lighter polar molecules. Generally, the mass of the molecules and the London forces are more important than the additional dipole-dipole forces.

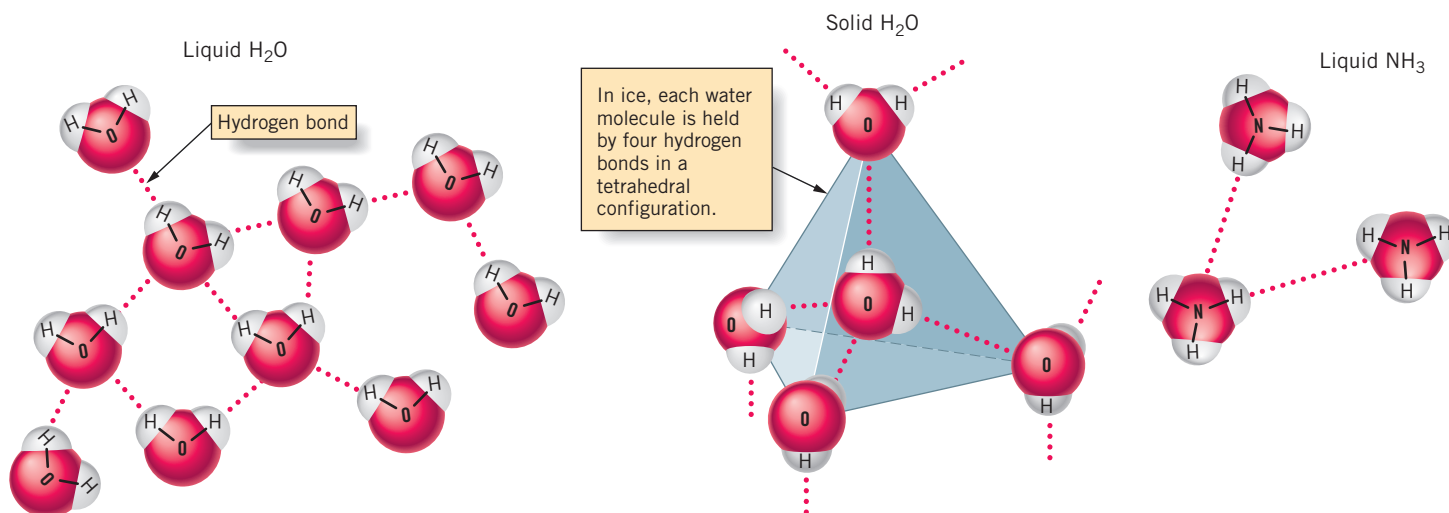
### 11-2.3 Hydrogen Bonding

In Section 8-5, we discussed trends in the size of atoms. Atoms of the elements to the upper right in the periodic table are the smallest. In Chapter 9, we also mentioned that these same atoms (fluorine, oxygen, and nitrogen in particular) are the most electronegative elements. This means that these small, highly electronegative atoms tend to attract a significant amount of negative charge to themselves

when chemically bonded to other atoms. As an example, consider molecules of water. There is a large difference in electronegativity between oxygen and hydrogen ( $3.5 - 2.1 = 1.4$ ). This difference is not enough to indicate an ionic bond, but it does point to a highly polar covalent bond. In Chapter 9, we discussed the geometry of water molecules. According to VSEPR theory, the mutually repulsive effect of the two electron pairs on the oxygen atom and the two bonded pairs causes the electron pairs and the hydrogen atoms to be located at the corners of a rough tetrahedron. (See Figure 11-4a.) Since this structure gives  $\text{H}_2\text{O}$  a V-shaped molecular geometry, the bond dipoles do not cancel and the water molecule is significantly polar. (See Figure 11-4b.) The partial positive charge is centered on the hydrogen atoms at two of the corners of the tetrahedron, and the partial negative charge is centered on the electron pairs at the other two corners. As shown in Figure 11-5, in solid ice, hydrogen atoms on two different water molecules interact with the two electron pairs on one water molecule. In liquid water, the structure is less orderly because the interactions between molecules are more random. Individual and groups of water molecules can slide past one another in the liquid state.



**FIGURE 11-4** Structure of Water Water molecules are polar because they are V-shaped.



**FIGURE 11-5** Hydrogen Bonding  $\text{H}_2\text{O}$  molecules in both liquid and solid states, as well as  $\text{NH}_3$  molecules, are attracted by hydrogen bonds.

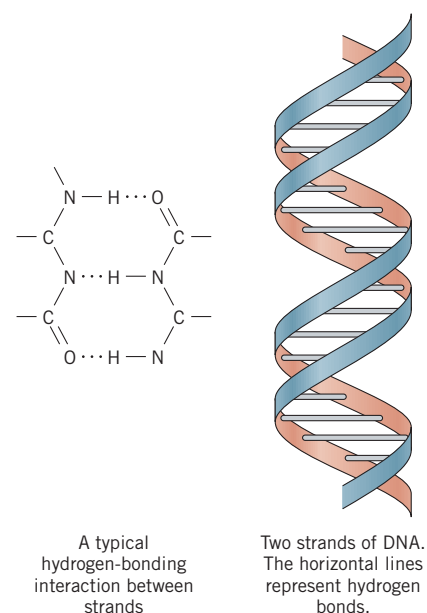


In the solid state, the  $\text{H}_2\text{O}$  molecules have a relatively open structure compared to the liquid state. The more compact structure in the liquid state accounts for its higher density and thus why ice cubes float in water. (See Figure 11-5.)

The interactions between a partially positive hydrogen atom on one molecule and the electron pair of the oxygen on another molecule provide an example of a moderately strong force called a hydrogen bond. A **hydrogen bond** is generally restricted to molecules that have an  $\text{N}-\text{H}$ ,  $\text{O}-\text{H}$ , or  $\text{F}-\text{H}$  bond, where the hydrogen in these bonds interacts with an unshared electron pair on an  $\text{F}$ ,  $\text{O}$ , or  $\text{N}$  atom of another molecule. Hydrogen bonding usually involves only these three atoms because of their high electronegativities and small size. This interaction at first may seem like a case of an extreme dipole–dipole attraction. In fact, it is more complex than that. A hydrogen bond is not nearly as strong as a regular covalent bond (about 1/10 or less as strong), but it is considerably stronger than typical dipole–dipole attractions. Whereas dipole–dipole attractions usually do not have a large effect on the physical properties of the compound, *hydrogen bonding has a significant effect on the properties of a compound.* (In this case, it is like getting 15–20 extra-credit points on a 100-point test. It would most likely make a difference.) Consider the water molecule. It has a very small molar mass of 18 g/mol. If only London forces were present, it would be a gas at temperatures as low as  $-75^\circ\text{C}$ . Even if regular dipole–dipole attractions were present, it would still boil at a very low temperature. The presence of hydrogen bonding between water molecules provides the “glue” that holds the molecules together so that the substance exists as a liquid and even a solid under normal conditions on this planet. Other compounds whose properties are altered considerably by the presence of hydrogen bonding are ammonia ( $\text{NH}_3$ ) and hydrogen fluoride ( $\text{HF}$ ).

Hydrogen bonding is also important in the huge, complex molecules on which life is based. Consider, for example, a molecule of DNA, the “messenger of life.” DNA is an extremely large molecule composed of two strands of covalently bonded atoms offset from each other in a helical arrangement (somewhat like the railings on each side of a spiral staircase). One of the miracles of life is that these two strands can separate from each other and replicate themselves from smaller molecules. The two strands can separate because they are held together by hydrogen bonds, much like Velcro holds two pieces of clothing together. The hydrogen bonds are not as strong as the covalent bonds within the strands (see Figure 11-6), so the two strands can break apart under the right circumstances. When DNA unravels, the hydrogen bonds are broken but not the covalent bonds.

Hydrogen bonds also play an important role in the structure of proteins. Proteins are made of amino acids, which contain  $\text{N}-\text{H}$  bonds, and also have oxygen atoms with unshared electron pairs for the hydrogen bonds to form. A protein is made up of thousands of individual amino acids, so there are potentially thousands of sites along a protein where hydrogen bonds can occur. The fact that proteins can form into sheets to build muscle, or twist into specific shapes to make enzymes, is due in large part to their ability to join together into hydrogen bonds.



**FIGURE 11-6 Hydrogen Bonding in DNA** The double-helix structure of DNA consists of two strands twisted about each other. The strands are connected by hydrogen bonds

**EXERCISE 11-2(a) KNOWLEDGE:** Identify the type of intermolecular force described below.

- caused by a permanent charge separation
- caused by random fluctuations in the electron cloud
- is dependent on the size of the molecule
- occurs only with the largest electronegativity differences
- found in polar molecules
- is about 1/10 the strength of a covalent bond

**ASSESSING THE OBJECTIVE FOR SECTION 11-2**

**EXERCISE 11-2(b) ANALYSIS:** Write the Lewis structures for  $\text{BCl}_3$ ,  $\text{NCl}_3$ , and  $\text{HNCl}_2$ .

- (a) What are the intermolecular forces between molecules in each case?  
 (b) Which is more likely to be in a condensed state at a given temperature? Which is least likely?

**EXERCISE 11-2(c) ANALYSIS:** Rank the following molecules on the basis of increasing intermolecular forces:  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{NH}_2$ .

**EXERCISE 11-2(d) SYNTHESIS:** Of  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ , at room temperature one is a solid, one is a liquid, and one is a gas. Which is which? On what basis did you decide?

For additional practice, work chapter problems 11-6, 11-9, 11-14, and 11-17.

**OBJECTIVE FOR SECTION 11-3**

Classify a solid as ionic, molecular, network, or metallic.

## 11-3 THE SOLID STATE: MELTING POINT



**LOOKING AHEAD!** Heat is a measure of kinetic energy, the energy of motion. Therefore, heating a solid substance increases the motion of the molecules or ions. Eventually, heat and motion overcome the forces holding the molecules or ions in place and the lattice breaks down or melts. We will discuss different types of solids in this section and how intermolecular forces affect the temperature at which they melt. ■

On a hot summer afternoon, ice cream melts too fast and water evaporates quickly. In fact, we may all feel as if we are “melting.” The process of melting is understandable from kinetic theory. As the temperature goes up, the average kinetic energy of molecules increases, which means that they move faster and faster. The increased motion of the molecules eventually overcomes whatever forces are holding the solid or liquid molecules together, and a phase change occurs. It’s like a feeling that most of us have experienced. Sometimes we just get too “fidgety” to stay seated and we have to move around.

Why do some solids melt at a certain temperature while others require a higher temperature to melt? The situation is analogous to what happens in an earthquake that begins slowly and intensifies. At first, only the flimsiest buildings collapse. As the earthquake intensifies, stronger and sturdier buildings are affected and collapse. The buildings with the strongest structure may collapse only in the strongest quake. Heating solids is much like subjecting them to an earthquake. A rising temperature causes the molecules or ions of a solid to vibrate more and more vigorously. The flimsiest solids, whose basic particles are not firmly attached to each other, are the first to collapse, so they melt or vaporize at the lower temperatures. At higher temperatures, solids whose particles have stronger attractive forces change to the liquid state. The stronger the forces holding the particles together, the higher the temperature needed to cause melting.

### 11-3.1 Amorphous and Crystalline Solids

There are basically two general categories of solids: amorphous and crystalline. **Amorphous solids** are so named because they have no defined shape. The basic particles in amorphous solids are not located in any particular positions. Examples of amorphous solids are glass, rubber, and many plastics. In **crystalline solids**, the molecules or ions are arranged in a regular, symmetrical structure called a **crystal lattice**. A salt crystal, a piece of quartz, and many minerals found on Earth naturally form solids with discrete geometric patterns. These symmetrical shapes reflect the ordered arrangements of the molecules or ions that lie within. (See Figure 11-7.)



Aquamarine



Fluorite



Dolomite

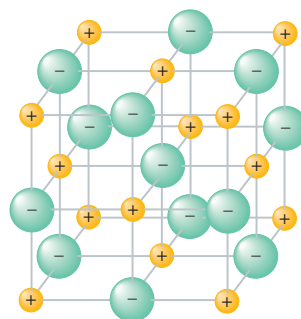
**FIGURE 11-7 Crystalline Solids** The minerals shown here are crystalline solids that are ionic compounds. Their symmetrical shapes reflect the ordered geometry of the ions within.

In this section, we are interested in how heat causes a change from the solid to the liquid state. *The temperature at which a pure crystalline solid melts (the melting point) is a definite and constant physical property.* When pure crystalline solids melt, the added heat causes a phase change and the temperature remains constant. When amorphous solids melt, the melting process is a gradual softening that occurs over a temperature range.

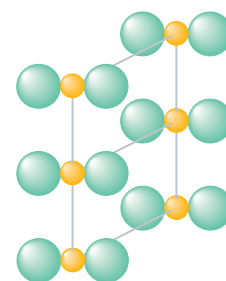
Different types of solids have different melting characteristics. We will examine the four types of solids individually.

### 11-3.2 Ionic Solids

**Ionic solids** are crystalline solids in which ions are the basic particles making up the crystal lattice. (See Figure 11-8a.) Forces between oppositely charged ions are quite strong, especially when compared to forces between individual molecules. The strong ion–ion forces result in solid compounds that have relatively high melting points, as high as 3000°C, for example, for ZrN. As mentioned in Chapter 2 and 9, ionic compounds are the material of rocks and minerals. They are always solids at room temperature. Ionic compounds are also very hard and brittle (they shatter into pieces when struck).



(a) An ionic solid



(b) A molecular solid

### 11-3.3 Molecular Solids

In **molecular solids**, the basic particles of the crystal lattice are individual molecules, which are held together by London forces and, in some cases, dipole–dipole attractions or hydrogen bonding. (See Figure 11-8b.) These attractions are not

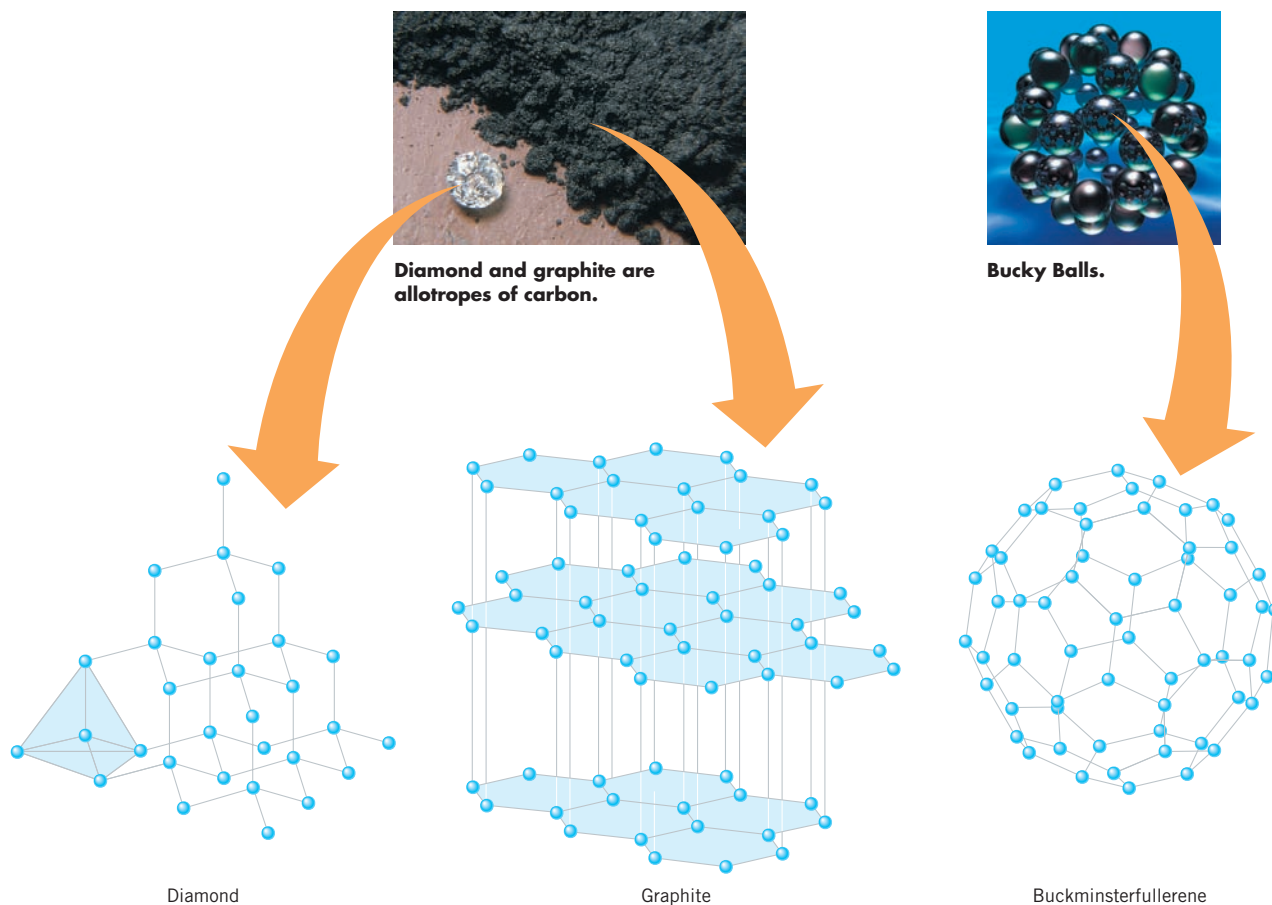
nearly as strong as the ion–ion attractions found in ionic compounds. As a result, molecular solids have low melting points compared to ionic solids. These melting points range from very low for small, nonpolar molecules such as  $\text{N}_2$  and  $\text{CH}_4$  to well above room temperature for large molecules such as table sugar, where large molecules are attracted to each other by hydrogen bonds.

**FIGURE 11-8 Ionic and Molecular Solids** (a) In ionic compounds, ions occupy lattice points. (b) In molecular solids, molecules occupy lattice points.

### 11-3.4 Network Solids

There are a few examples of solids where the atoms are covalently bonded throughout the entire sample of the solid. These are known as **network solids** and generally have very high melting points. Examples of such solids are the two familiar allotropes of carbon—*diamond* and *graphite*. (See Figure 11-9.) In diamond, each carbon is in the center of a tetrahedron and is bonded to four other carbons at the corners of the tetrahedron. These carbons are bonded to four other carbons and so forth throughout the entire crystal. The compact arrangement of atoms makes diamond the hardest material known. To melt diamond, a large number of covalent bonds must be broken, which requires a high temperature to supply the large amount of energy needed. The melting point of diamond is so high (over  $4100^{\circ}\text{C}$ ) as to be difficult to establish.

It is hard to believe that an ordinary chunk of charcoal is chemically the same as a precious diamond. The charcoal is mostly composed of graphite, which is another allotrope of carbon. (Diamond is formed deep in Earth's mantle from graphite at extremely high temperatures and pressures.) In graphite, the carbons are arranged in parallel planar sheets. Since these sheets can slip past one another, graphite is used as a lubricant and as the “lead” in pencils. A third allotrope of carbon, buckminsterfullerene, was not identified until 1985 and is composed of carbon atoms bonded in spherical shapes somewhat like a soccer ball. It was named after the architect Buckminster Fuller, the designer of the geodesic dome that also reminds one of this allotrope. These bucky balls, as they are sometimes called, come in a variety of sizes. The two most familiar have the formulas  $\text{C}_{60}$  and  $\text{C}_{70}$ . Although an important application of this discovery has not yet been forthcoming, we can expect to hear more about

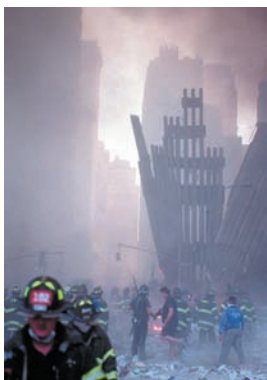


**FIGURE 11-9** The Allotropes of Carbon There are three allotropes of carbon—diamond, graphite and buckminsterfullerene.





## The Melting Point of Iron and the World Trade Center



Iron has been the most important metal for thousands of years. Of all of the metals, how did iron gain this exalted position? First, iron ore is plentiful and widely available. Second, the reduction of the ore can be accomplished with charcoal, limestone, and a hot fire. But most importantly, it is a strong metal that can support many times its weight in other materials. All large

structures like skyscrapers and dams are supported by iron (actually an alloy, known as steel) or concrete reinforced with iron bars.

But as was tragically illustrated in the destruction of the World Trade Center towers on September 11, 2001, it loses strength at high temperatures. The melting point of iron is  $1535^{\circ}\text{C}$ , which is quite high. However, changes in the internal structure of the metal begin around  $900^{\circ}\text{C}$ , and it begins to lose its strength. When the airplanes struck the towers, the strong steel beams, reinforced with concrete, did their job and withstood these powerful collisions. But large amounts of jet fuel ignited inside the buildings, raising the temperature to an estimated  $1000^{\circ}\text{C}$ . Eventually, the heat

caused the metal to soften and collapse from the weight of the floors.

How can iron be protected from high temperatures? In the past, it was coated with asbestos.\* Asbestos is a fibrous form of silica that occurs naturally in the earth. It has a high melting point and is a poor conductor of heat. Iron coated with asbestos or similar materials is effectively insulated from heat at least long enough for a typical fire to burn out. In the case of the World Trade Center, the iron was indeed covered by a protective coating, but the force of the collisions blew it away, exposing the metal to the extreme heat.

The space shuttle must also be protected from heat during its reentry into the atmosphere. As the shuttle encounters air at  $17,000\text{ mi/hr}$ , the friction heats the bottom surface to  $1650^{\circ}\text{C}$ . This temperature would melt most metals, including iron. *Refractory ceramic* tiles are used in this case. A ceramic is a mineral or a mixture of minerals (e.g., quartz and clays) that have been mixed and heated to about  $900^{\circ}\text{C}$ . Dishes and vases are two of many ceramics used in our daily lives. Refractory ceramics have particularly high melting points (above  $2000^{\circ}\text{C}$ ) and incorporate metal oxides such as aluminum oxide. Bricks of these ceramics protect the underside of the spacecraft, which is exposed to the heat.

Iron will continue to support our infrastructure. Research continues, however, on various ways to make it stronger and protect it from the effects of extreme heat.

\*Asbestos coatings are no longer applied because they have been found to cause lung disease, including lung cancer, when the small fibers are inhaled over a period of time.

this form of carbon in the future. Graphite, like diamond, is a network solid and has a very high melting point, but buckminsterfullerene is a molecular solid.

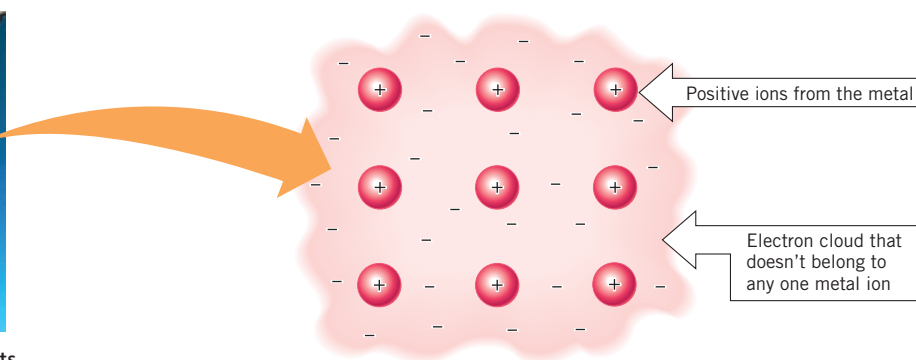
Another example of a network solid is quartz. It is the major component of ordinary sand and also forms the backbone structure of several gemstones, such as amethyst. The formula of quartz,  $\text{SiO}_2$ , represents an empirical formula, since the oxygen atoms in this compound are each attached to two silicon atoms, forming a network throughout the crystal. Quartz also has a high melting point ( $1610^{\circ}\text{C}$ ).

### 11-3.5 Metallic Solids

Metals are also crystalline solids. As mentioned in Section 8-5, the outer electrons of metals are loosely held. *In metallic solids, the positive metal ions occupy regular positions in the crystal lattice, with the valence electrons moving freely among these positive ions.* (See Figure 11-10.) This is the reason metals are good conductors of electricity. All metals except mercury (melting point  $-39^{\circ}\text{C}$ ) are solids at room temperature. Some, like the alkali metals, are soft and melt at comparatively low temperatures. Others, such as iron, are hard and have high melting points. Tungsten has one of the highest melting points of any substance known ( $3380^{\circ}\text{C}$ ). Metals are generally ductile (can be drawn into wires) and malleable (can be pounded into sheets).



Tungsten is used in drill bits because of its strength and high melting point.



**FIGURE 11-10 Metallic Solids** In metals, positive ions occupy the lattice points.

### ASSESSING THE OBJECTIVES FOR SECTION 11-3

#### EXERCISE 11-3(a) KNOWLEDGE: Fill in the blanks.

The two types of solids are \_\_\_\_\_ and \_\_\_\_\_. \_\_\_\_\_ solids have a definite melting point. Of the four types of crystalline solids, \_\_\_\_\_ solids are composed of ions and are always solids at room temperature. \_\_\_\_\_ solids have covalent bonds throughout the crystal. An allotrope of carbon that has a very high melting point is \_\_\_\_\_. Molecular solids are usually soft and melt at \_\_\_\_\_ temperatures. \_\_\_\_\_ solids have positive ions in a sea of \_\_\_\_\_.

#### EXERCISE 11-3(b) KNOWLEDGE: Identify the type(s) of solid that fit the following descriptions.

- |                           |                                  |
|---------------------------|----------------------------------|
| (a) easily malleable      | (d) wide range of melting points |
| (b) generally low melting | (e) brittle                      |
| (c) high melting          | (f) ductile                      |

#### EXERCISE 11-3(c) ANALYSIS: Choose the one in the pair with the higher melting point.

- (a) W or Fe   (b)  $\text{CaF}_2$  or  $\text{SeF}_2$    (c)  $\text{SiO}_2$  or  $\text{CO}_2$    (d) Sn or Hg

#### EXERCISE 11-3(d) SYNTHESIS: Identify the type of molecular solid each of the following chemicals is. Estimate the order of increasing melting points among them: $\text{H}_2\text{O}(s)$ , $\text{C}(s)$ , $\text{CS}_2(s)$ , KF, Sn

*For additional practice, work chapter problems 11-19, 11-20, 11-24, and 11-25.*

### PART A SUMMARY

#### KEY TERMS

- 11-2** Molecules in the condensed states are held together by **intermolecular forces**. p. 334
- 11-2.1** All molecules are attracted to each other by **London forces**, but in nonpolar compounds these act exclusively. p. 334
- 11-2.2** Polar compounds have **dipole-dipole attractions** in addition to London forces. p. 335
- 11-2.3** An interaction involving an electropositive hydrogen and highly electronegative atoms is known as **hydrogen bonding**. p. 337
- 11-3.1** The molecules in **amorphous solids** have no order, but the particles in **crystalline solids** exist in a **crystal lattice**. p. 338
- 11-3.2** The lattice positions in an **ionic solid** are occupied by ions. p. 339
- 11-3.3** The lattice positions in **molecular solids** are occupied by molecules. p. 339
- 11-3.4** The bonding in **network solids** extends throughout the entire crystal. p. 340
- 11-3.5** A **metallic solid** can be thought of as metal cations in a sea of electrons. p. 341



## SUMMARY CHART

| Solids and Forces |                  |                    |                                      |
|-------------------|------------------|--------------------|--------------------------------------|
| Type of Solid     | Forces           | Compounds          | Examples                             |
| Molecular         | London           | all molecules      | CCl <sub>4</sub> , CO <sub>2</sub>   |
|                   | Dipole–dipole    | polar molecules    | SO <sub>2</sub> , CH <sub>3</sub> Cl |
|                   | Hydrogen bonding | mainly O—H and N—H | NH <sub>2</sub> Cl, HOCl             |
| Ionic             | Ion–ion          | Ionic compounds    | NaCl, K <sub>2</sub> SO <sub>4</sub> |
| Network           | Covalent bonds   |                    | SiO <sub>2</sub> , diamond           |
| Metallic          | Cation–electron  | Solid metals       | Fe, Ni, Co                           |

**PART B**  
THE LIQUID STATE AND  
CHANGES IN STATE

## SETTING A GOAL

- You will learn about properties of the liquid state and examine how energy is associated with phase changes.

## OBJECTIVES

- 11-4 (a)** List and define physical properties of the liquid state. **(b)** Discuss the relationship between intermolecular forces and liquid properties.
- 11-5** Given the appropriate heats of fusion and vaporization, calculate the energy required to melt and vaporize a given compound.
- 11-6 (a)** Describe the changes that occur on the molecular level in a heating curve. **(b)** Calculate the energy required for a change in temperature or physical state.

## 11-4 THE LIQUID STATE: SURFACE TENSION, VISCOSITY, AND BOILING POINT



**LOOKING AHEAD!** All the free elements and compounds, even those that make up our atmosphere, can be found in the solid state if the temperature is low enough. As the temperature rises, these solids, one by one, melt to form the liquid state. We now shift our focus to some properties of the liquid state. ■

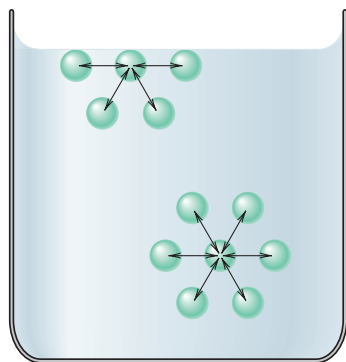
▶ **OBJECTIVES FOR SECTION 11-4**

**(a)** List and define physical properties of the liquid state. **(b)** Discuss the relationship between intermolecular forces and liquid properties.

Intermediate between the complete disorder of molecules in the gaseous state and the high order of the crystal lattice in the solid state lies the liquid state. Here, the basic particles are still held close together, so liquids remain condensed as in the solid state. On the other hand, the basic particles can move past one another. In this respect, the liquid state is like the gaseous state. At a lower temperature, liquids freeze to the solid state, and at some higher temperature, liquids vaporize to the gaseous state. Melting point and boiling point are two properties of liquids that are dependent on their intermolecular forces. Other physical properties, too, are also related to these forces, such as surface tension and viscosity. We will discuss surface tension first.

### 11-4.1 Surface Tension

Have you ever noticed that certain insects can walk on water? Also, if one carefully sets a needle or a small metal grate on water, it remains on the surface despite the fact that the metal is much denser than water. (See Figure 11-11.) This tells us that there is some tendency for the surface of the water to stay together. **Surface tension**



(a) Molecules on the surface are pulled down and to the sides.



(b) An insect can walk on water.



(c) The metal grid floats on the surface.

**FIGURE 11-11 Surface Tension** The unequal attraction for molecules on the surface accounts for surface tension.

is the force that causes the surface of a liquid to contract. Because of surface tension, drops of liquid are spherical. A molecule within the body of the liquid is equally attracted in all directions by the intermolecular forces. Molecules on the surface are pulled to the side and downward, but not upward. This unequal attraction means that a portion of a liquid will tend to have a minimum amount of surface area. A liquid placed on a flat surface draws itself into a “bead,” or into a sphere if it is suspended in space. Although raindrops are not completely spherical because of gravity, water released in the space shuttle forms perfectly spherical drops. The force that is required to break through a surface relates to its surface tension. Water obviously has a high enough surface tension to support small insects. Other liquids, where the intermolecular forces are greater, have higher surface tensions.

Dissolved soaps reduce the surface tension of water, thus allowing the surface to expand and “wet” clothes or skin rather than form beads. An insect would do well to avoid trying to walk on soapy water. Because of the reduced surface tension, the bug would sink. In this context, we think of “wetness” as the ability of a liquid to cover a surface. While we generally think of water or any liquid as being wet, clearly some are wetter than others. If you’ve ever examined liquid mercury (hopefully not for very long), you would notice just how *not wet* it is. The strong metallic bonds, while not strong enough to make it a solid at room temperature like other metals, do give it a high surface tension.

### 11-4.2 Viscosity

We all know it seems to take forever to pour ketchup on french fries when we are hungry. Ketchup is more viscous than water. The **viscosity** of a liquid is a measure of its resistance to flow. Water and gasoline flow freely because they have low viscosity. Motor oil and syrup flow slowly because they have high viscosity. The viscosity of a liquid depends to some extent on the intermolecular forces between molecules. Strong intermolecular attractions usually mean a more viscous liquid. Water is an exception—even though its molecules interact relatively strongly, it has a comparatively low viscosity. Compounds with long, complex molecules also tend to form viscous liquids because the molecules tangle together much like strands of spaghetti in a bowl.

A breakfast of pancakes with syrup on a cold morning is hard to beat. Unfortunately, the syrup barely moves when it is cold. A little warming of the syrup solves the problem. All liquids become less viscous as the temperature increases. The higher kinetic energy of the molecules counteracts the intermolecular forces, allowing the molecules to move past one another more easily. (See Figure 11-12.)



**FIGURE 11-12 Viscosity** Syrup is a viscous liquid.

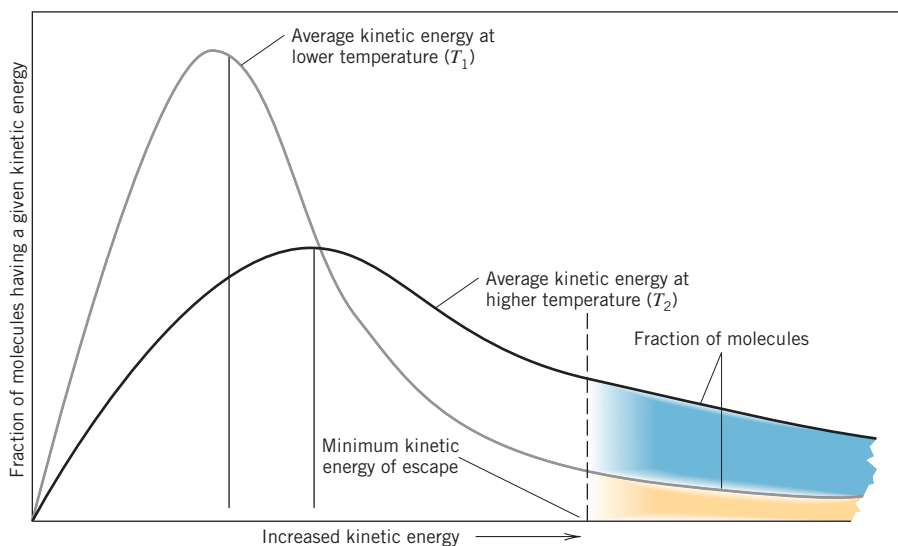
### 11-4.3 Vapor Pressure

Perhaps one of the most accepted facts of life is that wet things eventually become dry. *Liquid changes to the gaseous state in a process known as vaporization.* When vaporization occurs at temperatures lower than the boiling point, it is known as **evaporation**. In order for a molecule of a liquid to escape to the vapor state, however, it must overcome the intermolecular forces attracting it to its neighbors in the liquid. Two conditions allow a molecule in a liquid to escape the liquid state to the gaseous state. First, it must be at or near the surface of the liquid. Second, it must have at least the minimum amount of kinetic energy needed to overcome the intermolecular forces. So why don't all molecules on the surface escape? To answer this, we must recall that at a given temperature, the molecules have a wide range of kinetic energies. The temperature relates to the *average* kinetic energy. The distribution of kinetic energies of the molecules at two temperatures ( $T_1$  and  $T_2$ ) can be represented graphically as in Figure 11-13. The unbroken vertical lines represent the average kinetic energy at each of these two temperatures.  $T_2$  represents a higher temperature than  $T_1$  because it has a higher average. The broken vertical line represents the minimum kinetic energy that a molecule must have in order to escape from the surface. Notice that a small fraction of molecules have the minimum energy at  $T_1$ , but a larger fraction of molecules have the minimum energy at the higher temperature,  $T_2$ . As a result, a liquid evaporates faster at a higher temperature.

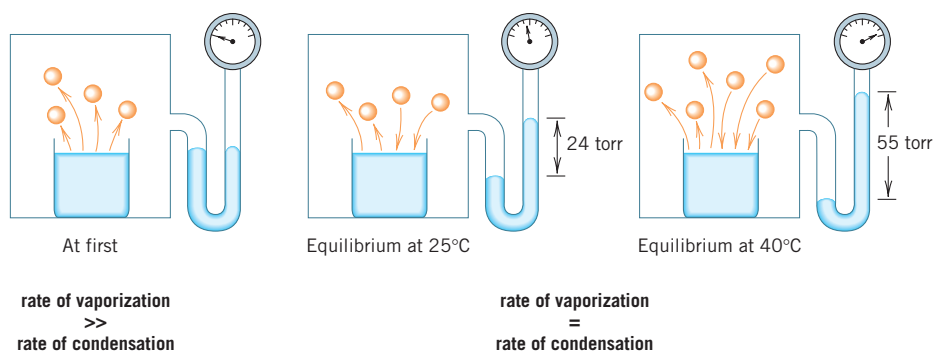
If only the molecules with the highest kinetic energy escape to the vapor state, what effect does that have on the liquid left behind? The effect is similar to what would happen if the top 10% of the grades were left out when the average of the last chemistry test was computed. The remaining average would be lower. When the molecules with the highest kinetic energy escape, the average kinetic energy of the molecules remaining in the liquid state is lowered. This means that the liquid will be cooled and the gas above the water will be correspondingly heated.

The cooling effect of evaporating water is important to health maintenance in warm climates. Perspiration covers our bodies with a layer of water when it is warm. The evaporation of this liquid cools the water on our bodies and us along with it. The cool feeling after a hot shower is not just a feeling but a reality. Our perspiration cools us but can make life more miserable for the other people in a crowded room. Evaporation cools the liquid but heats the air. If water is allowed to evaporate under a vacuum, the evaporation process occurs faster. In fact, the water cools enough to freeze. Certain food products, such as some instant coffees, advertise that they are "freeze dried." Instant coffee is made by first making a coffee solution and then removing the water, leaving coffee crystals. Boiling the coffee solution to remove the water presumably affects the taste. Thus, removing the water at lower temperatures (freeze drying) should preserve the flavor.

Now, instead of letting the water vapor escape to the surroundings, we can measure the buildup of pressure by placing a beaker of water in a closed glass container so that the vapor molecules are trapped. Attached to the apparatus is an open-ended mercury manometer for measuring the increase in pressure within the container. We will assume that initially the air is completely dry, meaning that any water vapor will come from our beaker of water. Before any water evaporates, the manometer indicates the same pressure inside and outside the container. As the



**FIGURE 11-13**  
**Distribution of Kinetic Energies at Two Temperatures** The average kinetic energy is higher at  $T_2$  than at  $T_1$ .



**FIGURE 11-14**  
**Equilibrium Vapor Pressure** A given fraction of molecules escape to the vapor state above a liquid.

that state. *The change of state from the gaseous to the liquid state is known as **condensation**.* As more liquid molecules enter the gaseous state, more gaseous molecules enter the liquid state. Eventually, a point is reached where the rate of evaporation equals the rate of condensation, and the pressure remains constant. That is, for every molecule that goes from the liquid to the gaseous state, a molecule goes from the gaseous to the liquid state. The system is said to have reached a point of *equilibrium*. (See Figure 11-14.)

The difference in the levels of the manometer at the dry state and when the pressure has reached equilibrium is the pressure exerted by the water vapor. *The pressure exerted by the vapor above its liquid at a given temperature is called its **equilibrium vapor pressure** or simply **vapor pressure**.* At a higher temperature, more molecules have the minimum energy needed to escape and, as a result, the vapor pressure is higher. (We say the liquid has become more *volatile*, meaning that it has a higher tendency to vaporize.) Solids may also have an equilibrium vapor pressure. *The vaporization of a solid is known as **sublimation**.* Dry ice (solid  $\text{CO}_2$ ) has a high vapor pressure and sublimates rapidly. Ordinary ice also has a small but significant vapor pressure. A thin layer of snow will vaporize away even if the temperature remains below the melting point of ice.

In the experiment described above, the vapor pressure at first increases rapidly but then slowly reaches the equilibrium vapor pressure. We notice this same effect on humid summer days. The closer the actual vapor pressure of water is to the equilibrium vapor pressure, the slower the rate of evaporation. The relative humidity measures how near the air is to saturation with vapor at a particular temperature. For example, if the relative humidity is 60% and the equilibrium vapor pressure of water at this temperature is 30 torr, the actual vapor pressure of water in the atmosphere is about  $0.60 \times 30 \text{ torr} = 18 \text{ torr}$ . The higher the humidity, the slower the evaporation and the less efficient our personal air-conditioning system provided by perspiration. “It’s not the heat, it’s the humidity.” In fact, both factors affect our comfort level. On the weather report, the combined effect of heat and humidity is called the *heat index*. This tells us how much hotter it actually feels because of the humidity.

How does the vapor pressure for various liquids at a given temperature relate to their intermolecular force? Clearly, molecules that are held more strongly to the surface will require greater energies to vaporize. That means that a smaller percentage will have the required energy to escape, and the rate of evaporation will be slower. On the other hand, the reverse process—getting a gaseous molecule to “stick” to the surface—will be easier and occur more rapidly. Therefore, liquids with weak intermolecular forces have higher vapor pressures, and liquids with stronger intermolecular forces have lower vapor pressures (i.e., are less volatile) at the same temperature. It is no wonder that the odor of gasoline can be found in a warm garage after a recent fill-up. The smell of acetone fills the bathroom if you’ve used it to remove fingernail polish. Both of these liquids have weak forces and relatively high vapor pressures at room temperature.



Solid naphthalene (moth balls) sublimates. The vapor kills moths.



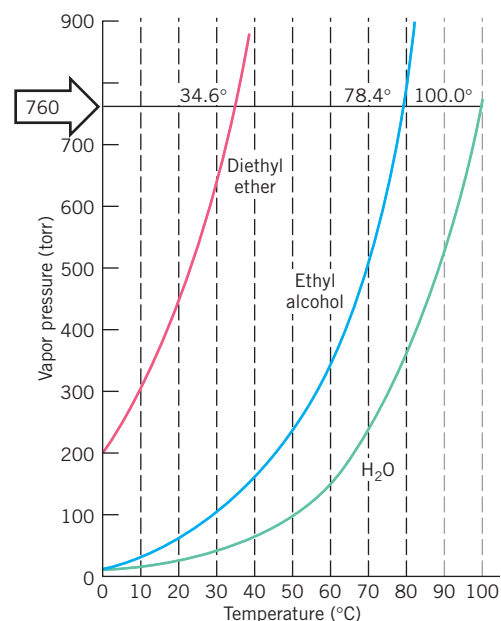
### 11-4.4 The Boiling Point

The vapor pressure of liquids varies regularly as a function of temperature. This is represented graphically in Figure 11-15. The vapor pressure curves of water, diethyl ether, and ethyl alcohol are included. Notice that the vapor pressure of water at 100°C is equal to the pressure of the atmosphere (760 torr).

When the vapor pressure of a liquid equals the restraining pressure, bubbles of vapor form in the liquid and rise to the surface. This is the **boiling point** of the liquid. The boiling point depends on the restraining pressure.

The **normal boiling point** of a liquid is the temperature at which the vapor pressure is equal to 760 torr. Diethyl ether and ethyl alcohol are more volatile than water, which means that their vapor pressures reach 1 atm at temperatures below that of water. They boil at around 34°C and 78°C, respectively, at 1 atm pressure. At other atmospheric pressures, the boiling points of liquids are different. For example, on Pikes Peak in Colorado, water boils at 86°C because the atmospheric pressure is only 450 torr. The highest point on Earth is the top of Mt. Everest. Water boils at 76°C at this elevation. Cooking takes much longer at high elevations and may not even kill all harmful bacteria because of the lower boiling point of water. Appliances called pressure cookers are sometimes used. They retain some of the water vapor, thus increasing the pressure inside the cooker and increasing the boiling point.

The temperature at which a liquid begins to boil also depends on the attractive forces between the basic particles. Ionic compounds naturally have very high boiling points and molecular compounds have much lower ones. Of the molecular compounds, those that have large molecules or that also have hydrogen bonding have the highest boiling points. The effect of hydrogen bonding has a rather dramatic effect on boiling points. For example, consider the boiling points of the Group VIA hydrogen compounds: H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te. The molar masses of these compounds increase in the order listed. Thus London forces should increase in the same order and, as a result, so should the intermolecular attractions. From this result alone, we may predict steadily higher boiling points for these compounds. Note in Table 11-1 that this is indeed the case for H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te. However, the boiling point of H<sub>2</sub>O, by far the highest, is way out of line. The explanation for the unusually high boiling point of water is that hydrogen bonding provides significant intermolecular interactions. The other three compounds are polar, but the normal dipole–dipole attractions do not seem to have a major effect on the boiling points compared with the trend in London forces. In Table 11-1, the boiling points of Group VA and Group VIIA hydrogen compounds are also listed. Hydrogen bonding explains the unusually high boiling points of NH<sub>3</sub> and HF compared with other hydrogen compounds in their group.



**FIGURE 11-15 Vapor Pressure and Temperature** The boiling points of these liquids are the temperatures at which the vapor pressures equal 760 torr.

**TABLE 11-1** Boiling Points (°C) of Some Binary Hydrogen Compounds

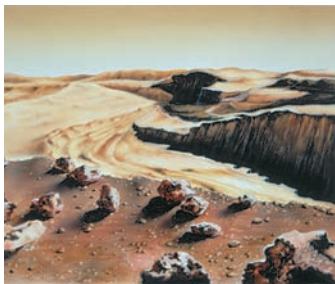
| GROUP | SECOND PERIOD        | THIRD PERIOD         | FOURTH PERIOD         | FIFTH PERIOD           |
|-------|----------------------|----------------------|-----------------------|------------------------|
| VIIA  | HF 17                | HCl -84              | HBr -70               | HI -37                 |
| VIA   | H <sub>2</sub> O 100 | H <sub>2</sub> S -61 | H <sub>2</sub> Se -42 | H <sub>2</sub> Te -2.0 |
| VA    | NH <sub>3</sub> -33  | PH <sub>3</sub> -88  | AsH <sub>3</sub> -62  | SbH <sub>3</sub> -18   |

MAKING

IT

REAL

## The Oceans of Mars



Water once flowed on Mars and maybe still does.

This magnificent planet where we live exists at a perfect distance from the sun. We receive just the right amount of energy so that water can exist in the liquid state. Of course, it is solid in the colder regions, and the discomfort of a humid day tells us it is also present in the gaseous

state. The exchange of water among the three states is a continual process powered by the energy from the sun. It also moderates and distributes heat around Earth.

Are there oceans on other planets? In the 1970s the scientific world was shocked when spacecraft sent back photos of what appeared to be dry riverbeds on the surface of our neighboring planet, Mars. Scientists have been intrigued and excited ever since about the possibility of oceans of water on Mars. The existence of liquid water implies the possibility that life may have existed on this planet (and maybe still does). More recent visits, including that of the Phoenix polar lander in 2008, confirmed the existence of ancient but now dry lakebeds. Current conditions on the surface of Mars would not be suitable for the liquid state of water to exist. The atmospheric pressure on the surface is between 6 and 8 torr, which is about 1% of the pressure on Earth. At this low pressure, water would

boil at about 5°C, so the liquid range would only be from 0°C to 5°C. The temperature actually varies from about –75°C at the poles to around 10°C at the equator. Even if the liquid state existed at 3° or 4°C, it would quickly evaporate in the thin atmosphere and freeze from the evaporative process.

Apparently, 1 to 2 billion years ago, the temperature and pressure could have been much like Earth's, meaning that liquid water could have existed in many places. What happened to all the water on Mars? For a long time, we thought it all must have escaped into space. Data reported in 2007 indicated that much of it could still be there. It is either frozen at the surface at its poles or lies in layers beneath the surface. Very recent evidence seems to suggest that some sort of liquid water, perhaps very acidic or briny, has flowed on the surface within our lifetimes. These chemicals would lower the melting point of the water so that, perhaps for brief periods, it could exist on the surface. We will know much more in the next few years as more space probes orbit the planet and some make soft landings.

Farther out in space lies a moon of Saturn known as Titan. As mentioned in the Setting the Stage in Chapter 3, the *Cassini* spacecraft showed a rugged terrain that appeared to be eroded by flowing liquids. It has a thick, hazy atmosphere where the cold temperature (–180°C) and pressure of 1.6 atm are just right for oceans of methane (CH<sub>4</sub>). It is speculated that there may be weather patterns there similar to those on Earth, except that the rain in this plain is mostly methane.

### ASSESSING THE OBJECTIVES FOR SECTION 11-4

#### EXERCISE 11-4(a) KNOWLEDGE: Fill in the blanks.

In the liquid state, \_\_\_\_\_ causes water to form spherical drops. \_\_\_\_\_ is a property relating to the rate of flow. When evaporation of a liquid occurs, the remaining liquid becomes \_\_\_\_\_. The equilibrium \_\_\_\_\_ is the pressure exerted by the gas at a given \_\_\_\_\_. The vaporization of a solid is known as \_\_\_\_\_. The normal boiling point is the temperature at which the \_\_\_\_\_ is equal to 760 torr.

#### EXERCISE 11-4(b) KNOWLEDGE: Do the following properties result from strong or weak intermolecular forces?

- |                          |                           |
|--------------------------|---------------------------|
| (a) a high boiling point | (c) a high vapor pressure |
| (b) a low viscosity      | (d) a low surface tension |



**EXERCISE 11-4(c) ANALYSIS:** Refer to Figure 11-15 to answer the following.

- (a) What is the boiling point of water at an altitude where the pressure is 550 torr?  
 (b) At what pressure will diethyl ether boil at 20°C?

**EXERCISE 11-4(d) SYNTHESIS:** At a given temperature, substance A has a vapor pressure of 850 torr and substance B has a vapor pressure of 620 torr. What can you say about the physical states of the two substances at this temperature? What can you reasonably conclude about their respective viscosities and surface tensions?

For additional practice, work chapter problems 11-29, 11-32, 11-37, 11-38, and 11-41.

## 11-5 ENERGY AND CHANGES IN STATE



**LOOKING AHEAD!** The energy required to cause a phase change is specific for a particular substance. The amount of that energy is the subject of this section. We will see that the energy required to melt a solid or vaporize a liquid depends on the nature of the solid or liquid. ■

Large lakes and oceans moderate the climate in a number of ways. When one of the American Great Lakes freezes in winter, heat is released to the surroundings by this process. This heat has the same effect as a giant natural furnace and helps keep the air temperature from falling as much as it otherwise would. Since the Great Lakes do not usually completely freeze over, heat is released all through the winter from the freezing process. On the downside, spring is delayed in this region because the melting ice absorbs heat and keeps the temperature from rising as much as it otherwise would. Regions of Siberia, in Russia, lie about as far north as Minnesota but have few large lakes. As a result, it is much colder there in the winter but also much hotter in the summer.

An ice cube at its melting point of 0°C remains in the solid state indefinitely unless energy is supplied. The addition of sufficient energy causes the solid to change to the liquid state yet remain at 0°C. The same is true for a pure liquid at its boiling point. That is, a specific amount of energy must be supplied to change the liquid to vapor at its boiling point. The opposite processes (i.e., fusion and condensation) *release* the same amount of energy as was absorbed in the reverse processes. (See Figure 11-16.)

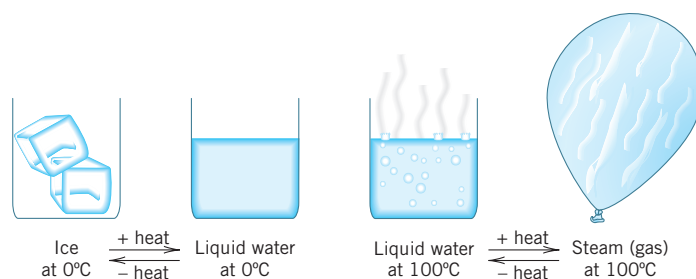
We understand that the temperature at which a substance melts and boils depends on the forces between the basic particles. The amount of energy it takes to cause changes in physical state also depends on the magnitude of these forces. We will first consider the energy involved in transitions between the solid and the liquid states (melting and freezing) and then transitions between the liquid and the gaseous states (boiling and condensation).

### 11-5.1 Melting and Freezing

We are all aware that ice melts in the hot sun and that water changes to ice in the freezer. Melting [i.e.,  $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ ] is an endothermic process—so heat must be supplied as in the hot sun. Freezing [i.e.,  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ ] is an exothermic process—so heat must be removed as in a freezer. The same amount of heat energy

### OBJECTIVE FOR SECTION 11-5

Given the appropriate heats of fusion and vaporization, calculate the energy required to melt and vaporize a given compound.



**FIGURE 11-16 Heat and Changes in State** Application or removal of heat causes a change in state at the melting point or boiling point of a substance.

**TABLE 11-2** Heats of Fusion and Melting Points

| COMPOUND             | TYPE OF COMPOUND                     | HEAT OF FUSION (Cal/g) | HEAT OF FUSION (J/g) | MELTING POINT (°C) |
|----------------------|--------------------------------------|------------------------|----------------------|--------------------|
| NaCl                 | ionic                                | 124                    | 519                  | 801                |
| H <sub>2</sub> O     | polar covalent<br>(hydrogen bonding) | 79.8                   | 334                  | 0                  |
| ethyl alcohol        | polar covalent<br>(hydrogen bonding) | 24.9                   | 104                  | -114               |
| ethyl ether          | polar covalent                       | 22.2                   | 92.5                 | -116               |
| benzene              | nonpolar covalent                    | 30.4                   | 127                  | 5.5                |
| carbon tetrachloride | nonpolar covalent                    | 4.2                    | 17.6                 | -24                |

is released when a given amount of liquid freezes as would be required if the same amount of solid were to melt at the melting point. Each compound requires a specific amount of heat energy to melt a specific mass of sample. *The heat of fusion of a substance is the amount of heat in calories or joules required to melt one gram of the substance.* Table 11-2 lists the heats of fusion and the melting points of several substances. Note that sodium chloride, which is ionic, has the strongest attractions between particles of those listed and thus has the highest melting point and the highest heat of fusion.

Nonpolar compounds of low molar mass have comparatively small heats of fusion. Water, because of hydrogen bonds, has a rather high heat of fusion for such a light molecule. In fact, it is this relatively high heat of fusion that helps make water so effective at moderating climate, such as described for the Great Lakes in the winter.

**EXAMPLE 11-1****Calculating the Heat Released by Freezing**

How many kilojoules of heat are released when 185 g of water freezes?

**PROCEDURE**

The heat of fusion can be used as a conversion factor relating mass in grams to joules.

$$\text{mass} \times \text{heat of fusion} = \text{heat}$$

**SOLUTION**

$$185 \text{ g} \times \frac{334 \text{ J}}{\text{g}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = \underline{\underline{61.8 \text{ kJ}}}$$

**ANALYSIS**

Of course, this problem could be calculated in the other direction as well, determining how many grams freeze when a certain amount of energy is removed or how much melts when a given amount of energy is applied. Make certain to use the heat of fusion for the specific compound being melted or frozen. Can you determine what mass of ethyl alcohol can be melted with 40.0 kJ of energy? Answer: 385 grams.

**SYNTHESIS**

Table 11-3 in the next section lists the heats of vaporization of several compounds. This is the energy necessary to break the forces between solid particles and allow them to flow past one another. In the next section, we'll look at heats of vaporization. This is the energy needed to break the forces between liquid particles and allow them to expand into the gaseous state. What's your prediction as to which value is greater for a given substance, heat of fusion or heat of vaporization? Read on to find out.

**11-5.2 Boiling and Condensation**

If we want to boil water, we place the container of water on the stove or in the microwave. The vaporization of a liquid [e.g.,  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ ] requires energy and so is also an endothermic process. The opposite process, condensation, is

**TABLE 11-3** Heats of Vaporization and Boiling Points

| COMPOUND             | TYPE OF COMPOUND                     | HEAT OF VAPORIZATION (Cal/g) | HEAT OF VAPORIZATION (J/g) | NORMAL BOILING POINT (°C) |
|----------------------|--------------------------------------|------------------------------|----------------------------|---------------------------|
| NaCl                 | ionic                                | 3130                         | 13,100                     | 1465                      |
| H <sub>2</sub> O     | polar covalent<br>(hydrogen bonding) | 540                          | 2260                       | 100                       |
| ethyl alcohol        | polar covalent<br>(hydrogen bonding) | 204                          | 854                        | 78.5                      |
| ethyl ether          | polar covalent                       | 89.6                         | 375                        | 34.6                      |
| benzene              | nonpolar covalent                    | 94                           | 393                        | 80                        |
| carbon tetrachloride | nonpolar covalent                    | 46                           | 192                        | 76                        |

exothermic. As with melting and freezing, the same amount of energy is released when a given amount of vapor condenses [e.g.,  $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$ ] as would be required if the same amount of liquid were to vaporize at the boiling point. Each compound also requires a specific amount of heat energy to vaporize a specific mass of the sample. *The heat of vaporization of a substance is the amount of heat in calories or joules required to vaporize one gram of the substance.* The heats of vaporization and the boiling points of several substances are given in Table 11-3.

Note again that water has an unusually high heat of vaporization compared with other molecular compounds. Once again, the strength and number of hydrogen bonds between H<sub>2</sub>O molecules are responsible.

The heats of fusion and vaporization concern how heat can cause phase changes at a constant temperature. When only one phase is present, the application of heat results in an increased temperature of the phase. All pure solids, liquids, and gases have a physical property that we previously defined as specific heat. (See Table 3-2 in section 3-5.1.) *Specific heat refers to the amount of heat required to raise one gram of a substance one degree Celsius.* We observed that water also has an unusually high specific heat compared with other compounds or elements. The specific heats for the solid and gaseous states of water are not the same as for the liquid state, however.



The heat required to vaporize water is comparatively large.

**EXAMPLE 11-2****Calculating the Heat Released by Condensation and Cooling**

Steam causes more severe burns than an equal mass of water at the same temperature. Compare the heat released in calories when 3.00 g of water at 100°C cools to 60°C with the heat released when 3.00 g of steam at 100°C condenses and then cools to 60°C.

**PROCEDURE**

There are two processes to consider. The first is the heat released when the liquid is cooled from 100°C to 60°C, or a change of 40°C. The second is the heat released when the gas condenses at 100°C.

Use the specific heat of water as a conversion factor to convert mass and temperature change to calories.

$$\text{mass} \times \text{specific heat} \times \Delta T = \text{heat}$$

Use the heat of vaporization as a conversion factor to convert mass to calories.

$$\text{mass} \times \text{heat of vaporization} = \text{heat}$$

**SOLUTION**

Cooling of water:

$$3.00 \text{ g} \times (100 - 60)^\circ\text{C} \times \frac{1.00 \text{ cal}}{\text{g} \cdot ^\circ\text{C}} = \underline{\underline{120 \text{ cal}}}$$

Condensation of steam:

$$3.00 \text{ g} \times \frac{540 \text{ cal}}{\text{g}} = 1620 \text{ cal}$$

Total heat released from condensation and cooling =  $1620 + 120 = \underline{1740 \text{ cal}}$

### ANALYSIS

Note that almost 15 times more heat energy is released by the steam at  $100^\circ\text{C}$  than by the water at the same temperature.

### SYNTHESIS

There are many applications of the fact that steam at  $100^\circ\text{C}$  carries with it so much energy. Steam radiators allow steam to pass by its own power through buildings and carry large quantities of heat with it compared to hot water. Steamed vegetables cook quickly and thoroughly. Steam cleaning dislodges dirt that vacuuming could not remove. Initially, car manufacturers built steam-powered automobiles, which were popular until the internal combustion engine became popular. Can you think of other uses?

## ASSESSING THE OBJECTIVE FOR SECTION 11-5

**EXERCISE 11-5(a) KNOWLEDGE:** What are the units of heat of vaporization, heat of fusion, and specific heat?

**EXERCISE 11-5(b) ANALYSIS:** What mass of ethyl ether can be melted with 1.00 kJ of heat energy? (Refer to Table 11-2.)

**EXERCISE 11-5(c) ANALYSIS:** How much energy is required to vaporize 35.0 g of benzene? (Refer to Table 11-3.)

**EXERCISE 11-5(d) SYNTHESIS:** Refrigerators cool because a liquid extracts heat when it is vaporized. Before the synthesis of Freon ( $\text{CF}_2\text{Cl}_2$ ), ammonia ( $\text{NH}_3$ ) was used. The heat of vaporization of  $\text{NH}_3$  is 1.36 kJ/g and that of Freon is 161 J/g. Which is the better refrigerant on a mass basis? Which is the better refrigerant on a mole basis? What might be a reason we don't use ammonia today?

*For additional practice, work chapter problems 11-47, 11-54, 11-55, and 11-56.*

## OBJECTIVES FOR SECTION 11-6

(a) Describe the changes that occur on the molecular level in a heating curve. (b) Calculate the energy required for a change in temperature or physical state.

## 11-6 HEATING CURVE OF WATER



**LOOKING AHEAD!** In the final section of this chapter, we will summarize what happens when heat is applied to a chunk of ice from the freezer so that it eventually changes from a cold solid to a hot vapor. The added heat will cause three temperature changes and two phase changes. As each of these changes occurs, we will try to visualize how the molecules of  $\text{H}_2\text{O}$  are affected. ■

Assume that we take an ice cube cooled to  $-10^\circ\text{C}$  from the freezer compartment of the refrigerator. Imagine that the ice crystal could be magnified so that the motions and positions of the individual molecules could be seen. We would notice that all the molecules are in fixed positions and that ice is a crystalline molecular solid. The molecules are certainly in motion, but the motion consists mainly of vibrations about their fixed locations. We are now going to supply heat at a constant rate to the ice cube and observe the changes that occur. *The graphical representation of the temperature as a solid is heated through the two phase changes plotted as a function of the time of heating is called the heating curve.* (See Figure 11-17. Note that it is really a series of straight lines despite being called a curve.) There are five regions of interest in the curve.

### 11-6.1 Heating Ice

From  $-10^{\circ}\text{C}$ , the added heat causes an increase in kinetic energy in the crystal in the form of increased vibrations and rotations of the molecules about the fixed positions in the crystal lattice. Since only one phase is present, the temperature of the ice rises. The specific heat of a particular phase of a particular compound is a measure of the energy required to cause these kinetic energy changes. The larger the value of the specific heat, the more slowly the temperature rises. Figure 11-17a represents the temperature change as the ice is heated.

### 11-6.2 Melting Ice

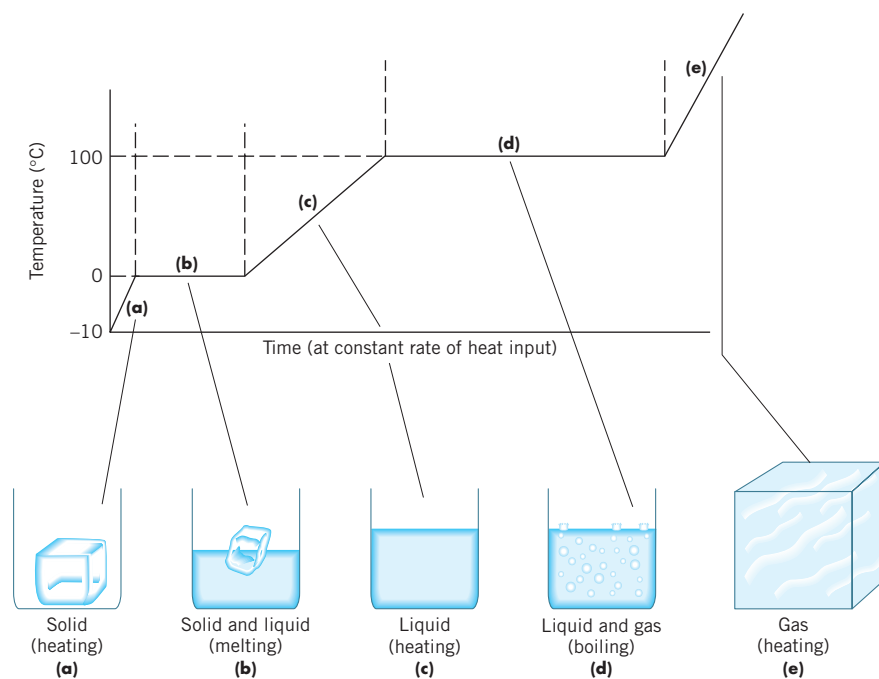
At  $0^{\circ}\text{C}$  (and 1 atm pressure), a phase change begins. The vibrations of the molecules become so great that some hydrogen bonds break and the molecules begin to move out of their fixed positions in the crystal lattice. What we notice is that the solid ice begins to melt but the temperature of the ice–water mixture remains constant. Not all the hydrogen bonds break, however, so groups of molecules still stick together in the liquid state. The added heat is now causing molecules to move apart rather than move faster. When particles that attract each other move apart, there is an increase in the potential energy (analogous to suspending a weight above the ground). Changes in potential energy do not relate to temperature, so the temperature remains constant while the ice is melting. A constant temperature as a solid melts is a property of pure matter. (See Figure 11-17b.) How long it takes a given solid to melt depends on the heat of fusion.

### 11-6.3 Heating Water

Between  $0^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ , only the liquid phase is present, so the added heat causes the temperature of the liquid to rise. Unlike in the solid state, the motion of water molecules in the liquid state includes translational motion (movement from point to point). The rate at which the temperature of a liquid rises depends on the specific heat of the liquid. Notice from the slope of the lines that the temperature does not appear to rise as fast in the liquid as in the solid. This is because the specific heat of water [ $4.184\text{ J}/(\text{g} \cdot ^{\circ}\text{C})$ ] is about twice that of ice [ $2.05\text{ J}/(\text{g} \cdot ^{\circ}\text{C})$ ]. (See Figure 11-17c.)

### 11-6.4 Vaporizing Water

At  $100^{\circ}\text{C}$  (and 1 atm pressure), a second phase change begins. As the temperature of the liquid increases from  $0^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , the vapor pressure of the liquid has also been rising. At this temperature, the vapor pressure of water is equal to the atmospheric pressure, and the water begins to boil. The kinetic energy of the water molecules has now become great enough to break the remaining hydrogen bonds holding them in the liquid state. Just as in the melting process, the added heat is now causing molecules to move apart rather than increasing the kinetic energy of the molecules. As with melting, the added heat causes an increase in potential energy, and the temperature remains constant. How long it takes to vaporize a given liquid depends on the heat of vaporization of that liquid. Notice that it takes much longer to vaporize the water than to melt it. This is because the heat of vaporization of water is more than six times that of the heat of fusion. This makes sense. The amount of



**FIGURE 11-17 The Heating Curve of Water** The heating curve illustrates the temperature changes by heating the solid state through the liquid state to the gaseous state.



energy needed to allow molecules to slide past one another (melting) should be just a fraction of the energy needed for those molecules to completely pull apart from one another (boiling). (See Figure 11-17d.)

### 11-6.5 Heating Vapor

Above 100°C, we again have only one phase, so the added heat causes the temperature of the gas to increase. In the gaseous state, the kinetic energy of the gas molecules is great enough to overcome all the interactions between molecules. As a result, water vapor acts as any other gas and is subject to the gas laws discussed in the previous chapter. (See Figure 11-17e.) The vapor absorbs heat at its own unique rate, different from that of the liquid or solid. In the case of steam, the specific heat is again about half of water's [2.16 J/(g · °C)].

#### EXAMPLE 11-3

#### Calculating the Heat Involved in the Heating Curve

How many kilojoules of heat are required to convert 250 g of ice at  $-15^{\circ}\text{C}$  to steam at  $100^{\circ}\text{C}$ ?

#### PROCEDURE

There are four processes to consider. First (1) is the heating of the ice from  $-15^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ , or a total of  $15^{\circ}\text{C}$ . Second (2) is the melting of the ice at  $0^{\circ}\text{C}$ . Third (3) is the heating of the liquid from  $0^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , or a total of  $100^{\circ}\text{C}$ . And finally, fourth (4) is the vaporization of the liquid water to steam at  $100^{\circ}\text{C}$ . In summary, our processes are

$$\begin{array}{cccc} \text{heat ice (1),} & \text{melt ice (2)} & \text{heat liquid (3),} & \text{vaporize liquid (4)} \\ (1) & (2) & (3) & (4) \\ -15^{\circ}\text{C} \rightarrow 0^{\circ}\text{C} & \rightarrow 0^{\circ}\text{C} & \rightarrow 100^{\circ}\text{C} & \rightarrow 100^{\circ}\text{C} \end{array}$$

The heats of fusion and vaporization as well as the specific heats of ice and water (Table 3-2) are needed.

- To calculate the heat required to heat the ice to  $0^{\circ}\text{C}$ , use the specific heat of ice to convert mass and temperature change to heat.

$$\text{mass} \times \Delta T \times \text{sp. heat (ice)} = \text{heat}$$

- To calculate the heat required to melt the ice, use the heat of fusion to convert mass to heat.

$$\text{mass} \times \text{heat of fusion} = \text{heat}$$

- To calculate the heat required to heat the water, use the specific heat of water to convert mass and temperature change to heat.

$$\text{mass} \times \Delta T \times \text{sp. heat (water)} = \text{heat}$$

- To calculate the heat required to vaporize the water, use the heat of vaporization to convert mass to heat.

$$\text{mass} \times \text{heat of vaporization} = \text{heat}$$

#### SOLUTION

To heat ice from  $-15^{\circ}\text{C}$  to its melting point ( $0^{\circ}\text{C}$ ), or a total of  $15^{\circ}\text{C}$ :

$$250 \text{ g} \times 15^{\circ}\text{C} \times 2.06 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 7.7 \text{ kJ}$$

To melt the ice at  $0^{\circ}\text{C}$ :

$$250 \text{ g} \times 334 \frac{\text{J}}{\text{g}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 83.5 \text{ kJ}$$

To heat the water from  $0^{\circ}\text{C}$  to its boiling point ( $100^{\circ}\text{C}$ ), or a total of  $100^{\circ}\text{C}$ :

$$250 \text{ g} \times 100^{\circ}\text{C} \times 4.18 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 105 \text{ kJ}$$

To vaporize the water at  $100^{\circ}\text{C}$ :

$$250 \text{ g} \times 2260 \frac{\text{J}}{\text{g}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 565 \text{ kJ}$$

$$\text{total} = 7.7 + 83.5 + 105 + 565 = \underline{\underline{761 \text{ kJ}}}$$

**ANALYSIS**

The trouble that many students have with a problem of this type is the difficulty in viewing it as five separate calculations, although all have been solved previously. There's a tendency to look for one overriding equation where all variables can be plugged in simultaneously. But because the curve is not really a single curve, but five discrete lines, we *must* see it as five individual calculations, each one dictated by a different conversion factor. The heat changes of the single phases (solid, liquid, and gas) are determined by the specific heats of each phase. The phase changes themselves are determined by the heats of fusion and vaporization. Note also the units of each factor. Heats of fusion and vaporization are J/g, while specific heats are J/(g · °C). There is a temperature factor here because temperature changes. There is no temperature factor for fusion or vaporization because these processes occur at constant temperature.

**SYNTHESIS**

What would the heating curve of ethyl alcohol look like compared to that of water? The intermolecular forces in the alcohol are slightly weaker. Is the slope of the liquid line greater or smaller than in water? Are the lengths of the phase changes longer or shorter than in water? Would the phase changes occur at higher or lower temperatures?

**ASSESSING THE OBJECTIVES FOR SECTION 11-6**

**EXERCISE 11-6(a) KNOWLEDGE:** Are the following processes endothermic or exothermic?

(a) melting (b) boiling (c) freezing (d) evaporating (e) condensing

**EXERCISE 11-6(b) KNOWLEDGE:** In which of the following does the potential energy of the molecules increase? In which does the kinetic energy increase?

(a) melting (c) freezing (e) condensing  
(b) boiling (d) heating a liquid (f) cooling a solid

**EXERCISE 11-6(c) ANALYSIS:** Calculate the energy needed to melt 40.0 g of ice at 0°C and then raise its temperature to 50°C.

**EXERCISE 11-6(d) ANALYSIS:** How much water at 25°C can be frozen if 32.0 kJ is removed?

*For additional practice, work chapter problems 11-70 and 11-76.*

**PART B SUMMARY****KEY TERMS**

- 11-4.1** The measure of how difficult it is to break the surface of a liquid is its **surface tension**. p. 343
- 11-4.2** The measure of how rapidly a liquid flows is its **viscosity**. p. 344
- 11-4.3** When a liquid has an **equilibrium vapor pressure** it undergoes **vaporization** or **evaporation**. pp. 345-346
- 11-4.3** Gases undergo **condensation** to the liquid state. The solid state may undergo **sublimation** to the gaseous state. p. 346
- 11-4.4** The temperature at which the vapor pressure of a liquid equals the restraining pressure is the **boiling point**. The temperature at which the vapor pressure of the liquid is 1 atmosphere is the **normal boiling point**. p. 347
- 11-5.1** A measure of the amount of energy needed to cause melting is the **heat of fusion**. p. 350
- 11-5.2** A measure of the amount of energy needed to cause vaporization is the **heat of vaporization**. p. 351
- 11-6** The **heating curve** of a compound traces the changes in phases and the changes in temperature of the phases. p. 352

## SUMMARY CHART

| What Happens When Heat is Applied to a Phase or Phases |   |               |                    |                                 |
|--|---|---------------|--------------------|---------------------------------|
| Phase  | What Happens  | Energy Change | Temperature Change | Relevant Thermodynamic Equation |
| Solid  | Particles move faster about fixed positions.                | K. E.         | $T$ increases      | Sp. heat of solid               |
| Solid, liquid  | Particles break attractions and move past each other.       | P. E.         | $T$ constant       | Heat of fusion                  |
| Liquid   | Particles move faster, which includes translational motion. | K. E.         | $T$ increases      | Sp. heat of liquid              |
| Liquid, vapor  | Particles break final attractions as they escape to vapor.  | P. E.         | $T$ constant       | Heat of vaporization            |
| Vapor  | Particles move faster in gaseous state.                     | K. E.         | $T$ increase       | Sp. heat of gas                 |

## CHAPTER SUMMARY

This chapter gives the liquid and solid state their proper consideration. The most significant difference between these “condensed” states and the gaseous state is that cohesive forces hold the basic particles together and the basic particles occupy a significant part of the volume. Motions are confined to vibrations about fixed positions in the solid state or vibrational and translational motion in the liquid state. For this reason, solids and liquids are essentially incompressible, undergo little thermal expansion, and have definite volumes and high densities.

The temperature at which a molecular substance undergoes a phase transition (melting or boiling) depends on the **intermolecular forces** between molecules. **London forces** occur between all molecules but act exclusively for nonpolar molecules. These forces depend to a large extent on the size of the molecules. Compounds composed of heavy molecules generally have higher melting points than lighter ones. If a molecule has a permanent dipole, it has **dipole–dipole attractions** between molecules in addition to London forces. Compounds composed of polar molecules usually have higher melting and boiling points than nonpolar compounds of similar molar mass. **Hydrogen bonding** is a particular type of electrostatic interaction that has a significant effect on physical properties. It involves hydrogen bonded to an F, O, or N interacting with an electron pair on an F, O, or N on another molecule. Hydrogen bonding is responsible for many of the unusual properties of water.

We first examined the solid state of matter. Solids may be either **amorphous** or **crystalline**. Most solids are crystalline, which means they have atoms, ions, or molecules occupying fixed positions in a **crystal lattice**. They display sharp and definite melting points. There are four types of crystalline solids. **Ionic solids** are composed of ions as

the basic particles in the crystal lattice. The ion–ion attractions are strong, so ionic compounds are solids at room temperature. **Molecular solids** are composed of molecules in the crystal lattice. The melting points of such solids depend on the intermolecular forces between molecules. Generally, they are soft solids melting at lower temperatures than ionic solids. **Network solids** are somewhat rare but generally melt at high temperatures because covalent bonds must be broken to cause melting. Of the three allotropes of carbon, diamond and graphite melt at high temperatures. The third allotrope of carbon, buckminsterfullerene, is a molecular solid. **Metallic solids** have metal cations at the crystal lattice positions surrounded by a sea of electrons. These solids have melting points that range from low to very high temperatures.

The liquid state is intermediate between the solid and gaseous states. The cohesive forces between the basic particles in the liquid state are evident because of the liquid’s **surface tension** and **viscosity**. Some molecules in the liquid state may overcome these cohesive forces and escape to the gaseous state. When the process of **vaporization** is exactly counteracted by the process of **condensation**, an **equilibrium vapor pressure** above the liquid is established. The **boiling point** of the liquid relates to its vapor pressure. The **normal boiling point** is the temperature at which the vapor pressure equals 1 atm. **Evaporation** occurs when the liquid vaporizes below the boiling point. A solid may also vaporize in a process known as **sublimation**.

Melting and boiling each take place at a specific temperature for most substances. It also takes a specific amount of energy to change one gram of solid to liquid, which is known as the **heat of fusion**, and a specific amount of energy to change one gram of liquid to vapor, which is known as the **heat of vaporization**. The magni-

tudes of these quantities depend on the forces between the basic particles of the solid or liquid. A substance with a high melting point usually has a high heat of fusion and a high heat of vaporization. Much of the information on phase transitions can be shown in a **heating curve**. The rate of heating of a single phase is dependent on the specific heat of that phase. The times required for a solid to melt

and a liquid to boil at a given pressure depend on the magnitudes of the heat of fusion and vaporization, respectively. The heating curve of a pure substance shows that, when two phases are present during a phase change, the temperature remains constant. When melting or boiling is occurring, the applied heat energy is increasing the potential energy of the system rather than the kinetic energy.

| OBJECTIVES |  |            |                |                            |
|------------|--|------------|----------------|----------------------------|
| SECTION    | YOU SHOULD BE ABLE TO...   | EXAMPLES   | EXERCISES      | CHAPTER PROBLEMS           |
| 11-1       | List the physical properties of solids and liquids that distinguish them from gases.   |            | 1a, 1b         | 1, 2, 4                    |
| 11-2       | Describe the types of intermolecular forces that can occur between two molecules and their relative strengths.               |            | 2a, 2b, 2c, 2d | 6, 7, 8, 9, 12, 13, 14, 17 |
| 11-3       | Classify a solid as ionic, molecular, network, or metallic.  |            | 3a, 3b         | 19, 21                     |
|            | Order solids by melting point.   |            | 3c, 3d         | 20, 22, 24, 25             |
| 11-4       | List and define physical properties of the liquid state.   |            | 4a, 4c         | 27, 31, 35                 |
|            | Discuss the relationship between intermolecular forces and liquid properties.  |            | 4b, 4d         | 29, 32, 37, 41, 42, 45, 46 |
| 11-5       | Given the appropriate heats of fusion and vaporization, calculate the energy required to melt and vaporize a given compound. | 11-1, 11-2 | 5a, 5b, 5c, 5d | 52, 54, 56, 58, 62, 64     |
| 11-6       | Describe the changes that occur on the molecular level in a heating curve.   |            | 6a, 6b         | 70, 71, 72                 |
|            | Calculate the energy required for a change in temperature or physical state.   | 11-3       | 6c, 6d         | 66, 68, 75, 77             |

## ANSWERS TO ASSESSING THE OBJECTIVES

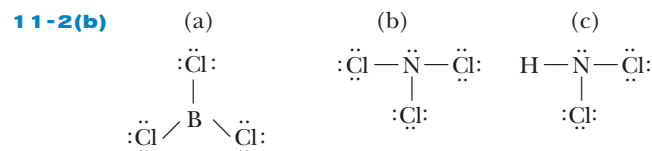
### PART A

#### EXERCISES

**11-1(a)** Compared to gases, liquids and solids have a **high** density and occupy a **fixed** volume. The molecules of the condensed states have appreciable **attractions** for each other.

**11-1(b)** Generally, solids have higher densities. The particles in solids are held together more tightly than in liquids. This implies that the forces between individual molecules in a solid are greater than those in a liquid.

**11-2(a)** (a) dipole–dipole force (b) London force (c) London force (d) hydrogen bonding (e) dipole–dipole force (f) hydrogen bonding



(a)  $\text{BCl}_3$ —London force only;  $\text{NCl}_3$ —Dipole–dipole force (and London force);  $\text{HNCl}_2$ —Hydrogen bonds (and

London force) (b)  $\text{HNCl}_2$  has the strongest force and so is most likely to be in a condensed phase.  $\text{BCl}_3$  has the weakest force and so is the most likely to be gaseous.

**11-2(c)**  $\text{C}_2\text{H}_6$  ( $-88^\circ\text{C}$ ) <  $\text{CH}_3\text{F}$  ( $-78^\circ\text{C}$ ) <  $\text{CH}_2\text{F}_2$  ( $-52^\circ\text{C}$ ) <  $\text{CH}_3\text{NH}_2$  ( $-6^\circ\text{C}$ )

**11-2(d)** All three are nonpolar molecules. Therefore, the only intermolecular forces present are London forces. Based on molecular size, we'd predict that  $\text{I}_2$  would have the strongest forces and  $\text{Cl}_2$  would have the weakest. The stronger the force, the more likely a molecule will be found in a condensed phase, so  $\text{I}_2$  is the solid,  $\text{Br}_2$  is the liquid, and  $\text{Cl}_2$  is the gas.

**11-3(a)** The two types of solids are **crystalline** and **amorphous**. **Crystalline** solids have a definite melting point. Of the four types of crystalline solids, **ionic** solids are composed of ions and are always solids at room temperature. **Network** solids have covalent bonds throughout the crystal. An allotrope of carbon that has a very high melting point is **diamond**. Molecular solids are usually soft and melt at **low** temperatures. **Metallic** solids have positive ions in a sea of **electrons**.

**11-3(b)** (a) metallic (b) molecular (c) ionic, network (d) metallic (e) ionic, network, molecular (f) metallic

**11-3(c)** (a) W (b)  $\text{CaF}_2$  (c)  $\text{SiO}_2$  (d) Sn

**11-3(d)**  $\text{H}_2\text{O}(s)$  is a molecular solid.  $\text{C}(s)$  is a network solid.  $\text{CS}_2(s)$  is a molecular solid.  $\text{KF}$  is an ionic solid.  $\text{Sn}$  is a metallic solid.

The network and ionic solids should have the highest melting points, and the molecular solids should have the lowest.  $\text{H}_2\text{O}(s)$  has hydrogen bonding, a stronger force than the London forces in  $\text{CS}_2(s)$ . Therefore, the order of increasing melting points should be  $\text{CS}_2 < \text{H}_2\text{O} < \text{Sn} < \text{KF} < \text{C}$ .

## PART B

### EXERCISES

**11-4(a)** In the liquid state, surface tension causes water to form spherical drops. Viscosity is a property relating to the rate of flow. When evaporation of a liquid occurs, the remaining liquid becomes cooler. The equilibrium vapor pressure is the pressure exerted by the gas at a given temperature. The vaporization of a solid is known as sublimation. The normal boiling point is the temperature at which the equilibrium vapor pressure is equal to 760 torr.

**11-4(b)** (a) strong (b) weak (c) weak (d) weak

**11-4(c)** (a) about  $92^\circ\text{C}$  (b) about 450 torr

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Nature of the Solid and Liquid States

#### (SECTION 11-1)

**11-1.** Liquids mix more slowly than gases. Why?

**11-2.** Why is a gas compressible, whereas a liquid is not compressible?

**11-3.** Describe why a drop of food coloring in a glass of water slowly becomes evenly distributed without the need for stirring.

**11-4.** What properties do liquids have in common with solids? With gases?

**11-5.** Review the densities of the solids listed in Table 2-1. In general, which have higher densities—solids or liquids? Why is this so?

#### Intermolecular Forces (SECTION 11-2)

**11-6.** Arrange the following in order of increasing magnitude of the London forces between their molecules.

(a)  $\text{CH}_4$  (b)  $\text{CCl}_4$  (c)  $\text{GeCl}_4$

**11-7.** Arrange the following in order of increasing magnitude of the London forces between their molecules or atoms.

(a) Ne (b) Xe (c)  $\text{N}_2$  (d)  $\text{SF}_6$

**11-8.** At room temperature,  $\text{Cl}_2$  is a gas,  $\text{Br}_2$  is a liquid, and  $\text{I}_2$  is a solid. Explain the trend.

**11-9.** At room temperature,  $\text{CO}_2$  is a gas and  $\text{CS}_2$  is a liquid. Why is this reasonable?

**11-10.** If  $\text{H}_2\text{O}$  were a linear molecule, could it have hydrogen-bonding interactions?

**11-11.** The  $\text{H}_2\text{S}$  molecule is also V-shaped, similar to  $\text{H}_2\text{O}$ , but it has a very small molecular dipole. How does one  $\text{H}_2\text{S}$  molecule interact with other  $\text{H}_2\text{S}$  molecules?

**11-4(d)** Substance A is a gas at that temperature. Substance B is a liquid. Because substance B has the stronger intermolecular forces, it has both a higher viscosity and a greater surface tension.

**11-5(a)** Heat of vaporization and heat of fusion are in J/g. They can also be expressed in kJ/mol. Specific heat has units of J/(g $\cdot$  $^\circ\text{C}$ ).

**11-5(b)** 10.8 g

**11-5(c)** 13.8 kJ

**11-5(d)**  $\text{NH}_3$  has a higher heat of vaporization by mass and can therefore extract more heat than Freon. Converted into kJ/mol, it's closer (23.1 kJ/mol for  $\text{NH}_3$  and 19.5 kJ/mol for  $\text{CF}_2\text{Cl}_2$ ), but  $\text{NH}_3$  is still the better refrigerant. However,  $\text{NH}_3$  is noxious-smelling and toxic. A leak would be unpleasant and perhaps dangerous.

**11-6(a)** (a) endothermic (b) endothermic (c) exothermic (d) endothermic (e) exothermic

**11-6(b)** Melting (a) and boiling (b) lead to an increase in potential energy for the molecules. Heating a liquid (d) leads to an increase in kinetic energy of the molecules.

**11-6(c)** 13.4 kJ to melt and 8.4 kJ to heat up, for a total of 21.8 kJ

**11-6(d)** 72.9 g of water

**11-12.** Write the Lewis structure of  $\text{NH}_3$ , with the electron pair and the hydrogens in a tetrahedral arrangement. (See Figure 11-4a.) How does one  $\text{NH}_3$  molecule interact with other  $\text{NH}_3$  molecules?

**11-13.** The  $\text{PH}_3$  molecule can be represented in a tetrahedral arrangement similar to  $\text{NH}_3$ . How does one  $\text{PH}_3$  molecule interact with other  $\text{PH}_3$  molecules?

**11-14.** Which of the following molecules have dipole–dipole attractions in a condensed state?

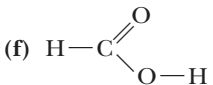
(a)  $\text{HBr}$  (d)  $\text{BF}_3$  (trigonal planar)  
(b)  $\text{SO}_2$  (nonlinear) (e)  $\text{N}_2$   
(c)  $\text{CO}_2$  (linear) (f)  $\text{CO}$

**11-15.** Which of the following molecules have dipole–dipole interactions in a condensed state?

(a)  $\text{SCl}_2$  (nonlinear) (d)  $\text{O}_3$   
(b)  $\text{PH}_3$  (e)  $\text{FCl}$   
(c)  $\text{CCl}_4$  (tetrahedral)

**11-16.** What is the difference between a covalent bond and hydrogen bonding?

**11-17.** Which of the following molecules can have hydrogen bonding in the liquid state?

(a)  $\text{HF}$   
(b)  $\text{NCl}_3$   
(c)  $\text{H}_2\text{NCl}$   
(d)  $\text{H}_2\text{O}$   
(e)  $\text{CH}_4$  (tetrahedral)  
(f)   
(g)  $\text{CH}_3\text{Cl}$  (tetrahedral)

**11-18.** Which should have stronger hydrogen bonding,  $\text{NH}_3$  or  $\text{H}_2\text{O}$ ?



### The Solid State (SECTION 11-2)

**11-19.** Identify the forces that must be overcome to cause melting in the following solids.

(a) KF (b) HF (c) HCl (d) F<sub>2</sub>

**11-20.** Rank the compounds in problem 11-19 in order of expected melting points (lowest one first).

**11-21.** Identify the forces that must be overcome to cause melting in the following solids.

(a) diamond (b) CF<sub>4</sub> (c) CrF<sub>2</sub> (d) SCl<sub>2</sub>

**11-22.** Rank the compounds in problem 11-21 in order of expected melting points (lowest one first).

**11-23.** The two Group IVA oxides, CO<sub>2</sub> and SiO<sub>2</sub>, have similar formulas but very different melting points. Why?

**11-24.** The two Group IIA fluorides, BF<sub>3</sub> and AlF<sub>3</sub>, have similar formulas but very different melting points. Why?

**11-25.** Lead forms two compounds with chlorine, PbCl<sub>2</sub> and PbCl<sub>4</sub>. The melting point of PbCl<sub>2</sub> is 501°C and that of PbCl<sub>4</sub> is -15°C. Interpret in terms of types of solids.

### The Liquid State (SECTION 11-4)

**11-26.** Why is motor oil more viscous than water? Does motor oil have a greater surface tension than water?

**11-27.** Explain how molecules of a liquid can go into the vapor state if the temperature is below the boiling point.

**11-28.** Why does a summer rainstorm lower the temperature?

**11-29.** Why does rubbing alcohol feel cool on the skin even if the alcohol is at room temperature when first applied?

**11-30.** Ethyl chloride boils at 12°C. When it is sprayed on the skin, it freezes a small part of the skin and thus serves as a local anesthetic. Explain how it cools the skin.

**11-31.** You have a sample of water at 90°C and a sample of water at 30°C. In which liquid does the temperature change at a faster rate when both are allowed to evaporate?

**11-32.** A beaker of a liquid with a vapor pressure of 350 torr at 25°C is set alongside a beaker of water, and both are allowed to evaporate. In which liquid does the temperature change at a faster rate? Why?

**11-33.** What is implied by the word *equilibrium* in *equilibrium vapor pressure*?

**11-34.** What is the difference between boiling point and normal boiling point?

**11-35.** A liquid has a vapor pressure of 850 torr at 75°C. Is the substance a gas or a liquid at 75°C and 1 atm pressure?

**11-36.** If the atmospheric pressure is 500 torr, what are the approximate boiling points of water, ethyl alcohol, and ethyl ether? (Refer to Figure 11-15.)

**11-37.** How can the boiling point of a pure liquid be raised?

**11-38.** On top of Mt. Everest, the atmospheric pressure is about 260 torr. What is the boiling point of ethyl alcohol at that pressure? If the temperature is 10°C, is ethyl ether a gas or a liquid under conditions on Mt. Everest? (Refer to Figure 11-15.)

**11-39.** The boiling point of water in Death Valley, California, is about 100.2°C. Why is the actual boiling point higher than the normal boiling point?

**11-40.** Propane is used as a fuel to heat rural homes where natural gas pipelines are not available. It is stored as a liquid under normal temperature conditions, although its normal boiling point is -42°C. How can propane remain a liquid in a tank when the temperature is well above its normal boiling point?

**11-41.** The normal boiling point of neon is -246°C and that of argon is -186°C. What accounts for this order of boiling points?

**11-42.** The boiling point of HCl is -84°C and that of HBr is -70°C. Why is this order reasonable on one account but opposite from what one would expect from a consideration of polarity? Which trend is more important in this case?

**11-43.** On Mars the temperature can reach as high as a comfortable 50°F (10°C) at the equator. The atmospheric pressure is about 8 torr on Mars, however. Can liquid water exist on Mars under these conditions? What would the atmospheric pressure have to be before liquid water could exist at this temperature? What would happen to a glass of water set out on the surface of Mars under these conditions? (Refer to Figure 11-15.)

### Energy and Changes of State (SECTION 11-6)

**11-44.** At a given temperature, one liquid has a vapor pressure of 240 torr and another measures 420 torr. Which liquid probably has the lower boiling point? Which probably has the lower heat of vaporization?

**11-45.** Ethyl ether (C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>) and ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) are both polar covalent molecules. What accounts for the considerably higher heat of vaporization for alcohol?

**11-46.** The heats of vaporization of liquid O<sub>2</sub>, liquid Ne, and liquid CH<sub>3</sub>OH are in the order Ne < O<sub>2</sub> < CH<sub>3</sub>OH. Why?

**11-47.** A given compound has a heat of fusion of about 600 cal/g. Is it likely to have a comparatively high or low melting point?

**11-48.** A given compound has a boiling point of -75°C. Is it likely to have a comparatively high or low heat of vaporization?

**11-49.** A given compound has a boiling point of 845°C. Is it likely to have a comparatively high or low melting point?

**11-50.** Graph the data in Table 11-1 for the Group VIA hydrogen compounds. Plot the boiling points on the y-axis and the molar masses of the compounds on the x-axis. What would be the expected boiling point of H<sub>2</sub>O if only London forces were important, as is the case with the other compounds in this series? (Determine from the graph.)

**11-51.** Graph the data in Table 11-1 for the Group VA hydrogen compounds. Plot the boiling points on the y-axis and the molar masses of the compounds on the x-axis. What would be the expected boiling point of NH<sub>3</sub> if only London forces were important, as is the case with the other compounds in this series?

**11-52.** How many kilojoules are required to vaporize 3.50 kg of H<sub>2</sub>O at its boiling point? (Refer to Table 11-3.)

**11-53.** How many joules of heat are released when an 18.0-g sample of benzene condenses at its boiling point? (Refer to Table 11-3.)

**11-54.** Molten ionic compounds are used as a method to store heat. How many kilojoules of heat are released when 8.37 kg of NaCl solidifies at its melting point? (Refer to Table 11-2.)

**11-55.** If 850 J of heat is added to solid H<sub>2</sub>O, NaCl, and benzene at their respective melting points, what mass of each is changed to a liquid? (Refer to Table 11-2.)

**11-56.** What mass of carbon tetrachloride can be vaporized by addition of 1.00 kJ of heat energy to the liquid at its boiling point? What mass of water would be vaporized by the same amount of heat? (Refer to Table 11-3.)

**11-57.** When a 25.0-g quantity of ethyl ether freezes, how many calories are liberated? When 25.0 g of water freezes, how many calories are liberated? In a large lake, which liquid would be more effective in modifying climate? How many joules of heat are required to melt 125 g of ethyl alcohol at its melting point? (Refer to Table 11-2.)

**11-58.** Air conditioners and refrigerators cool by vaporization of Freon. How many kcal of heat are removed by the vaporization of 1.00 kg of Freon? Will this be enough to freeze one can (325 mL) of soda? Assume the soda is essentially pure water at 0°C. (The heat of vaporization of Freon is 38.5 cal/g.)

**11-59.** Refrigerators cool because a liquid extracts heat when it is vaporized. Before the synthesis of Freon ( $\text{CF}_2\text{Cl}_2$ ), ammonia was used. Freon is nontoxic, and  $\text{NH}_3$  is a pungent and toxic gas. The heat of vaporization of  $\text{NH}_3$  is 1.36 kJ/g and that of Freon is 161 J/g. How many joules can be extracted by the vaporization of 450 g of each of these compounds? Which is the better refrigerant on a mass basis?

**11-60.** The heat of vaporization of  $\text{BCl}_3$  is 4.5 kcal/mol and that of  $\text{PCl}_3$  is 7.2 kcal/mol. There are two reasons that account for this order. What are they?

**11-61.** How many joules of heat are released when 275 g of steam at 100.0°C is condensed and cooled to room temperature (25.0°C)? (Refer to Table 11-3.)

**11-62.** How many kilocalories of heat are required to melt 0.135 kg of ice and then heat the liquid water to 75.0°C? (Refer to Table 11-2.)

**11-63.** How many calories of heat are needed to heat 120 g of ethyl alcohol from 25.5°C to its boiling point and then vaporize the alcohol? [The specific heat of alcohol is 0.590 cal/(g · °C). Refer to Table 11-3.]

**11-64.** Rubbing alcohol (isopropyl alcohol) helps reduce fevers by cooling the skin when it is rubbed on. How much heat is removed by the vaporization of 25.0 mL of alcohol? (The density of the alcohol is 0.786 g/mL and the heat of vaporization is 705 cal/g.)

**11-65.** How many calories of heat are required to change 132 g of ice at -20.0°C to steam at 100.0°C? [The specific heat of ice is 0.492 cal/(g · °C). Refer to Tables 11-2 and 11-3.]

**11-66.** How many kilojoules of heat are released when 2.66 kg of steam at 100.0°C is condensed, cooled, frozen, and then cooled to -25.0°C? [The specific heat of ice is 2.06 J/(g · °C). Refer to Tables 11-2 and 11-3.]

**\*11-67.** A sample of steam is condensed at 100.0°C and then cooled to 75.0°C. If 28.4 kJ of heat is released, what is the mass of the sample? (Refer to Table 11-3.)

**\*11-68.** What mass of ice at 0°C can be changed into steam at 100°C by 2.00 kJ of heat? (Refer to Tables 11-2 and 11-3.)

**\*11-69.** A 10.0-g sample of benzene is condensed from the vapor at its boiling point, and the liquid is allowed to cool. If 5000 J is released, what is the final temperature of the liquid benzene? [The specific heat of benzene is 1.72 J/(g · °C). Refer to Table 11-3.]

## The Heating Curve (SECTION 11-6)

**11-70.** Which of the following processes are endothermic?

- (a) freezing (c) boiling  
(b) melting (d) condensation

**11-71.** Which has the higher kinetic energy:  $\text{H}_2\text{O}$  molecules in the form of ice at 0°C or in the form of liquid water at 0°C?

**11-72.** Which has the higher potential energy:  $\text{H}_2\text{O}$  molecules in the form of ice at 0°C or in the form of liquid water at 0°C?

**11-73.** Which has the higher potential energy:  $\text{H}_2\text{O}$  molecules in the form of steam at 100°C or in the form of liquid water at 100°C?

**11-74.** If water is boiling and the flame supplying the heat is turned up, does the water become hotter? What happens?

**11-75.** How many kilocalories are released when 18.0 g of steam at 100°C is condensed and cooled to ice at 0°C?

**\*11-76.** Construct a heating curve for carbon tetrachloride. Refer to Tables 11-2 and 11-3. The specific heat of the liquid is 1.51 J/g · °C. Assume that the specific heats of both the gas and solid are about half that of the liquid. How should the time of constant temperature for melting compare with that for boiling?

**\*11-77.** Construct a heating curve for ethyl ether. Refer to Tables 11-2 and 11-3. How should the time of constant temperature for melting compare with that for boiling? (Assume that the specific heats of the three phases of water are about four times those of ethyl ether.)

## General Problems

**11-78.** The following three compounds have similar molar masses:  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{CH}_3\text{OCH}_3$ , and  $\text{CO}_2$ . The temperatures at which these compounds boil are -78°C, -25°C, and 17°C. Match the boiling point with the compound and give the respective intermolecular forces that account for this order.

**11-79.** At room temperature,  $\text{SF}_6$  is a gas and  $\text{SnO}$  is a solid. Both have similar formula weights. What accounts for the difference in physical states of the two compounds?

**11-80.** At room temperature,  $\text{CH}_3\text{OH}$  is a liquid and  $\text{H}_2\text{CO}$  is a gas. Both are polar and have similar molar masses. What accounts for the difference in physical states of the two compounds?

**11-81.**  $\text{CH}_3\text{F}$  and  $\text{CH}_3\text{OH}$  have almost the same molar mass, and both are polar compounds. Yet  $\text{CH}_3\text{OH}$  boils at 65°C and  $\text{CH}_3\text{F}$  at -78°C. What accounts for the large difference?

**11-82.** The heat of fusion of gold is 15.3 cal/g and that of silver is 25.0 cal/g, yet it takes more heat to melt the same volume of gold as silver. Calculate the heat required to melt 10.0 mL each of silver and gold. (The density of silver is 10.5 g/mL and that of gold is 19.3 g/mL.)

**11-83.**  $\text{SiH}_4$ ,  $\text{PH}_3$ , and  $\text{H}_2\text{S}$  melt at -185°C, -133°C, and -85°C, respectively. Since all have about the same molar mass, what accounts for the order?

**11-84.** The boiling point of  $\text{F}_2$  is -188°C and that of  $\text{Cl}_2$  is -34°C, yet the boiling point of  $\text{HF}$  is much higher than that of  $\text{HCl}$ . Explain.

**11-85.** Nitrogen gas and carbon monoxide have the same molar masses. Carbon monoxide boils at a slightly higher temperature, however ( $-191^{\circ}\text{C}$  versus  $-196^{\circ}\text{C}$  for  $\text{N}_2$ ). Account for the difference.

**11-86.** Liquid sodium metal is used as a coolant in a certain type of experimental nuclear reactor. How many kilojoules does it take to heat 1.00 mol of sodium from a solid at its melting point of  $98^{\circ}\text{C}$  to vapor at its boiling point of  $883^{\circ}\text{C}$ ? [For sodium, the heat of fusion is  $113\text{ J/g}$ , the heat of vaporization is  $3.90\text{ kJ/g}$ , and the specific heat of liquid sodium is  $1.18\text{ J/(g}\cdot^{\circ}\text{C)}$ .]

**11-87.** The heat of fusion of iron is  $266\text{ J/g}$ . Iron is formed in industrial processes in the molten state and is solidified with water. The water vaporizes when it comes in contact with the liquid iron. What mass of water is needed to solidify or freeze 1.00 ton (2000 lb) of iron? (Assume that the water is originally at  $25.0^{\circ}\text{C}$  and that the steam remains at  $100.0^{\circ}\text{C}$ .)

**\*11-88.** On a hot, humid day the relative humidity is 70% of saturation. If the temperature is  $34^{\circ}\text{C}$ , the vapor pressure of water at 100% of saturation is 39.0 torr. What mass of water is in each 100 L of air under these conditions?

**11-89.** Chromium metal, which is used to make stainless steel, is obtained by reaction of chromium(III) oxide with elemental aluminum. How much heat energy is required to melt the chromium produced from 1.25 kg of chromium(III) oxide? The heat of fusion of chromium is  $21.0\text{ kJ/mol}$ .

**11-90.** The heat of fusion of chromium is  $21.0\text{ kJ/mol}$ , molybdenum is  $28.0\text{ kJ/mol}$ , and tungsten is  $35.0\text{ kJ/mol}$ . What mass (in kg) of each of these elements can be melted by the same amount of heat required to change 1.00 kg of liquid water at  $25^{\circ}\text{C}$  to steam at  $100^{\circ}\text{C}$ ?

**11-91.** A certain element melts at  $-39^{\circ}\text{C}$  and boils at  $357^{\circ}\text{C}$ . The specific heat of the liquid is  $0.139\text{ J/g}\cdot^{\circ}\text{C}$ . The element forms a  $+2$  ion. What is the element? What mass of the element can be melted at  $-39^{\circ}\text{C}$ , heated to its boiling point, and then vaporized at its boiling point by  $15.00\text{ kJ}$  of heat? The heat of fusion of the element is  $11.5\text{ J/g}$ , and the heat of vaporization is  $29.5\text{ J/g}$ .

**11-92.** A common element has a melting point of  $114^{\circ}\text{C}$ . The element forms a  $-1$  ion. What is the element? It has a vapor pressure of 90.5 torr at its melting point. If 50.0 g of the solid element were placed in a 1.00-L container at  $114^{\circ}\text{C}$  and 1.00 atm pressure, what percent of the element would eventually be in the vapor state?

**11-93.** Ice has a vapor pressure of 2.50 torr at  $-5^{\circ}\text{C}$ . Will 50.0 g of ice completely vaporize if placed in a room at  $-5^{\circ}\text{C}$  and 1.00 atm pressure with a volume 20.0 kL? Assume that the air in the room was originally dry.

**11-94.** Liquid air is composed mainly of  $\text{N}_2$  and  $\text{O}_2$ . At  $-196^{\circ}\text{C}$ , the vapor pressure of  $\text{N}_2$  is 760 torr. Would you expect the vapor pressure of  $\text{O}_2$  to be larger or smaller than 760 torr at this temperature? Would liquid  $\text{O}_2$  boil at a higher or lower temperature than liquid  $\text{N}_2$ ? Explain.

## STUDENT WORKSHOP

### Constructing a Heating Curve for Ethanol

**Purpose:** To plot the change of temperature due to the absorption of energy for a chemical as it changes phase from solid to liquid to gas. (Work in groups of three or four. Estimated time: 25 min.)

We will create a plot of temperature versus added energy in joules for a 1.0-g sample of ethanol over a temperature range of  $-180^{\circ}\text{C}$  to  $180^{\circ}\text{C}$ . The relevant values for your calculations are:

|  |  |   |
|--|--|---|
| sp. heat (solid) = $0.54\text{ J/g}\cdot^{\circ}\text{C}$  | melting point = $-114^{\circ}\text{C}$ | heat of vaporization = $854\text{ J/g}$ |
| sp. heat (liquid) = $2.44\text{ J/g}\cdot^{\circ}\text{C}$ | boiling point = $78^{\circ}\text{C}$   |   |
| sp. heat (gas) = $0.81\text{ J/g}\cdot^{\circ}\text{C}$    | heat of fusion = $104\text{ J/g}$      |   |

1. Calculate the following amounts of energy:

- Joules to heat 1.0 g of solid ethanol from  $-180^{\circ}\text{C}$  to  $-114^{\circ}\text{C}$
- Joules to melt 1.0 g of solid ethanol
- Joules to heat 1.0 g of liquid ethanol from  $-114^{\circ}\text{C}$  to  $78^{\circ}\text{C}$
- Joules to boil 1.0 g of liquid ethanol
- Joules to heat 1.0 g of gaseous ethanol from  $78^{\circ}\text{C}$  to  $180^{\circ}\text{C}$

2. On graph paper (turned sideways), scale the  $x$ -axis in joules from 0 to 1600 (this should be the approximate total energy required). Scale the  $y$ -axis from  $-180$  to 180 (about  $10^{\circ}\text{C}$  per square should do).

3. Make your plot with 5 distinct straight lines:

- Line 1: Joules increase by the amount in 1(a); temperature increases from  $-180^{\circ}\text{C}$  to  $-114^{\circ}\text{C}$ .
- Line 2: Joules increase by the amount in 1(b); no temperature increase (a straight line).

- Line 3: Joules increase by the amount in 1(c); temperature increases from  $-114^{\circ}\text{C}$  to  $78^{\circ}\text{C}$ .
- Line 4: Joules increase by the amount in 1(d); no temperature increase.
- Line 5: Joules increase by the amount in 1(e); temperature increases from  $78^{\circ}\text{C}$  to  $180^{\circ}\text{C}$ .

4. Label the lines a, b, c, d, and e, respectively.

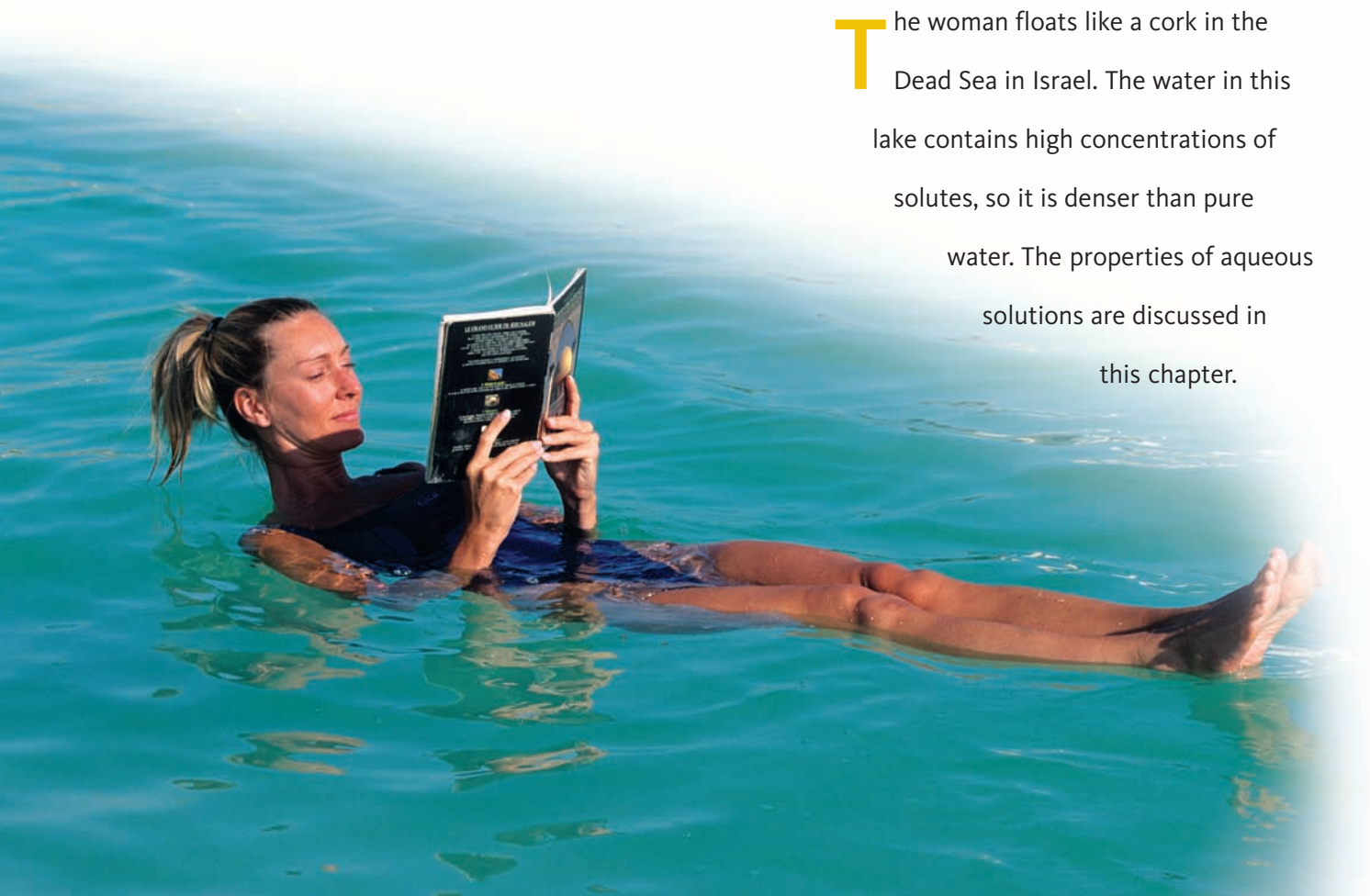
5. Answer the following questions:

- Why is line d significantly longer than line b?
- Why does line c slope more than lines a or e?
- How does your graph compare to the graph in Figure 11-6? What are the similarities? What are the differences?
- Over what range on your graph would you represent the energy needed to completely boil 1.0 g of ethanol that was originally at  $25^{\circ}\text{C}$ ?

# CHAPTER 12

## Aqueous Solutions

The woman floats like a cork in the Dead Sea in Israel. The water in this lake contains high concentrations of solutes, so it is denser than pure water. The properties of aqueous solutions are discussed in this chapter.





**PART A**  
**SOLUTIONS AND THE**  
**QUANTITIES INVOLVED**

**12-1** The Nature of Aqueous Solutions

**12-2** The Effects of Temperature and Pressure on Solubility



**MAKING IT REAL**

*Hyperbaric Therapy*

**12-3** Concentration: Percent by Mass

**12-4** Concentration: Molarity

**12-5** Stoichiometry Involving Solutions

**PART B**  
**THE EFFECTS OF SOLUTES**  
**ON THE PROPERTIES OF**  
**WATER**

**12-6** Electrical Properties of Solutions

**12-7** Colligative Properties of Solutions



**MAKING IT REAL**

*Osmosis in a Diaper*

**SETTING THE STAGE** The sound and sensation that we feel from the rhythmic pounding of waves against a silvery ocean beach are among nature's most tranquil gifts. This endless body of liquid seems to extend forever past the horizon. Actually, the ocean covers two-thirds of the surface of Earth and in places it is nearly 6 miles deep. But we can't drink this water, nor can we use it to irrigate crops. This water is far from pure; it contains a high concentration of dissolved compounds as well as suspended matter. On the other hand, the blood coursing in our veins is one example of how our life also depends on this same ability of water to dissolve substances. This red waterway dissolves oxygen and nutrients for life processes and then carries away dissolved waste products for removal by the lungs and kidneys. In fact, water is indispensable for any life-form as we know it.

The ability of water to act as a solvent is the emphasis of this chapter. In the last chapter, we examined the unusual properties of this important compound. Most of the unique properties of water can be attributed to hydrogen bonding between molecules.

In Part A in this chapter, we will examine how water acts as such a powerful solvent for many ionic and polar covalent compounds. Also important is how we measure the amount of solute present in a given amount of solvent and how this relates to the stoichiometry of reactions that take place in aqueous solution. In Part B we will discuss how the presence of a solute changes the physical properties of a solvent.

**PART A**  
**SOLUTIONS AND THE**  
**QUANTITIES INVOLVED**

**SETTING A GOAL**

- You will learn how water acts to dissolve specific types of compounds and how concentrations of solutes are expressed and used.

**OBJECTIVES**

- 12-1** Describe the role of water in the formation of aqueous solutions of ionic compounds, strong acids, and polar molecules.
- 12-2 (a)** Define terms associated with solubility. **(b)** Predict the effects of temperature and pressure on solubility.
- 12-3** Perform calculations of concentration involving percent by mass.
- 12-4 (a)** Perform calculations of concentration involving molarity. **(b)** Perform calculations involving the dilution of concentrated solutions.
- 12-5** Perform calculations involving titrations and other solution stoichiometry.

▶ **OBJECTIVE FOR SECTION 12-1**

Describe the role of water in the formation of aqueous solutions of ionic compounds, strong acids, and polar molecules.

## 12-1 THE NATURE OF AQUEOUS SOLUTIONS



**LOOKING AHEAD!** The composition of a solution is familiar territory.

In Chapter 3, we defined a solution as a homogeneous mixture of a solute (that which dissolves) in a solvent (the medium that dissolves the solute—usually a liquid). In this section we will look into the process of how and why a solute is dispersed into a solvent. ■

### 12-1.1 Mixtures of Two Liquids

First, we will briefly consider the mixing of two liquids. *If homogeneous mixing occurs when the solvent and solute are both liquids, we say that the two liquids are **miscible**. If two liquids do not mix to form a solution, we say that they are **immiscible** and remain as a heterogeneous mixture with two liquid phases.* Oil and water, for example, are immiscible and thus form a heterogeneous mixture with two obvious phases. Alcohol and water are miscible and form a solution with one phase. This was previously discussed in Section 3-3.2 and illustrated in Figure 3-5. Other types of homogeneous mixtures that qualify as solutions are any mixture of gases, which was discussed in Chapter 10, and metal alloys, discussed in Section 3-3.3.

### 12-1.2 The Formation of Aqueous Solutions of Ionic Compounds

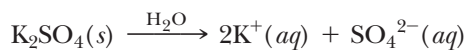
In this chapter, we will be primarily concerned with solutions formed by solids and liquids dissolved in water as the solvent. (See Figure 12-1.) The dissolving of table salt, NaCl, is typical of what happens when an ionic compound is placed in water. Recall that this solid compound is composed of alternating Na<sup>+</sup> ions and Cl<sup>-</sup> ions in a three-dimensional crystal lattice. In Chapters 9 and 11, we discussed how water is a polar compound with a positive dipole located on the hydrogen atoms and negative dipoles located on the unshared pairs of electrons on the oxygen. The water molecules are moderately attracted to each other by hydrogen bonds, but in the presence of the ionic crystal a stronger attraction between the ions in the solid and the dipoles of water exists. (See Figure 12-2.) Certainly, strong forces hold the solid crystal together (ion-ion), but the forces between the water molecules and the ions act to lift the ions on the surface of the solid out of the crystal lattice and into the



**FIGURE 12-1 A Solution**  
 A solution (the red liquid) is a homogeneous mixture of solute (the solid chromium compound) and solvent (water). The solution is in the same physical state as the solvent.



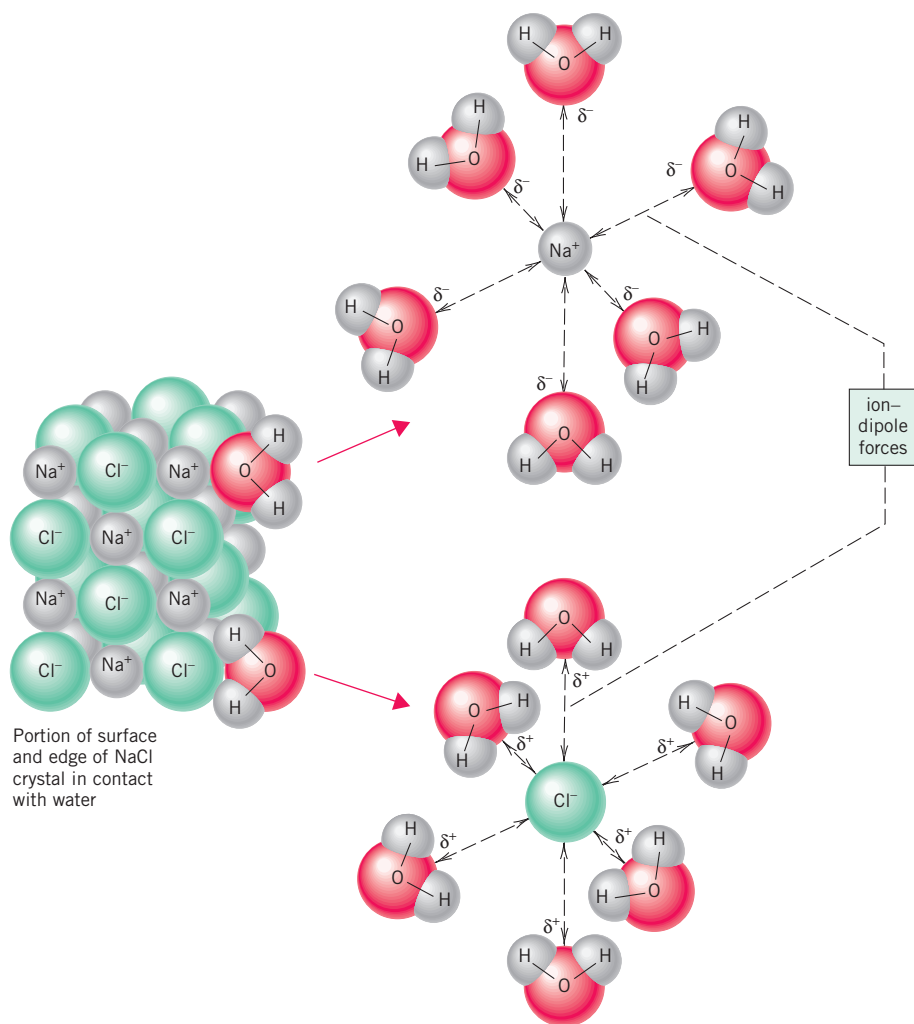
aqueous medium. *The interactions between the ions and dipoles of solvent molecules are referred to as ion-dipole forces.* An individual ion-dipole force is not as strong as one ion-ion force, but there are many ion-dipole forces at work. As a result, a tug-of-war develops between the ion-ion forces, holding the crystal together, and the ion-dipole forces, pulling the ions into solution. In the case of NaCl, the solution forces are strong enough to lift the ions, one by one, into the solvent. Since the ions in solution are now surrounded by water molecules, we say that the ions are *hydrated*. In solution, the positive and negative ions are no longer associated with one another. In fact, the charges on the ions are diminished or insulated from each other by the “escort” of hydrating water molecules around each ion. As before, we represent the solution of the ionic compound as going from the ions in the crystal lattice on the left to the hydrated ions on the right. Two examples of the solution of ionic compounds are as follows.



The  $\text{H}_2\text{O}$  (above the reaction arrow) represents a large, undetermined number of water molecules needed to break up the crystal and hydrate the ions. The  $(aq)$  after the symbol of each ion indicates that it is hydrated in the solution. Of course, not all ionic compounds dissolve to an appreciable extent in water. In these cases, the ion-ion forces are considerably stronger than the ion-dipole attractions, so the solid crystal remains essentially intact when placed in water. For example, ancient marble (i.e.,  $\text{CaCO}_3$ ) sculptures have suffered the indignities of weather for centuries with little deterioration.

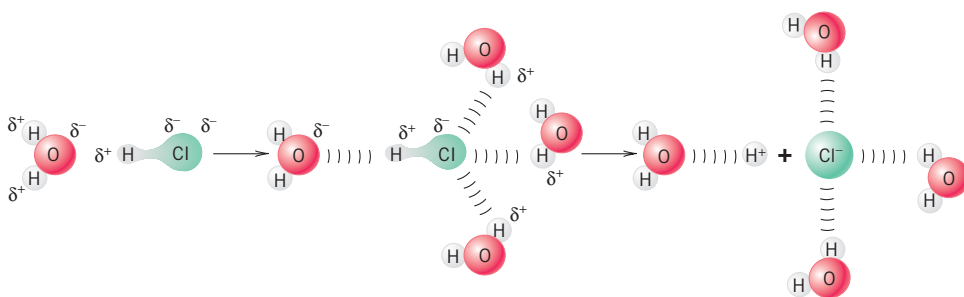
### 12-1.3 Formation of Aqueous Solutions of Molecular Compounds

In addition to soluble ionic compounds, acids are molecular compounds that dissolve in water with the formation of ions in a process known as **ionization**. An example is the HCl molecule, which in the pure gaseous state is held together by a single covalent bond. This is a very polar molecule, however, with the chlorine having a partial negative charge and the hydrogen a partial positive charge. When dissolved in water, a tug-of-war develops. On one side, the  $\text{H}_2\text{O}$  molecules tend to pull the HCl apart as a result of the dipole-dipole interactions. On the other side, the HCl covalent bond serves to hold the molecule together. For HCl, the  $\text{H}_2\text{O}$  molecules



**FIGURE 12-2** Interaction of Water and Ionic Compounds

There is an electrostatic interaction between the polar water molecules and the ions. This is an ion-dipole force.



**FIGURE 12-3** Interaction of HCl and H<sub>2</sub>O The dipole–dipole interaction between H<sub>2</sub>O and HCl leads to breaking of the HCl bond.

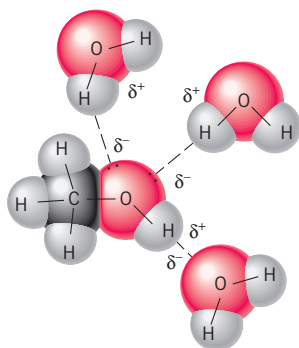
neutral atoms. In water, the breaking of the H—Cl bond leads to the formation of hydrated H<sup>+</sup> and Cl<sup>−</sup> ions. The ionization process is illustrated in Figure 12-3. For clarity, we have shown only four water molecules, but actually many more are involved in the interaction. We will have much more to say about the reaction of acids in water in the next chapter. Ionization is represented by the equation



Other polar molecules dissolve in water without the formation of ions. In these cases, the dipole–dipole interactions between solute and solvent do not lead to ionization, so the neutral solute molecule remains intact in solution. Methyl alcohol, a liquid, is a polar molecular compound that is miscible with water without ionization. (See Figure 12-4.)

If a molecule is nonpolar, there are no centers of positive and negative charge to interact with the dipoles of water. Since the water molecules are moderately attracted to one another by hydrogen bonding, there is no tendency for the water molecules to interact with a solute molecule. *As a result, most nonpolar compounds do not dissolve in polar solvents such as water.* On the other hand, nonpolar compounds do tend to dissolve in nonpolar solvents such as benzene or carbon tetrachloride. This happens because neither solvent nor solute molecules are held together by particularly strong forces, so they are free to mix. For example, if we wish to dissolve a grease stain (i.e., grease is composed of nonpolar molecules), we know that plain water does not work but a nonpolar solvent such as gasoline does. Within chemistry circles, a well-known phrase sums up the tendency of one chemical to dissolve another: “Like dissolves like.” This simply means that, in most cases, *polar solvents dissolve ionic or polar molecular compounds, and nonpolar solvents dissolve nonpolar compounds.*

Why should we be so concerned about dissolving things, anyway? A great deal of time and effort are spent trying to find the right solvent for all sorts of chemical compounds in industry. That is because chemical reactions occur easier and faster in solution. Because of the close packing of molecules in a solid, it is difficult to allow two different reacting molecules to come together. Thus, the proper solvent is needed so the solid can enter the liquid phase.



**FIGURE 12-4** Methyl Alcohol in Water For some polar covalent molecules in water, there are only dipole–dipole attractions between solute and water molecules.

### ASSESSING THE OBJECTIVE FOR SECTION 12-1

**EXERCISE 12-1(a) KNOWLEDGE:** Are the following compounds soluble in water?

- (a) NaI      (b) H<sub>2</sub>SO<sub>4</sub>      (c) CCl<sub>4</sub>      (d) NH<sub>2</sub>CH<sub>3</sub>      (e) FeCl<sub>3</sub>

**EXERCISE 12-1(b) KNOWLEDGE:** Write symbols for the aqueous form of each compound, including state symbols [for example, Na<sup>+</sup>(aq) + Cl<sup>−</sup>(aq)]. All dissolve in water.

- (a) (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>      (b) HNO<sub>3</sub>      (c) CH<sub>3</sub>— $\overset{\text{O}}{\parallel}$ —CH<sub>3</sub>      (d) ZnBr<sub>2</sub>

**EXERCISE 12-1(c) ANALYSIS:** What kinds of forces form between the following?

(a) water and  $\text{Zn}(\text{NO}_3)_2$       (b) water and  $\text{CH}_3\text{CH}_2\text{OH}$       (c)  $\text{CCl}_4$  and  $\text{C}_6\text{H}_{14}$

**EXERCISE 12-1(d) SYNTHESIS:** When a compound like  $\text{KF}(s)$  dissolves in water, we say that it dissociates. When a compound like  $\text{HNO}_3(l)$  dissolves in water, we say that it ionizes. What do these terms mean, and why is there a difference?

For additional practice, work chapter problems 12-1, 12-3, 12-4, and 12-6.

## 12-2 THE EFFECTS OF TEMPERATURE AND PRESSURE ON SOLUBILITY

### OBJECTIVES FOR SECTION 12-2

(a) Define terms associated with solubility. (b) Predict the effects of temperature and pressure on solubility.



**LOOKING AHEAD!** The terms used to define the relative amount of a substance that dissolves almost constitute a separate vocabulary. Besides the terms that we use, in this section we are also interested in how temperature affects the solubility of compounds. ■

The **solubility** of a solute is defined as the maximum amount that dissolves in a given amount of solvent at a specified temperature. The terms *soluble* and *insoluble* were introduced in Section 5-5.1. In fact, these terms are somewhat arbitrary since every compound has an upper limit of solubility and many compounds that we designate as insoluble actually have a limited solubility. So there is no clear boundary between soluble and insoluble compounds.

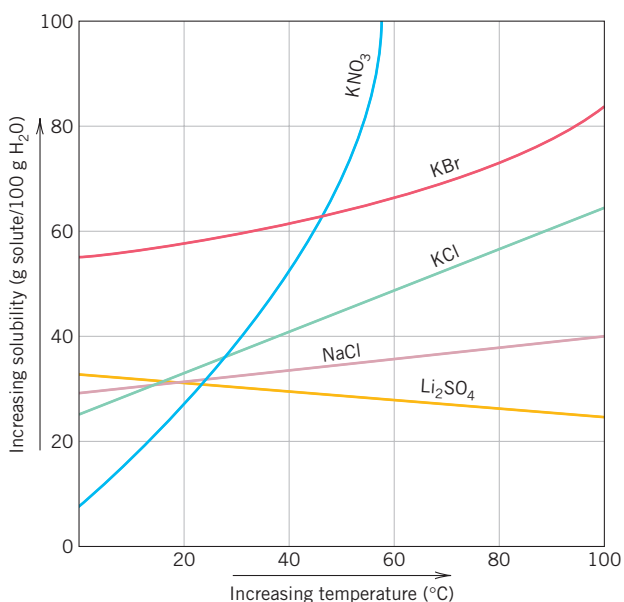
### 12-2.1 Saturation of a Solution

Now consider the amount of solute that dissolves in a solvent. When a specific amount of solvent contains the maximum amount of dissolved solute, the solution is said to be **saturated**. If less than the maximum amount is present, the solution is **unsaturated**. In certain unusual situations, an unstable condition may exist in which there is actually more solute present in solution than its solubility would indicate. Such a solution is said to be **supersaturated**. Supersaturated solutions often shed the excess solute if a tiny “seed” crystal of solute is added or if the solution is shaken. The excess solute solidifies and collects at the bottom of the container as a precipitate.

Given that certain compounds are soluble in water, how do we express the **concentration**, which is the amount of solute present in a given amount of solvent or solution? Several units are available, and the one we choose depends on the application involved. Some units emphasize the mass of solute and some the number of particles (moles) of solute. Some relate the solute to the mass of solvent, the mass of the solution, or the volume of solution. The first concentration unit that we will discuss expresses the amount of solute present in a saturated solution as mass of solute present in 100 g of solvent (g solute/100 g  $\text{H}_2\text{O}$  in the case of aqueous solutions). The solubilities of several compounds in water are listed in Table 12-1. For example, note that 205 g of sugar dissolved in 100 g (100 mL) of water produces a saturated solution at  $20^\circ\text{C}$ . Also notice that  $\text{PbSO}_4$ ,  $\text{Mg}(\text{OH})_2$ , and  $\text{AgCl}$  have very low solubilities

**TABLE 12-1** Solubilities of Compounds (at  $20^\circ\text{C}$ )

| COMPOUND                 | SOLUBILITY<br>(g SOLUTE/100 g $\text{H}_2\text{O}$ ) |
|--------------------------|--|
| sucrose (table sugar)    | 205  |
| HCl                      | 63   |
| NaCl                     | 36   |
| $\text{KNO}_3$           | 28   |
| $\text{PbSO}_4$          | 0.04   |
| $\text{Mg}(\text{OH})_2$ | 0.01   |
| $\text{AgCl}$            | $1.9 \times 10^{-4}$                                 |



**FIGURE 12-5 Solubility and Temperature** The solubility of most solids increases as temperature increases.

and thus are usually considered as insoluble (or, more accurately, *sparingly soluble*). In Chapter 5, we indicated that whenever both ions involved in one of these insoluble compounds (e.g.,  $\text{Mg}^{2+}$  and  $\text{OH}^-$ ) are mixed from separate solutions, a precipitate of that compound forms [e.g.,  $\text{Mg}(\text{OH})_2$ ]. The other compounds listed are considered *soluble*, although to various extents. Table 5-3 can be used as an aid in determining whether compounds of some common anions are considered soluble or essentially insoluble.

### 12-2.2 The Effect of Temperature on the Solubility of Solids in Water

It is apparent that the nature of a solute affects its solubility in water. Temperature is also an important factor. From practical experience, most of us know that more sugar or salt dissolves in hot water than in cold. This is generally true. *Most solids and liquids are more soluble in water at higher temperatures.* In Figure 12-5, the solubilities of several ionic compounds are graphed as a function of temperature. Note that all except  $\text{Li}_2\text{SO}_4$  are more soluble as the temperature

increases. The information shown in Figure 12-5 has important laboratory implications. An impure solid can be purified by a process called **recrystallization**. In this procedure, a solution is saturated with the solute to be purified at a high temperature, such as the boiling point of the solution. Insoluble impurities are then filtered from the hot solution. As the solution is allowed to cool, the solvent can hold less and less solute. The excess solute precipitates from the solution as it cools (if it does not become supersaturated). This solid, now more pure, can then be filtered from the cold solution. The soluble impurities, as well as some of the original compound still in solution, pass through the filter. For example, if 100 g of water is saturated with KBr at its boiling point near  $100^\circ\text{C}$ , it contains 85 g of dissolved KBr. If the solution is cooled to  $0^\circ\text{C}$  in an ice bath, the water can now contain only 55 g of dissolved salt. The difference (i.e.,  $85\text{ g} - 55\text{ g} = 30\text{ g}$ ) forms a precipitate. (See Figure 12-6.)



**FIGURE 12-6 Recrystallization** A hot, saturated solution of KBr is being prepared on the left. A precipitate has formed in the cold solution on the right because of its lower solubility.





### 12-2.3 The Effect of Temperature on the Solubility of Gases in Water

Despite their nonpolar nature, many gases also dissolve in water to a small extent (e.g.,  $O_2$ ,  $N_2$ , and  $CO_2$ ). Indeed, the presence of dissolved oxygen in water provides the means of life for fish and other aquatic animals. *Unlike solids, gases become less soluble as the temperature increases.* This can be witnessed by observing water being heated. As the temperature increases, the water tends to fizz somewhat as the dissolved gases are expelled. High temperatures in lakes can be a danger to aquatic animals and may cause fish kills. The lower solubility of oxygen at the higher temperatures can lead to an oxygen-depleted lake.



Fish maintain life by extracting dissolved oxygen from water.

### 12-2.4 The Effect of Pressure on Solubility

The solubility of solids and liquids in a liquid is not affected to any extent by the external pressure. However, this is not true of the solubility of gases in liquids. The solubility of a gas in a liquid relates to the partial pressure of that gas above the liquid. This is known as **Henry's law**, which states that the solubility of a gas is proportional to the partial pressure of that gas above the solution.

$$\text{solubility} = k P_{\text{gas}}$$

If you have ever opened a carbonated beverage, you have experienced Henry's law. A sealed can of soda contains carbon dioxide gas above the liquid under modest pressure. When the can is opened, the pressure of carbon dioxide above the liquid



### Hyperbaric Therapy



Hyperbaric cylinder.

However, the high pressure of air that is inhaled increases the concentration of dissolved  $N_2$  in the blood. If the diver comes to the surface too quickly (high pressure to low pressure), the lower pressure in the lungs causes  $N_2$  to come out of solution and form bubbles of  $N_2$  in the blood and cells. This is a condition known as *the bends* and can be fatal if the lungs are not quickly repressurized. A careful diver knows to return to the surface very slowly, pausing at specific intervals until the excess nitrogen is expelled from the blood.

Treatment of the bends requires that the patient be placed in a hyperbaric chamber as soon as possible. The person is completely enclosed in the chamber, where pressures of 2–3 atm of pure oxygen are applied. The higher pressure forces the nitrogen back into solution in

A scuba diver needs to be very much aware of Henry's law. As a diver descends in the ocean, the pressure of the water increases. As a result, the diver must inhale air under high pressure from a tank.

the blood, and the pure oxygen speeds the purging of the system of nitrogen. The pressure in the chamber is slowly brought back to normal.

Hyperbaric chambers are also used in the treatment of carbon monoxide and cyanide poisoning. Both of these substances attach to the hemoglobin in the blood, thus blocking it from attaching to molecular oxygen in the lungs. In effect, the victim suffocates. The partial pressure of oxygen in the chamber is 10 to 15 times the normal partial pressure in the atmosphere (about 0.20 atm). Under these conditions, the concentration of dissolved oxygen in the blood is from 10 to 15 times normal. Oxygen is transported to the tissues in solution, thus bypassing the normal hemoglobin transport. The high concentration of oxygen in the blood also helps purge the system of carbon monoxide. Eventually, the patient is revived through blood transfusions or the regeneration of new red blood cells.

Hyperbaric treatment has a large variety of other uses, especially in treating hard-to-heal wounds, such as those found in diabetics, or wounds in remote areas, such as the ankles and feet. The high concentration of oxygen destroys bacteria, which thrive in a low-oxygen environment. This treatment is becoming more popular to treat more and more conditions that seem to respond to a high concentration of oxygen.



decreases as it escapes. The lowering of the partial pressure of the carbon dioxide results in the decreased solubility of carbon dioxide, and bubbles of  $\text{CO}_2$  gas evolve from the solution. As time goes on, the carbon dioxide will continue to escape and the soda eventually goes flat. (Keeping an open can in a refrigerator will extend its carbonated life—see Section 12-2.3). An understanding of Henry's law is also very important for scuba divers, as discussed in Making it Real, "Hyperbaric Therapy."

**ASSESSING THE  
OBJECTIVES FOR  
SECTION 12-2**

**EXERCISE 12-2(a) KNOWLEDGE:** Fill in the blanks.

If a soluble compound dissolves to the limit of its solubility at a given temperature, the solution is \_\_\_\_\_; if the solute is not dissolved to the limit, the solution is \_\_\_\_\_. If more solute is present than indicated by its solubility, the solution is \_\_\_\_\_ and the excess solute may eventually form a \_\_\_\_\_. Solids generally become \_\_\_\_\_ soluble at higher temperatures, whereas gases become \_\_\_\_\_ soluble. An increase in partial pressure of a gas above a liquid \_\_\_\_\_ its solubility.

**EXERCISE 12-2(b) KNOWLEDGE:** Under what conditions of temperature and pressure will the following be most soluble?

- (a)  $\text{Cl}_2$       (b)  $\text{Na}_2\text{SO}_4$

**EXERCISE 12-2(c) ANALYSIS:** Referring to Figure 12-5, describe each of the following solutions as saturated, unsaturated, or supersaturated. (All are in 100 g of  $\text{H}_2\text{O}$ .)

- (a) 60 g of  $\text{KBr}$  at  $20^\circ\text{C}$       (c) 50 g of  $\text{KCl}$  at  $60^\circ\text{C}$   
(b) 40 g of  $\text{KNO}_3$  at  $40^\circ\text{C}$       (d) 20 g of  $\text{NaCl}$  at  $40^\circ\text{C}$

**EXERCISE 12-2(d) SYNTHESIS:** While working in lab, you want to dissolve a large crystal (about 3 g in size) of  $\text{CaCl}_2$ . What types of things could you do to speed the dissolving process?

*For additional practice, work chapter problems 12-9, 12-11, and 12-12.*

**▶ OBJECTIVE FOR  
SECTION 12-3**

Perform calculations of concentration involving percent by mass.

## 12-3 CONCENTRATION: PERCENT BY MASS



**LOOKING AHEAD!** A *concentrated* solution means that a large amount of a given solute is present in a given amount of solvent. A *dilute* solution means that comparatively little of the same solute is present. Obviously, we need more quantitative methods of expressing concentrations for laboratory situations. ■

In the previous discussion, the concentration unit (g solute/100 g solvent) related mass of solute to *solvent*. A second type of unit relates mass of solute to mass of *solution*, which contains both solute and solvent. **Percent by mass** expresses the mass of solute per 100 grams of solution. Therefore, in 100 g of a solution that is 25% by mass  $\text{HCl}$ , there are 25 g of  $\text{HCl}$  and 75 g of  $\text{H}_2\text{O}$ . The formula for percent by mass is

$$\begin{aligned} \% \text{ by mass (solute)} &= \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\% \\ &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \end{aligned}$$

**EXAMPLE 12-1****Calculating Mass Percent**

What is the percent by mass of NaCl if 1.75 g of NaCl is dissolved in 5.85 g of H<sub>2</sub>O?

**PROCEDURE**

Find the total mass of the solution and then the percent of NaCl.

**SOLUTION**

The total mass of solution is

$$\begin{array}{r} 1.75 \text{ g NaCl (solute)} \\ 5.85 \text{ g H}_2\text{O (solvent)} \\ \hline 7.60 \text{ g solution} \end{array}$$

$$\frac{1.75 \text{ g NaCl}}{7.60 \text{ g solution}} \times 100\% = \underline{\underline{23.0\% \text{ by mass NaCl}}}$$

**ANALYSIS**

In general, percent is always calculated by taking what you're looking for, dividing by the total, and then multiplying by 100%. To calculate your percentage on a test, take the number correct, divide by the total number of points available, and multiply by 100%. In our example, we're looking at the % salt. So take the mass of salt, divide by the total mass of solution, and multiply by 100%. What would be the percent by mass of the water? Is there a quick way to find it? Something to realize is that the sum of the mass percents of all the components of a solution must add to 100%. In a two-component system like salt and water, the percent by mass of the water is quickly determined to be 77%.

**SYNTHESIS**

Percent by mass is used frequently in the allied health professions. The calculations involved are relatively friendly, and you do not need to know the chemical composition of the components involved. Simply determining the masses is sufficient. Furthermore, general practices call for specific concentrations of solutions, whose creation has been standardized by the industry. This makes the creation of these solutions a bit more fail-safe in an industry that cannot afford miscalculations and errors.

**EXAMPLE 12-2****Calculating Amount of Solute from Mass Percent**

A solution is 14.0% by mass H<sub>2</sub>SO<sub>4</sub>. What quantity (in moles) of H<sub>2</sub>SO<sub>4</sub> is in 155 g of solution?

**PROCEDURE**

1. Find the mass of H<sub>2</sub>SO<sub>4</sub> in the solution by multiplying the mass of compound by the percent in fraction form.
2. Convert mass to moles using the molar mass of H<sub>2</sub>SO<sub>4</sub>.

**SOLUTION**

$$1. 155 \text{ g solution} \times \frac{14.0 \text{ g H}_2\text{SO}_4}{100 \text{ g solution}} = 21.7 \text{ g H}_2\text{SO}_4$$

2. The molar mass is

$$2.016 \text{ g (H)} + 32.07 \text{ g (S)} + 64.00 \text{ g (O)} = 98.09 \text{ g/mol}$$

$$21.7 \text{ g H}_2\text{SO}_4 \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \text{ g H}_2\text{SO}_4} = \underline{\underline{0.221 \text{ mol H}_2\text{SO}_4}}$$

**ANALYSIS**

Any problem using mass percent will use one of three conversion factors. When we say that a solution is 14.0% solute, we can use any of these relationships: 14.0 g solute/100 g solution, 14.0 g solute/86.0 g solvent, or 86.0 g solvent/100 g solution. Which to use depends on the question that is being asked. Look for references to the amount of solute, solvent, or solution in the problem to find the appropriate conversion factor.

**SYNTHESIS**

Along with percent by mass, which is often designated "(w/w)" or "(weight per weight)" to avoid confusion, we can create a short list of concentration calculations that all depend upon measuring the amount of solute and solvent either by mass or volume. For

example, percent of mass per unit volume, or (w/v), is used frequently in measurements of human bodily fluids. The concentration of solutes in blood is often expressed in terms of w/v percent. For example, a 0.89% (w/v) solution of a saline solution (NaCl) has the same concentration of ions as human blood. Percent by volume (v/v) is useful when both solute and solvent are liquids, such as the concentration of alcohol in alcoholic beverages. A wine that lists its alcohol content at 11.5% means that there are 11.5 mL of pure ethyl alcohol present in each 100 mL of solution. In all cases, knowing the chemical formulas of the components is unnecessary, since the units of mass and volume can be measured directly. This has the advantage of easy preparation of solutions. The drawback is that these concentrations are chemically irrelevant if we wish to use the solutions for a chemical reaction. A new, more useful concentration calculation, which takes into account the identity of the solute, will be forthcoming.

### 12-3.1 Parts per Million and Parts per Billion

Percent by mass is equivalent to *parts per hundred*. When concentrations are very low, however, two closely related units become more convenient. These units are **parts per million (ppm)** and **parts per billion (ppb)**. For example, the concentration of carbon dioxide in the atmosphere is currently 0.0380%. It is more conveniently represented as 380 ppm. (It is unfortunately increasing by about 3 ppm each year.) Dioxin, a synthetic chemical linked to cancer, is measured in the soil in units of ppb.

Parts per million is obtained by multiplying the ratio of the mass of solute to mass of solution by  $10^6$  ppm rather than 100%. Parts per billion is obtained by multiplying the same ratio by  $10^9$  ppb. For example, if a solution has a mass of 1.00 kg and contains only 3.0 mg of a solute, it has the following concentration in percent by mass, ppm, and ppb.

$$\begin{aligned} \frac{3.0 \times 10^{-3} \text{ g (solute)}}{1.0 \times 10^3 \text{ g (solution)}} \times 100\% &= \underline{3.0 \times 10^{-4}\%} \\ \frac{3.0 \times 10^{-3} \text{ g}}{1.0 \times 10^3 \text{ g}} \times 10^6 \text{ ppm} &= \underline{3.0 \text{ ppm}} \\ \frac{3.0 \times 10^{-3} \text{ g}}{1.0 \times 10^3 \text{ g}} \times 10^9 \text{ ppb} &= \underline{3.0 \times 10^3 \text{ ppb}} \end{aligned}$$

In this case, the most convenient expression of concentration is in units of ppm.

In the examples cited, the units, ppm and ppb, refer to the mass of the solution. In the case of the concentration of  $\text{CO}_2$  in the atmosphere, the ppm refers to 1 million particles (molecules of compounds or atoms of noble gases) in the atmosphere. Thus, there are currently 380  $\text{CO}_2$  molecules per million molecules.

#### EXAMPLE 12-3

##### Calculating ppm and ppb of a Solution

What is the concentration in ppm and ppb of a solution if it is  $8.8 \times 10^{-5}\%$  by mass solute?

##### PROCEDURE

Find the mass of solute per gram of solution and multiply by  $10^6$  for ppm or  $10^9$  for ppb.

##### SOLUTION

$$\begin{aligned} \frac{8.8 \times 10^{-5}\%}{100\%} &= \frac{8.8 \times 10^{-7} \text{ g solute}}{\text{g solution}} \\ \frac{8.8 \times 10^{-7} \text{ g solute}}{\text{g solution}} \times 10^6 \text{ ppm} &= \underline{0.88 \text{ ppm}} \\ \frac{8.8 \times 10^{-7} \text{ g solute}}{\text{g solution}} \times 10^9 \text{ ppb} &= \underline{880 \text{ ppb}} \end{aligned}$$

##### ANALYSIS

The units ppm and ppb can look quite imposing, but if you're comfortable using percents, then conversions become natural. The procedures are virtually identical. If you scored 80% on a test, and the test had 60 questions, you'd multiply

$\frac{60 \times 80\%}{100\%}$ , to see how many you got right (48 questions). If you had 25 g of water that had an 880 ppb concentration of lead in it, you'd multiply  $\frac{25 \text{ g} \times 880 \text{ ppb}}{10^9 \text{ ppb}}$  to see the mass of toxin ( $2.2 \times 10^{-5}$  g of Pb).

### SYNTHESIS

Choosing the appropriate concentration unit (% , ppm, ppb, or even ppt!) is a choice left to the scientist to discern the most reasonable unit. People are most comfortable dealing with numbers that fall between 1 and 1000. Beyond that range, they begin to look too large and unwieldy. Once they become decimals, their significance diminishes with size. But in the 1 to 1000 range, we are mentally prepared to compare and react to them in comparison to other data. As a rule of thumb, then, most scientists, agencies, health professionals, and others presenting data will choose units so that the data fall comfortably in that range. With our choices above, concentrations of most things that we measure can be manipulated into one of those units.

### ASSESSING THE OBJECTIVE FOR SECTION 12-3

**EXERCISE 12-3(a) KNOWLEDGE:** What are the three ratios that can be written involving the masses of solute, solvent, and solution for an 8.0% aqueous solution of KBr?

**EXERCISE 12-3(b) ANALYSIS:** What is the percent by mass if 15.0 g of  $\text{NH}_4\text{Cl}$  is dissolved in 45.0 g of water?

**EXERCISE 12-3(c) ANALYSIS:** How much solvent is needed to make a 14.0% by mass solution using 25.0 g of solute?

**EXERCISE 12-3(d) SYNTHESIS:** A sample of river water contained 2.50 mg of  $\text{Ba}^{2+}$  contaminant in a 10.0-kg sample. What is the amount of  $\text{Ba}^{2+}$  expressed in the following measurements?

(a) percent    (b) ppm    (c) ppb

Which of these is the most appropriate way to report the concentration?

For additional practice, work chapter problems 12-13, 12-16, 12-17, 12-18, and 12-19.

## 12-4 CONCENTRATION: MOLARITY



**LOOKING AHEAD!** In the laboratory, it is more convenient to measure the volume of a solution rather than its mass. In stoichiometry, recall that we are interested primarily in the mole relationships, so it is also important to have a unit that expresses the solute in moles rather than mass. Such a unit is discussed in this section. ■

### 12-4.1 Calculations Involving Molarity

Graduated cylinders, burets, or other readily available laboratory apparatus allow easy measurement of the volume of a solution. When a substance is in an aqueous solution, the most convenient way to measure the amount is by measuring the volume of the solution. **Molarity (M)** is defined as the number of moles of solute ( $n$ ) per volume in liters ( $V$ ) of solution. Although molarity may be shown without units, it is understood to have units of  $\text{mol/L}$ . This is expressed as follows in equation form.

$$M = \frac{n \text{ (moles of solute)}}{V \text{ (liters of solution)}}$$

The following examples illustrate the calculation of molarity and its use in determining the amount of solute in a specific solution.

### OBJECTIVES FOR SECTION 12-4

(a) Perform calculations of concentration involving molarity. (b) Perform calculations involving the dilution of concentrated solutions.



Solution volume is measured by burets, pipettes, and volumetric flasks.

**EXAMPLE 12-4****Calculating Molarity**

What is the molarity of  $\text{H}_2\text{SO}_4$  in a solution if 49.0 g of  $\text{H}_2\text{SO}_4$  is present in 250 mL of solution?

**PROCEDURE**

Write down the formula for molarity and what you have been given, and then solve for what's requested. Recall that the volume is expressed in liters in this calculation.

**SOLUTION**

$$M = \frac{n}{V}$$

$$n = 49.0 \text{ g H}_2\text{SO}_4 \times \frac{1 \text{ mol}}{98.09 \text{ g H}_2\text{SO}_4} = 0.500 \text{ mol}$$

$$V = 250 \text{ mL} \times \frac{10^{-3} \text{ L}}{\text{mL}} = 0.250 \text{ L}$$

$$\frac{n}{V} = \frac{0.500 \text{ mol}}{0.250 \text{ L}} = \underline{\underline{2.00 \text{ M}}}$$

**EXAMPLE 12-5****Calculating the Amount of Solute from Molarity**

What mass of HCl is present in 155 mL of a 0.540 M solution?

**PROCEDURE**

Volume must be expressed in liters. Molarity has units of mol/L. A quantity in grams requires the molar mass of HCl to convert to moles.

**SOLUTION**

$$M = \frac{n}{V} \quad n = M \times V$$

$$M = 0.540 \text{ mol/L}$$

$$V = 155 \text{ mL} = 0.155 \text{ L}$$

$$n = 0.540 \text{ mol/L} \times 0.155 \text{ L} = 0.0837 \text{ mol HCl}$$

$$0.0837 \text{ mol HCl} \times \frac{36.46 \text{ g}}{\text{mol HCl}} = \underline{\underline{3.05 \text{ g HCl}}}$$

**EXAMPLE 12-6****Calculating Molarity from Percent by Mass**

Concentrated laboratory acid is 35.0% by mass HCl and has a density of 1.18 g/mL. What is its molarity?

**PROCEDURE**

Since a volume was not given, you can start with any volume you want since this is an intensive property. The molarity will be the *same* for 1 mL as for 25 L. To make the problem as simple as possible, assume that you have exactly 1 L of solution ( $V = 1.00 \text{ L}$ ) and go from there. The number of moles of HCl ( $n$ ) in 1 L can be obtained as follows.

1. Find the mass of 1 L from the density.
2. Find the mass of HCl in 1 L using the percent by mass and the mass of 1 L.
3. Convert the mass of HCl to moles of HCl.

**SOLUTION**

Assume that  $V = 1.00 \text{ L}$

1. The mass of 1.00 L ( $10^3 \text{ mL}$ ) is

$$10^3 \text{ mL} \times 1.18 \text{ g/mL} = 1180 \text{ g solution}$$



2. The mass of HCl in 1.00 L is

$$1180 \text{ g-solution} \times \frac{35.0 \text{ g HCl}}{100 \text{ g-solution}} = 413 \text{ g HCl}$$

3. The number of moles of HCl in 1.00 L is

$$413 \text{ g} \times \frac{1 \text{ mol}}{36.46 \text{ g}} = 11.3 \text{ mol HCl}$$

$$\frac{n}{V} = \frac{11.3 \text{ mol}}{1.00 \text{ L}} = \underline{\underline{11.3 \text{ M}}}$$

### ANALYSIS

All the examples above are solved by the factor-label method. If you've mastered that problem-solving technique, then by this time the calculations should be straightforward. Remember to write down all the given information and the units. Also, remember to express molarity as mol/L. Most importantly, remember that the liters in molarity are liters of solution, not solvent. This has implications for the formation of solutions, as we will see in future discussions.

### SYNTHESIS

What if you were sent into the laboratory to make a specific molarity of solution? How would you do it? First, of course, you'd calculate the amount of solute you'd need for the required volume. Generally, the volumes we make are very specific, such as 100 mL, 250 mL, 500 mL, or 1000 mL. That is because we use volumetric flasks to ensure that our volumes are as accurate as possible. Then just mix the amount of solute in the required amount of solvent and stir? No! The solid itself takes up some volume. Until it has been made into a solution, we can't be sure how its volume will be accounted for. So you should transfer the solid into the flask as quantitatively as possible (use a funnel, rinse the weighing boat), and then fill up the flask halfway with solvent. This allows you to swirl until *all* the solute is dissolved. Then and only then can you fill the remainder of the flask with solvent. Toward the top, it is crucial that you do not exceed the line marked on the volumetric flask. You can always add more pure solvent, but you won't be able to remove it. Most scientists would use an eyedropper or disposable pipette to get the solvent exactly to the volume line. At this point, simply cap the flask and invert it several times to ensure thorough mixing, and your (very accurate) solution is made.



A student adds solvent with a pipette to a volumetric flask.

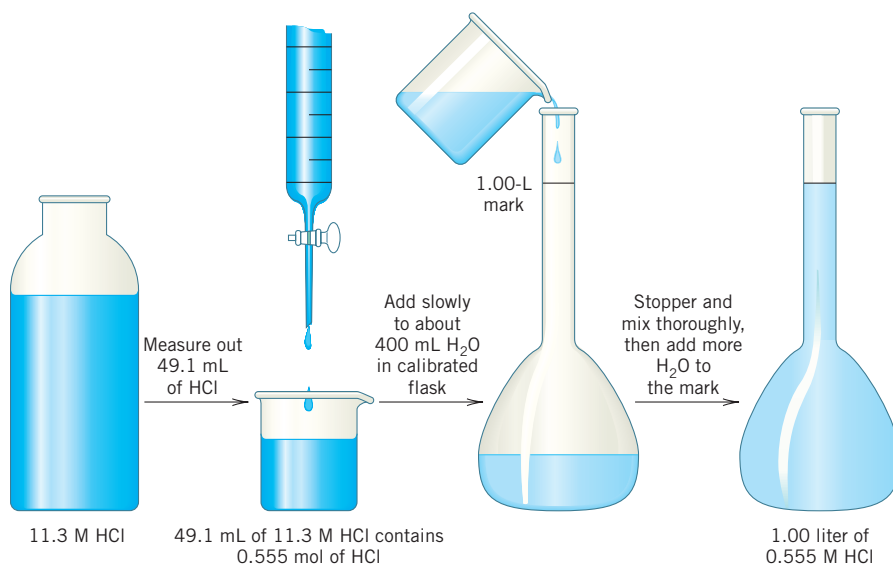
## 12-4.2 Dilution of Concentrated Solutions

From soft drinks to medicine, many products are transported as concentrated solutions. Before being sold, these products are carefully diluted to the desired concentration. Dilution is a straightforward procedure requiring a simple calculation. In our laboratory situations, we may be called on to prepare 200 mL of a 2.0 M solution from a large supply of a 6.0 M HCl solution. We simply need to know what volume of the more concentrated solution is needed. (See Figure 12-7.) In the following discussion, the number of moles in the dilute solution is designated  $n_d$ , and the volume and molarity of that solution are designated  $V_d$  and  $M_d$ , respectively. First we will calculate the number of moles of solute present in the dilute solution we want to prepare.

$$M_d \times V_d = n_d$$

The moles of solute taken from the concentrated solution are designated  $n_c$ . The moles of solute in the concentrated solution relate to the volume and molarity of the concentrated solution.

$$M_c \times V_c = n_c$$



**FIGURE 12-7** Dilution of Concentrated HCl (Note: Never add water directly to concentrated acid, because it may splatter and cause severe burns.)

Since all the solute used in the dilute solution comes from the concentrated solution, adding more solvent does not change the number of moles. Therefore,

$$\text{moles solute} = n_d = n_c$$

Because, in algebra, quantities equal to the same quantity are equal to each other, we have the simple relationship between the dilute solution and the volume and molarity of the concentrated solution that is used:

$$M_c \times V_c = M_d \times V_d$$

### EXAMPLE 12-7

#### Calculating the Volume of a Concentrated Solution

What volume of 11.3 M HCl must be mixed with water to make 1.00 L of 0.555 M HCl? (See also Figure 12-7.)

#### PROCEDURE

Rearrange the dilution formula to solve for the requested variable.

$$M_c \times V_c = M_d \times V_d \quad V_c = \frac{M_d \times V_d}{M_c}$$

#### SOLUTION

$$\begin{aligned} M_c &= 11.3 \text{ M} & M_d &= 0.555 \text{ M} \\ V_c &= ? & V_d &= 1.00 \text{ L} \\ V_c &= \frac{0.555 \text{ mol/L} \times 1.00 \text{ L}}{11.3 \text{ mol/L}} = 0.0491 \text{ L} = \underline{\underline{49.1 \text{ mL}}} \end{aligned}$$

#### ANALYSIS

We have the same issue here that we had when we were making solutions from solutes directly. The total volume calculated is the volume of the solution. So, in this problem, 49.1 mL of HCl would be measured out (probably with a buret) and then added to a 1.0-L volumetric flask. The volume of water added would then be the amount necessary to bring the total volume up to 1.0 L. This will, of course, be very close to 950.9 mL, but because volumes are not necessarily additive, the exact amount may be a little off from this value. Filling up to the 1.0-L line on the volumetric flask assures that the proper amount is added.

#### SYNTHESIS

This problem illustrates a concept that you learned in lab: When diluting an acid (or other concentrated compound), do you pour the concentrated solution into the water or pour the water into the concentrated solution? The catchphrase is “add acid.” Diluting acids is often very exothermic, and splattering may occur. The proper procedure of pouring the concentrated solution into the solvent ensures that any splatter is from a more dilute solution, rather than a more concentrated one; it is therefore considered the safer route.

### EXAMPLE 12-8

#### Calculating the Molarity of a Dilute Solution

What is the molarity of a solution of KCl that is prepared by dilution of 855 mL of a 0.475 M solution to a volume of 1.25 L?

#### PROCEDURE

Solve the algebraic equation for  $M_d$ .

$$M_c \times V_c = M_d \times V_d \quad M_d = \frac{M_c \times V_c}{V_d}$$

#### SOLUTION

$$\begin{aligned} M_c &= 0.475 \text{ M} & M_d &= ? \\ V_c &= 855 \text{ mL} = 0.855 \text{ L} & V_d &= 1.25 \text{ L} \\ M_d &= \frac{0.475 \text{ M} \times 0.855 \text{ L}}{1.25 \text{ L}} = \underline{\underline{0.325 \text{ M}}} \end{aligned}$$

**ANALYSIS**

The key concept in working dilution problems is that while the volume of solution goes up, and the concentration of solution goes down, the overall number of moles of solute never changes. The same number of moles are present before the dilution and afterwards. Though it goes beyond the scope of this text, this concept can be stretched to allow calculations when the dilution is not occurring with water but instead with a more dilute solution of the compound. If you wanted, for instance, to turn your 1.0 M  $\text{NH}_3$  into 3.0 M  $\text{NH}_3$  by adding 9.0 M  $\text{NH}_3$ , determining the total number of moles before and after the dilution, and then converting into the  $M \times V$  relationship, would allow you to solve the problem.

**SYNTHESIS**

Dilution is a process that occurs frequently in lab. Why so prevalent? Because manufacturers find that it is more convenient to produce and ship solutions that are concentrated. It makes a more convenient use of space and weight and costs less. Furthermore, end users can use the dilution formula to scale-down the concentrations to whatever value is needed for their particular use. We can always dilute, but without the original solute, we can't make commercial solutions more concentrated. As a result, acids are sold at very high concentrations (18 M for  $\text{H}_2\text{SO}_4$ , 12 M for HCl). Hence, there are numerous safety procedures in place whenever we deal with commercial bottles.

**ASSESSING THE OBJECTIVES FOR SECTION 12-4**

**EXERCISE 12-4(a) KNOWLEDGE:** What is the concentration if 0.500 mol of NaOH is present in 0.250 L of solution?

**EXERCISE 12-4(b) KNOWLEDGE:** What is the concentration if 1.00 L of 0.400 M HCl is diluted to 2.00 L?

**EXERCISE 12-4(c) ANALYSIS:** What mass of KI is needed to make 500 mL of 0.0750 M solution?

**EXERCISE 12-4(d) ANALYSIS:** What volume of 6.00 M  $\text{H}_2\text{SO}_4(aq)$  is needed to prepare 250 mL of 0.400 M  $\text{H}_2\text{SO}_4(aq)$ ?

**EXERCISE 12-4(e) SYNTHESIS:** Describe how you would make 250.0 mL of 0.500 M NaCl solution using the following:

- (a) solid NaCl      (b) a 3.00 M solution of NaCl(*aq*)

*For additional practice, work chapter problems 12-23, 12-27, and 12-30.*

**12-5 STOICHIOMETRY INVOLVING SOLUTIONS****OBJECTIVE FOR SECTION 12-5**

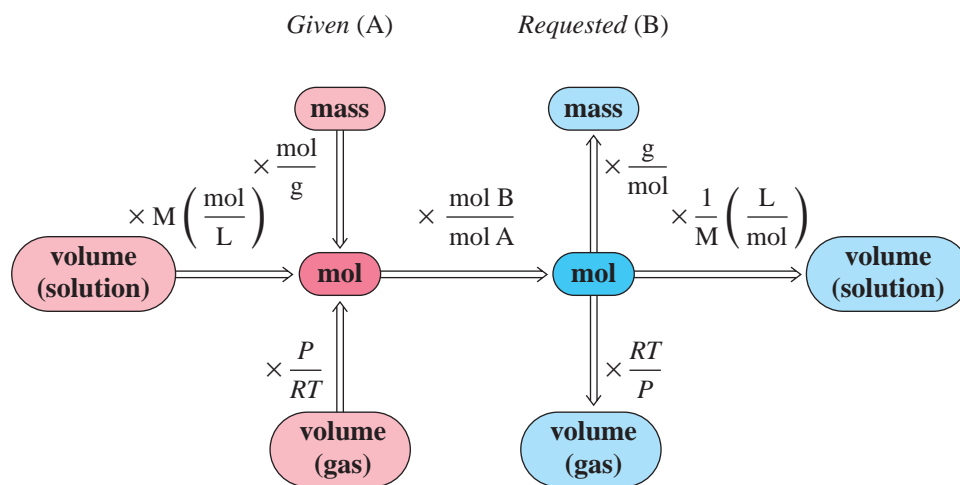
Perform calculations involving titrations and other solution stoichiometry.



**LOOKING AHEAD!** Previously, in Chapter 7, we related the moles of a substance to its molar mass and number of molecules. The volume of a gas at a specific temperature and pressure also relates to moles, so gases were included in stoichiometry problems in Chapter 10. The inclusion of solutions by means of molarity into our general stoichiometry scheme is discussed in this section. ■

**12-5.1 Stoichiometry and Molarity**

It is obvious by now that a large number of important chemical reactions take place in aqueous solution. With the use of molarity, the volume of a solution provides a direct path to the number of moles of a reactant or product. Conversion of the given information into moles has always been the first step in solving a stoichiometry problem. In Figure 12-8, the general scheme for working stoichiometry problems has been extended to include volumes of solutions. The following examples also illustrate the inclusion of solutions in stoichiometry problems.

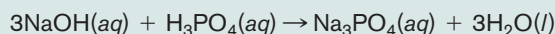


**FIGURE 12-8** General Procedure for Stoichiometry Problems

### EXAMPLE 12-9

#### Calculating the Volume of a Reactant

Given the balanced equation

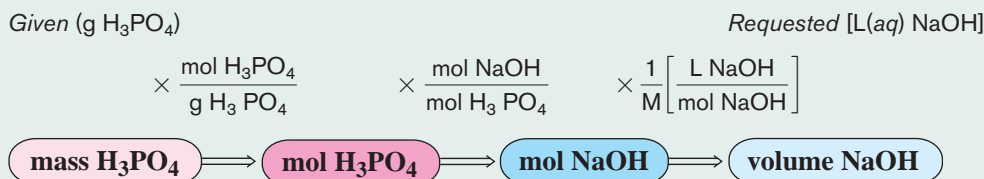


what volume of 0.250 M NaOH is required to react completely with 4.90 g of  $\text{H}_3\text{PO}_4$ ?

#### PROCEDURE

1. Convert mass of  $\text{H}_3\text{PO}_4$  to moles using the molar mass of  $\text{H}_3\text{PO}_4$ .
2. Convert moles of  $\text{H}_3\text{PO}_4$  to moles of NaOH using the mole ratio from the balanced equation.
3. Convert moles of NaOH to volume using the equation for molarity.

The complete unit map for this problem is shown below.



#### SOLUTION

$$4.90 \text{ g H}_3\text{PO}_4 \times \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g H}_3\text{PO}_4} \times \frac{3 \text{ mol NaOH}}{1 \text{ mol H}_3\text{PO}_4} = 0.150 \text{ mol NaOH}$$

$$\text{vol NaOH} = \frac{\text{mol NaOH}}{M} = \frac{0.150 \text{ mol}}{0.250 \text{ mol/L}} = \underline{\underline{0.600 \text{ L}}}$$

#### ANALYSIS

In Section 7-1, we introduced the mass-to-mass stoichiometry problem. This problem is an example of a mass-to-volume (solution) calculation. The similarities are important. Compare the unit map in Example 7-3 in Section 7-1.3 to the one in this example. The only difference in units is in the last conversion factor, where molarity is used to calculate volume, rather than molar mass for the purpose of converting to grams. Otherwise, the procedure is identical. Substitution of a second molarity value for the second reactant would allow for a volume-to-volume calculation, negating the need to calculate a molar mass entirely. See Example 12-10.

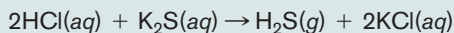
#### SYNTHESIS

These problems are actually more common than the original stoichiometry problems presented in Chapter 7 simply because they represent reactions occurring in solution. The vast majority of chemical reactions are solution reactions rather than solid-phase reactions because of the mixing that occurs in solution. It's hard for solids to react together at all, and if they do, reaction times are generally slow. Solutions allow dissolved chemicals to mix thoroughly, bringing reactant molecule right up to reactant molecule and significantly increasing reaction rates.

## EXAMPLE 12-10

## Calculating the Volume of a Gas from a Solution

Given the balanced equation

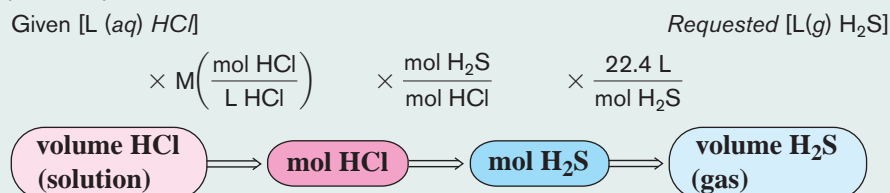


what volume of  $\text{H}_2\text{S}$  measured at STP would be evolved from 1.65 L of a 0.552 M HCl solution with excess  $\text{K}_2\text{S}$  present?

## PROCEDURE

1. Convert volume and molarity of HCl to moles of HCl.
2. Convert moles of HCl to moles of  $\text{H}_2\text{S}$  using mole ratio from the balanced equation.
3. Convert moles of  $\text{H}_2\text{S}$  to volume of  $\text{H}_2\text{S}$  using the molar volume.

The complete unit map for the problem is shown below.



## SOLUTION

$$V(\text{solution}) \times M(\text{HCl}) = n(\text{HCl})$$

$$1.65 \text{ L} \times 0.552 \text{ mol/L} = 0.911 \text{ mol HCl}$$

Since the volume of the gas is at STP, the molar volume relationship can be used rather than the ideal gas law.

$$0.911 \text{ mol HCl} \times \frac{1 \text{ mol H}_2\text{S}}{2 \text{ mol HCl}} \times \frac{22.4 \text{ L (STP)}}{\text{mol H}_2\text{S}} = \underline{\underline{10.2 \text{ L (STP)}}}$$

## ANALYSIS

This problem combines two different volume problems. One is a volume of solution and requires the use of molarity. The other is a volume of a gas and requires a gas law relationship, which was discussed in Chapter 10. Sometimes students get the two confused. Try to visualize the aqueous solution and the gas being evolved as the HCl solution is added. The solution to any stoichiometry problem lies in using the proper conversion factor: molar mass for grams, 22.4 L/mol for gases at STP, the ideal gas law for volumes at other conditions, and molarity for solutions.

## SYNTHESIS

Which conversion factors would be necessary to determine the number of *molecules* of a product that could be produced from a given volume of reactant solution? Starting with the volume, we would need the molarity of the solution, the mole ratio between reactant and product, and finally Avogadro's number. The unit map for this calculation is

$$\frac{\text{mol (reactant)}}{\text{L}} \times \frac{\text{mol (product)}}{\text{mol (reactant)}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol (product)}}$$

## 12-5.2 Titrations

Quite often, laboratory experiments require that we establish the molarity of a solution from stoichiometry data. For example, environmental scientists encounter this situation frequently when they sample river water. To know whether the water is safe to drink, the concentrations of  $\text{Pb}^{2+}$ , or  $\text{Hg}^{2+}$ , or some other heavy metal contaminant has to be established. The concentrations are determined through a stoichiometric procedure known as a *titration*.

**Titration** are usually *volume-to-volume stoichiometry problems where a concentration is the unknown variable*. A measured volume of one reactant of known molarity is added to a known volume of the other reactant. The end of the reaction is generally noted by the addition of an *indicator*, which is a compound that provides a visual clue, such as a color change, that a reaction has been completed. When the indicator changes color, the titration is said to be at its *end point*, which is the point in the titration where



the moles of reactants are exactly stoichiometric. The molarity of the unknown solution can then be calculated. This is illustrated in Example 12-11.

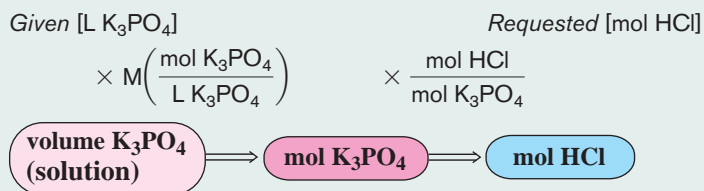
**EXAMPLE 12-11****Calculating an Unknown Concentration from Titration Data**

Given the reaction:  $3\text{HCl}(aq) + \text{K}_3\text{PO}_4(aq) \rightarrow \text{H}_3\text{PO}_4(aq) + 3\text{KCl}(aq)$

What is the concentration of an HCl solution if 25.0 mL reacts with 38.5 mL of 0.145 M  $\text{K}_3\text{PO}_4$  solution?

**PROCEDURE**

1. Convert volume in mL to volume in L.
2. Convert L and M of  $\text{K}_3\text{PO}_4$  to moles of  $\text{K}_3\text{PO}_4$  then moles of  $\text{K}_3\text{PO}_4$  to moles of HCl using the mole ratio from the balanced equation. The unit map for this conversion is shown below.



3. Convert moles and volume of HCl to molarity of HCl.

**SOLUTION**

$$38.5 \text{ mL} \times 1 \text{ L}/1000 \text{ mL} = 0.0385 \text{ L K}_3\text{PO}_4$$

$$25.0 \text{ mL} \times 1 \text{ L}/1000 \text{ mL} = 0.0250 \text{ L HCl}$$

$$0.0385 \text{ L K}_3\text{PO}_4 \times \frac{0.145 \text{ mol K}_3\text{PO}_4}{\text{L K}_3\text{PO}_4} \times \frac{3 \text{ mol HCl}}{1 \text{ mol K}_3\text{PO}_4} = 0.0167 \text{ mol HCl}$$

$$\text{Molarity} = \frac{\text{mol}}{\text{L}} = \frac{0.0167 \text{ mol}}{0.0250 \text{ L}} = \underline{\underline{0.668 \text{ M}}}$$

**ANALYSIS**

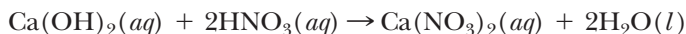
As a rule of thumb, concentrations above 1 M are considered fairly concentrated solutions. Concentrations below 0.1 M are considered dilute. The range between those two is what is frequently (though not exclusively) encountered. So when a value of 0.668 M is calculated for the molarity of a solution, it falls right in the range of common concentrations. The answer is very reasonable.

**SYNTHESIS**

Titration finds its biggest application in chemistry during acid–base reactions. There is generally a favorable reaction, and the accompanying change in the  $\text{H}^+$  (*aq*) concentration (see Chapter 13) is the primary factor that causes the indicator to change color. Most indicators change color very close to the end point, making for a wide range of available indicators. The stoichiometry of the reaction is usually very straightforward and can be determined easily from the formulas of the acid and base.

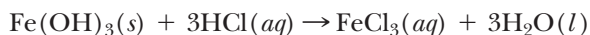
**ASSESSING THE OBJECTIVE FOR SECTION 12-5**

**EXERCISE 12-5(a) ANALYSIS:** For the reaction



What volume of 0.125 M of  $\text{Ca}(\text{OH})_2$  reacts with 15.0 mL of 0.225 M  $\text{HNO}_3$ ?

**EXERCISE 12-5(b) ANALYSIS:** For the reaction



What is the concentration of a solution of HCl if 33.5 mL reacts with 1.50 g of  $\text{Fe}(\text{OH})_3$ ?

**EXERCISE 12-5(c) SYNTHESIS:** Sodium carbonate and hydrochloric acid react together to form carbon dioxide, water, and sodium chloride. If 50.0 mL of an HCl solution reacts with an excess of sodium carbonate to form 3.50 L of  $\text{CO}_2$  at STP, what is the concentration of the HCl solution?

For additional practice, work chapter problems 12-43, 12-46, 12-49, and 12-51.

**PART A**  
**SUMMARY**

**KEY TERMS**

- 12-1.1** Two liquids are **miscible** if they form one phase and **immiscible** if they remain in two phases. p. 365
- 12-1.2** Ionic compounds dissolve in water as a result of **ion-dipole forces**. p. 366
- 12-1.3** Strong acids undergo **ionization** when dissolved in water. p. 366
- 12-2** The maximum amount of a solute that dissolves at a specific temperature is known as its **solubility**. p. 367
- 12-2.1** Depending on the amount of solute dissolved and its solubility, the solution may be **unsaturated**, **saturated**, or, in certain circumstances, **supersaturated**. p. 367
- 12-2.1** The **concentration** of a solute refers to the amount present in a certain amount of solvent or solution. p. 367
- 12-2.2** **Recrystallization** takes advantage of the difference in solubility of a substance at different temperatures. p. 368
- 12-2.4** According to **Henry's law**, the solubility of gases in a liquid relates to the pressure above the liquid. p. 369
- 12-3** Concentration may be measured as **percent by mass**. p. 370
- 12-3.1** **Parts per million (ppm)** or **parts per billion (ppb)** are used for small concentrations. p. 372
- 12-4** **Molarity (M)** is a concentration unit that emphasizes the volume of the solution. p. 373
- 12-5.2** During a **titration**, an indicator can be used to determine the end point of the experiment. p. 379

**SUMMARY CHART**

| Concentration Units   |                         |                        |  |
|---|-------------------------|------------------------|--|
| Concentration Unit  | Name                    | Relationship of solute | Use  |
| $\frac{\text{g solute}}{100 \text{ g solvent}}$                     | _____                   | Mass of solvent        | Solubility tables  |
| $\frac{\text{g solute}}{\text{g solution}} \times 100\%$            | Percent by mass         | Mass of solution       | High concentrations (above 0.01%)                                |
| $\frac{\text{g solute}}{\text{g solution}} \times 10^6 \text{ ppm}$ | Parts per million (ppm) | Mass of solution       | Low concentrations ( $> 10^{-4}\%$ )                             |
| $\frac{\text{g solute}}{\text{g solution}} \times 10^9 \text{ ppb}$ | Parts per billion (ppb) | Mass of solution       | Extremely low concentrations ( $> 10^{-7}\%$ )                   |
| $\frac{\text{mole solute}}{\text{L solution}}$                      | Molarity (M)            | Volume of solution     | Measuring molar amount with volume and in stoichiometry problems |

**PART B**  
**THE EFFECTS OF SOLUTES**  
**ON THE PROPERTIES OF**  
**WATER**

**SETTING A GOAL**

- You will learn how the physical properties of aqueous solutions differ from those of pure water.

**OBJECTIVES**

- 12-6** Explain the differences between nonelectrolytes, strong electrolytes, and weak electrolytes.
- 12-7 (a)** Explain how the presence of a solute in water affects its physical properties. **(b)** Calculate the boiling and melting points of aqueous solutions of nonelectrolytes and electrolytes.

▶ **OBJECTIVE FOR**  
**SECTION 12-6**

Explain the differences between nonelectrolytes, strong electrolytes, and weak electrolytes.

## 12-6 ELECTRICAL PROPERTIES OF SOLUTIONS



**LOOKING AHEAD!** The use of a hair dryer in the bathtub is extremely dangerous. Even though pure water is not a good conductor of electricity, ordinary tap water is because it contains a variety of dissolved compounds. It has long been known that the presence of a solute in water may affect its ability to conduct electricity. In this section, we will examine the electrical properties of water and aqueous solutions. ■

### 12-6.1 Conduction of Electricity

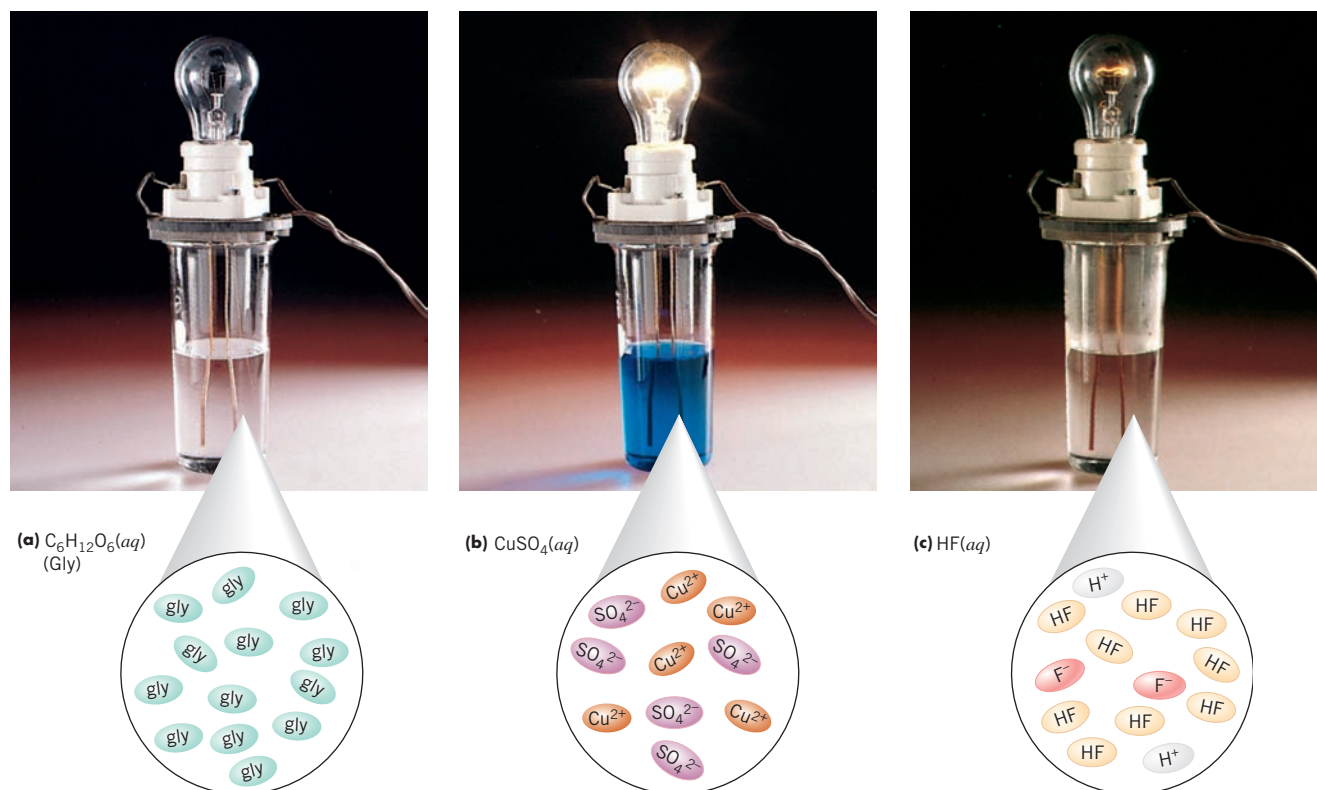
*Electricity is simply a flow of electrons through a substance called a **conductor**.* Metals are the most familiar conductors and, as such, find use in electrical wires. Because the outer electrons of metals are loosely held, they can be made to flow through a continuous length of wire. *Other substances resist the flow of electricity and are known as **nonconductors** or **insulators**.* Glass and wood are examples of nonconductors of electricity. When wires are attached to a charged battery and then to a lightbulb, the light shines brightly. If the wire is cut, the light goes out because the circuit is broken. If the two ends of the cut wire are now immersed in pure water, the light stays out, indicating that water does not conduct electricity under these circumstances. Now let's dissolve certain solutes in water and examine what happens. When compounds such as  $\text{CuSO}_4$  or  $\text{HCl}$  are dissolved in water, the effect is obvious. The light immediately begins to shine, indicating that the solution is a good conductor of electricity. (See Figure 12-9b.) *Compounds whose aqueous solutions conduct electricity are known as **electrolytes**.* (Some ionic compounds have limited solubility in water, but if their molten state conducts electricity, they are also classified as electrolytes.)

*We now understand that it is the presence of ions in the aqueous solution that allows the solution to conduct electricity.* Almost all soluble ionic compounds form ions in solution, and some polar covalent compounds also dissolve to form ions. For example, both  $\text{NaCl}$  (ionic) and  $\text{HCl}$  (polar covalent) are classified as electrolytes because they form ions in aqueous solution. As you will recall,  $\text{HCl}$  is a molecular compound in the pure state. However, in water it is ionized as described earlier in this chapter.

### 12-6.2 Nonelectrolytes and Electrolytes

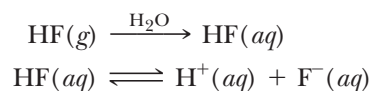
Other compounds such as sucrose (table sugar), glucose (blood sugar), and alcohol dissolve in water, but their solutions do not conduct electricity. *Compounds whose aqueous solutions do not conduct electricity are known as **nonelectrolytes**.* Nonelectrolytes are molecular compounds that dissolve in water without formation of ions. (See Figure 12-9a.)

There are two classes of electrolytes: strong electrolytes and weak electrolytes. *Solutions of **strong electrolytes** are good conductors of electricity.* Almost all salts and strong acids are present only as ions in aqueous solution (e.g.,  $\text{NaCl}$ ,  $\text{CuSO}_4$ , and  $\text{HCl}$ ) and are thus classified as strong electrolytes. (See Figure 12-9b.) *Solutions of **weak electrolytes** allow a*



**FIGURE 12-9 Nonelectrolytes, Strong Electrolytes, and Weak Electrolytes** (a) A solution of glucose sugar ( $C_6H_{12}O_6$ ) does not conduct electricity. (b) A  $CuSO_4$  solution is a strong electrolyte and conducts electricity. (c) A hydrofluoric acid solution [ $HF(aq)$ ] is a weak electrolyte and conducts a limited amount of electricity.

*limited amount of conduction.* When wires are immersed in solutions of weak electrolytes, the lightbulb glows, but very faintly. (See Figure 12-9c.) Even adding more of the solute does not help. Examples of weak electrolytes are ammonia ( $NH_3$ ) and hydrogen fluoride ( $HF$ ). Both of these gases are soluble in water but produce only a comparatively limited concentration of ions at any one time. For example, most of the dissolved  $HF$  remains as neutral molecules. Because the number of ions is small compared with the total number of  $HF$  molecules dissolved, the solution conducts only a limited amount of electricity. The ionization of  $HF$  is an example of a reversible reaction that reaches a point of equilibrium. The concept of equilibrium was discussed in relation to vapor pressure (Section 11-4.3) but will be discussed in more detail in Chapter 15. The solution and ionization of  $HF$  can be represented by the following equations.



(Note: Pure water actually does contain a very small concentration of ions, as we will discuss in the next chapter. However, the concentration of ions in pure water is too low to detect conduction with the electrical current described above.)

**EXERCISE 12-6(a) KNOWLEDGE:** Are the following descriptions of strong electrolytes, weak electrolytes, or nonelectrolytes?

- (a) describes all ionic compounds
- (b) solution causing a lightbulb to glow dimly
- (c) describes most molecular compounds
- (d) conducts electricity well

**ASSESSING THE  
OBJECTIVE FOR  
SECTION 12-6**

- (e) will not conduct electricity  
 (f) made from compounds that partially ionize in water

**EXERCISE 12-6(b) ANALYSIS:** Which of the following is the strong electrolyte, the weak electrolyte, and the nonelectrolyte:

- (a)  $\text{NH}_3$     (b)  $\text{KNO}_3$     (c)  $\text{CH}_3\text{OH}$

For additional practice, work chapter problems 12-51 and 12-52.

▶ **OBJECTIVES FOR SECTION 12-7**

(a) Explain how the presence of a solute in water affects its physical properties. (b) Calculate the boiling and melting points of aqueous solutions of nonelectrolytes and electrolytes.

## 12-7 COLLIGATIVE PROPERTIES OF SOLUTIONS



**LOOKING AHEAD!** We melt ice by spreading salt and put antifreeze in our car's radiator—we take these actions because the presence of solutes alters some important physical properties of pure water. We will examine why and how much the presence of solutes affects certain properties in this section. ■

The presence of a solute in water may or may not affect its conductivity, depending on whether the solute is an electrolyte or a nonelectrolyte. There are other properties of water, however, that are always affected to some extent by the presence of a solute. Consider again what was mentioned in Chapter 3 as characteristic of a pure substance. Recall that a pure substance has a distinct and unvarying melting point and boiling point (at a specific atmospheric pressure). Mixtures, such as aqueous solutions, freeze and boil over a range of temperatures that are lower (for freezing) and higher (for boiling) than those of the pure solvent. The effect of these changes is to extend the liquid range for the solvent. The more solute, the more the melting and boiling points are affected. A *property that depends only on the relative amounts of solute and solvent is known as a colligative property.*

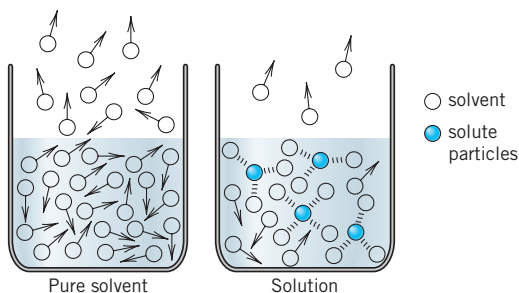
The conductivity of a solution depends on the nature of the particular solute. In contrast, colligative properties depend only on the amount or number of moles of particles present, not their identity. The particles may be small molecules, large molecules, or ions—only the total number is relevant. This is like many of the gas laws, which, you may recall, also depend only on the total number of moles of gas present.

### 12-7.1 Vapor Pressure

The Dead Sea in Israel and the Great Salt Lake in the United States contain large concentrations of solutes. These large bodies of water have no outlet to the ocean, so dissolved substances have accumulated, forming saturated solutions. Even though both bodies of water exist in semiarid regions with high summer temperatures, both lakes evaporate very slowly compared with a freshwater lake or even the ocean. If water in these lakes evaporated at the same rate as fresh water, both would nearly dry up in a matter of years. Why do they evaporate so slowly?

*The presence of a nonvolatile solute\* in a solvent lowers the equilibrium vapor pressure from that of the pure solvent.* (See Section 11-4.3.) It is not hard to understand why this occurs based on what we have discussed about the interactions between solute and solvent. Because of various attractive forces, solvent molecules surround solute molecules or ions. Solute molecules or ions thus tend to tie up the solvent molecules, which in effect prevents them from escaping to the vapor. The more solute particles present, the more solvent molecules that are held in the liquid phase. Thus the solution has a lower equilibrium vapor pressure than the pure solvent.

(See Figure 12-10.) As we might predict from this model, the more solute particles present, the lower the vapor pressure of the solution. **Vapor pressure lowering** affects the boiling point of the solution, as described next.



**FIGURE 12-10 Vapor Pressure Lowering** A nonvolatile solute reduces the number of solvent molecules escaping to the vapor.

\*A nonvolatile solute is one that has essentially no vapor pressure at the relevant temperatures.



## 12-7.2 Boiling Point

Adding salt to water raises the boiling point of the solution. Raising the boiling point means that food cooks a little faster, depending how much salt is dissolved. *A direct effect of the lowered vapor pressure of a solution is a higher boiling point than that of the solvent.* Recall that the normal boiling point of water is 100°C, which is the temperature at which its vapor pressure is equal to 760 torr. An aqueous solution, on the other hand, would not have a vapor pressure of 760 torr at 100°C—it would be lower than 760 torr. Thus, the solution would have to be heated above 100°C for the vapor pressure to reach 760 torr and begin boiling. Again, the more concentrated the solution, the lower the vapor pressure and the higher the boiling point.

The amount of **boiling-point elevation** is given by the equation

$$\Delta T_b = K_b m$$

where

$\Delta T_b$  = the number of Celsius (or Kelvin) degrees that the boiling point is raised

$K_b$  = a constant characteristic of the solvent [for water  $K_b = 0.512$  (°C · kg)/mol; other values of  $K_b$  are given for particular solvents in the problems]

$m$  = a concentration unit called molality.

**Molality** is a convenient concentration unit for this purpose since it emphasizes the relationship between the relative amounts of solute (expressed in moles) and mass of solvent (expressed in kg) present rather than the volume of the solution, as does molarity. Also, the molality of a solution is not affected by the temperature. (Since liquids expand to a small degree when heated, the volume of a solution, which is used in molarity, is affected by the temperature.) The definition of molality is

$$\text{molality } (m) = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

### EXAMPLE 12-12

#### Calculating Molality

What is the molality of methyl alcohol in a solution made by dissolving 18.5 g of methyl alcohol (CH<sub>3</sub>OH) in 850 g of water?

#### PROCEDURE

1. Convert mass of solute to mol of solute and g of solvent to kg of solvent.
2. Use these values to calculate molality.

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

#### SOLUTION

$$\begin{aligned} \text{mol solute} &= \frac{18.5 \text{ g}}{32.04 \text{ g/mol}} = 0.577 \text{ mol} \\ \text{kg solvent} &= \frac{850 \text{ g}}{10^3 \text{ g/kg}} = 0.850 \text{ kg} \\ \text{molality} &= \frac{0.577 \text{ mol}}{0.850 \text{ kg}} = \underline{\underline{0.679 m}} \end{aligned}$$

#### ANALYSIS

When water is the solvent, the value of the molarity and the molality differ by just a fraction of a percent. That is because 1.0 L of aqueous solution has a mass of about 1.0 kg. Should they be closer together for concentrated or dilute solutions? In fact, the more dilute the solution, the closer the mass of 1 L of the solution is to 1.0 kg (the mass of 1.0 L of pure water). Thus, they are closer for dilute solutions. For example, the molarity of a 1.0% solution of LiCl is 0.237, while the molality is 0.238. On the other hand, the molarity of a 10% solution of LiCl is 2.49, while the molality is 2.62.

**SYNTHESIS**

So what if the solvent isn't water? Most liquids that routinely serve as solvents have densities significantly less than water's. For example, ethyl alcohol, a common solvent, has a density of 0.789 g/mL (0.789 kg/L). If we assume a dilute solution where 1 L of solution weighs about the same as 1 L of solvent, the number of moles of solute would be divided by 1 L for molarity but 0.789 kg for molality. That will cause the molality to be noticeably higher than the molarity. For the few solvents with densities higher than water [e.g., methylene chloride (1.33 g/mL)], the molality would be lower than the molarity.

**EXAMPLE 12-13****Calculating the Boiling Point of a Solution**

What is the boiling point of an aqueous solution containing 468 g of sucrose ( $C_{12}H_{22}O_{11}$ ) in 350 g of water?

**PROCEDURE**

1. Convert g of solute (sucrose) to moles and g of solvent to kg.
2. Use these values and the value of  $K_b$  to calculate the temperature change.

$$\Delta T_b = K_b m = 0.512 (\text{°C} \cdot \text{kg})/\text{mol} \times \frac{\text{mol solute}}{\text{kg solvent}}$$

3. Calculate the actual boiling point from the temperature change.

**SOLUTION**

$$\text{mol solute} = \frac{468 \text{ g}}{342.5 \text{ g/mol}} = 1.37 \text{ mol}$$

$$\text{kg solvent} = \frac{350 \text{ g}}{10^3 \text{ g/kg}} = 0.350 \text{ kg}$$

$$\Delta T_b = 0.512 (\text{°C} \cdot \text{kg})/\text{mol} \times \frac{1.37 \text{ mol}}{0.350 \text{ kg}} = 2.00\text{°C}$$

$$\text{normal boiling point of water} = 100.0\text{°C}$$

$$\text{boiling point of the solution} = 100.0\text{°C} + \Delta T_b = 100.0 + 2.00 = \underline{\underline{102.0\text{°C}}}$$

**ANALYSIS**

In this problem the mass of solute is greater than the mass of solvent, yet it created an increase in boiling point of only 2°C. Why so small a change? In this case, it's because the solute is made of such heavy molecules. The atomic mass of the sucrose is 342.5 g/mol. If our solute had a molar mass of only 50 g/mol or so, what would our boiling point have been? 50 is about 7 times less than 342.5, which means there would be seven times as many particles and seven times the rise in temperature. The new boiling point would be closer to 114°C, a significant increase.

**SYNTHESIS**

This process of boiling-point elevation (or freezing-point depression, discussed in the next section) represented one of the earliest ways chemists had to determine the molar mass of an unknown compound. First, we determine whether the compound is soluble in a polar or a nonpolar solvent. Knowing the proper solvent and its value of  $K_b$ , we can then do the experiment. It requires that we dissolve a measured mass of the compound in a measured mass of solvent. We then measure the boiling point of the pure solvent, the boiling point of the solution, and, from these two values, the boiling-point elevation. From this we solve for the molality. Since we know the mass of solute and the mass of solvent, the only variable that is left is the molar mass. We could try the experiment using the same compound in other solvents to confirm our values.

**12-7.3 Freezing Point**

The icy, cold winds of winter can be very hard on automobiles. If there is not enough antifreeze in the radiator, the coolant water may freeze. This could ruin the radiator and even crack the engine block, because water expands when it freezes. We illustrate the same principle as antifreeze in radiators when we spread salt on ice-covered streets or sidewalks. In both of these cases, we take advantage of the fact that solutions have lower freezing points than pure solvents. *Just as the boiling point of a solution is higher than that of the pure solvent, the freezing point is lower.*

The amount of **freezing-point lowering** is given by the equation

$$\Delta T_f = K_f m$$

where

$\Delta T_f$  = the number of Celsius (or Kelvin) degrees that the freezing point is lowered

$K_f$  = a constant characteristic of the solvent [for water,  $K_f = 1.86$  ( $^{\circ}\text{C} \cdot \text{kg}$ )/mol]

$m$  = molality of the solution

### EXAMPLE 12-14

#### Calculating the Freezing Point of a Solution

What is the freezing point of the solution in Example 12-13?

#### PROCEDURE

$$\Delta T_f = K_f m = 1.86 (^{\circ}\text{C} \cdot \text{kg})/\text{mol} \times \frac{\text{mol solute}}{\text{kg solvent}}$$

#### SOLUTION

$$\Delta T_f = 1.86 (^{\circ}\text{C} \cdot \text{kg})/\text{mol} \times \frac{1.37 \text{ mol}}{0.350 \text{ kg}} = 7.28^{\circ}\text{C}$$

$$\text{freezing point of water} = 0.0^{\circ}\text{C}$$

$$\text{freezing point of the solution} = 0.0^{\circ}\text{C} - \Delta T_f = 0.0^{\circ}\text{C} - 7.3^{\circ}\text{C} = \underline{\underline{-7.3^{\circ}\text{C}}}$$

#### ANALYSIS

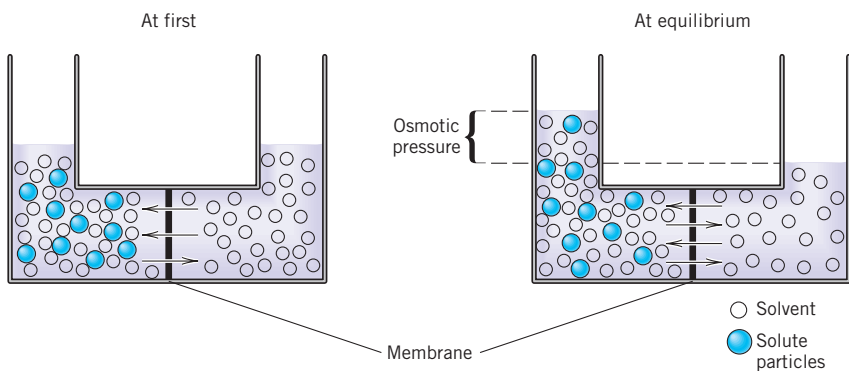
This problem stresses the concept of a *colligative* property. In Examples 12-13 and 12-14 nothing changed about the solution, since there are the same number of solute particles in each case. Yet notice that the effect on the melting point is more pronounced than the effect on the boiling point. Since  $K_f$  of water (1.86) is over three times larger than the  $K_b$  of water (0.512), the freezing-point depression is over three times larger as well (7.3 $^{\circ}\text{C}$  compared to 2 $^{\circ}\text{C}$ ). Because of the freezing-point *lowering* and boiling-point *elevation*, the liquid range in this example has been extended by over 9 $^{\circ}\text{C}$  (i.e.,  $-7.3^{\circ}\text{C}$  to  $102^{\circ}\text{C}$ ) for the solution compared to pure water. Permanent antifreeze not only protects the engine from freezing but in the summer it protects the water from boiling away. Until the late 1930s, methanol was used as antifreeze, but because it has a low boiling point, it would boil away in hot weather. It had to be removed and replaced with water when the weather warmed. Permanent antifreeze is now composed mostly of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ). A 1:1 mixture protects down to  $-40^{\circ}\text{C}$  (and up to about  $110^{\circ}\text{C}$ ), although less may be used depending on the locality. Ethylene glycol, however, is very poisonous compared to propylene glycol ( $\text{C}_3\text{H}_8\text{O}_2$ ), which is not. The latter is used in water-heating pipes in homes or other places where there is danger of accidental ingestion. (Because of its higher molar mass, however, it takes more propylene glycol to have the same effect as ethylene glycol.)

#### SYNTHESIS

Freezing-point depression is also used by chemists as a laboratory procedure to determine the molar mass of an unknown compound. See if you can calculate the molar mass of the compound in problem 12-87 in the chapter problems. Besides solubility, one looks for a solvent with the largest value for  $K_f$ . When you look at the equation for freezing-point depression, notice that the greater the value of  $K_f$ , the greater the freezing-point depression and the more precision (i.e., signifying figures) in the measurement. For example, a measured depression of  $12.2^{\circ}\text{C}$  in one solvent is more precise than one of  $1.3^{\circ}\text{C}$  for the same solute in another solvent. Chloroform ( $\text{CHCl}_3$ ) is very effective in this regard, since it has  $K_f = 30$ . One mole of solute in chloroform causes about 16 times as much freezing-point depression as in water. (This assumes that the solute is soluble in both solvents, which may not be the case.)

## 12-7.4 Osmotic Pressure

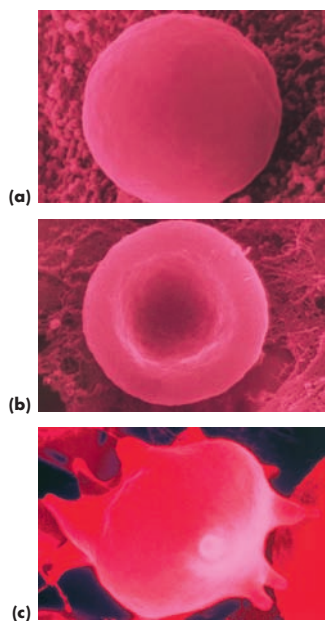
Food is preserved in salt water, drinking ocean water causes dehydration, tree and plant roots absorb water—these are all phenomena related to a colligative effect called osmosis. **Osmosis** is the tendency for a solvent to move through a thin porous membrane from a dilute solution to a more concentrated solution. The membrane is said to be *semipermeable*, which means that small solvent molecules can pass through but large hydrated solute species cannot. Figure 12-11 illustrates osmosis. On the right is a pure solvent and on the left, a solution. The two are separated by a semipermeable membrane. Solvent molecules can pass through the membrane in both directions, but the rate at which they diffuse to the right is lower because some of the water molecules on the left are held back by solute–solvent interactions. As a result of the uneven



**FIGURE 12-11 Osmotic Pressure** Osmosis causes dilution of the more concentrated solution.



Sodium chloride is used to melt ice from sidewalks, streets, and highways.



**FIGURE 12-12 Blood Cells** (a) In isotonic solution, red blood cells are spherical. (b) At higher ion concentration, osmotic flow removes water from the cell interior, shrinking the cell. (c) At lower ion concentration, osmotic flow pumps water into the cell and may cause it to burst.

passage of water molecules, the water level rises on the left and drops on the right. This creates increased pressure on the left, which eventually counteracts the osmosis, and equilibrium is established. *The extra pressure required to establish this equilibrium is known as the osmotic pressure.* Like other colligative properties, it depends on the concentration of the solute. In Figure 12-11, the more concentrated the solution on the left (less solvent), the higher the osmotic pressure.

In Figure 12-11, if pressure greater than the osmotic pressure is applied on the left, reverse osmosis takes place and solvent molecules move from the solution to the pure solvent. This process is used in desalination plants that convert seawater (a solution) to drinkable water. This is important in areas of the world such as the Middle East, where there is a shortage of fresh water.

### 12-7.5 Electrolytes and Colligative Properties

Our final point concerns the effect of electrolytes on colligative properties. Electrolytes have a more pronounced effect on colligative properties than do nonelectrolytes. The reason is that these properties depend only on how many particles are present regardless of whether the particle is a neutral molecule, a cation, or an anion. For example, one mole of NaCl dissolves in water to produce two moles of particles, one mole of  $\text{Na}^+$ , and one mole of  $\text{Cl}^-$ .



Thus one mole of NaCl lowers the freezing point approximately twice as much as one mole of a nonelectrolyte. This effect is put to good use in the U.S. Snow Belt, where sodium chloride is spread on snow and ice to cause melting even though the temperature is below freezing. Even more effective in melting ice is calcium chloride ( $\text{CaCl}_2$ ). This compound produces three moles of ions ( $\text{Ca}^{2+} + 2\text{Cl}^-$ ) per mole of solute and therefore is three times as effective per mole as a nonelectrolyte in lowering the freezing point. Calcium chloride is occasionally used on roads when the temperature is too low for sodium chloride to be effective. Aqueous electrolyte solutions are quite corrosive toward metals because of their electrical conductivity. This is why they are not used as an inexpensive antifreeze in automobile radiators.

We see an example of the osmosis process whenever we leave our hands in water for extended periods of time. The oils that protect our skin eventually wash away, allowing water to come in contact with the skin, which is a semipermeable membrane. The movement of excess water molecules from the outside of our skin to the more concentrated fluid in our bodies causes puffy wrinkling. Pickles are wrinkled for the opposite reason. The cells of the cucumber have been dehydrated by the salty brine solution. In fact, brine solutions preserve many foods because the concentrated solution of salt removes water from the cells of bacteria, thus killing the bacteria. Trees and plants obtain water by absorbing water through the semipermeable membranes in their roots into the more concentrated solution inside the root cells.

The concentration of solutes in the blood and other bodily fluids is important in the hydration and health of cells in our bodies. When the concentration of ions and other solutes in the blood or plasma is the same as that inside of a cell, the solution is said to be *isotonic*. In this case, there is no net movement of water into or out of the cell. If the concentration of solutes in the solutions around the cells is greater in the blood than in the cell, water moves out of the cell and dehydration occurs. If the opposite occurs, water moves into the cell and expands it. (See Figure 12-12.) In either case, destruction of the cells may occur in extreme cases. Intravenous solu-

tions, such as a glucose drip or injections in a saline solution, are isotonic with the blood so as not to dilute or concentrate the solution of the cells. As mentioned earlier in Example 12-2, a 0.89% (wt/v) saline solution is used as an isotonic solution.



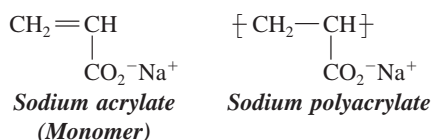
### Osmosis in a Diaper



Except for the fact that a baby seems to be unusually heavy, one might not realize just how wet a diaper has become. In the old days, a quick touch would tell the condition. Modern superabsorbent diapers make use of a chemical that has a tremendous ability to absorb water. In fact, such diapers contain a white powdery material that can absorb 200 to 500 times its weight in water. Not only is such a

diaper convenient for the diaper changer but it is also quite a bit more comfortable for the diaper wearer.

The compound used in these diapers is a polymeric material. The polymer used in diapers (sodium polyacrylate) is made of long chains of an ionic unit (called a monomer), sodium acrylate (shown below). Most familiar plastics such as Styrofoam cups, plastic bottles and bags, PVC pipes, and thousands of other everyday materials are made of various types of polymers. More detail about polymers is provided in Chapter 17.



The unique property of the diaper polymer is that its surface is semipermeable. Inside the surface, ions are present. The high concentration of ions inside causes water molecules to cross the membrane in the process of osmosis. The water then stays put inside the polymer. In fact, the diaper does not even feel wet, thus protecting the baby from nasty rashes. It is so effective that special “training diapers” can be used when it is time for baby to move on. These diapers are engineered to allow some wetness and discomfort as an incentive to become “trained.”

Consider the absorbent ability of these diapers. A 1-g quantity of the polyacrylate can absorb up to 500 g of water. If one had an 8-oz glass of water, it would take less than 500 mg of superabsorbent to turn the glass of water into a wiggly, gelatinous mass. A 700-lb quantity of superabsorbent would be enough to turn a good-size swimming pool into something like Jell-O.

In 1999, world production of this polymer was 980 million tons. Not all of that went into diapers (fortunately). It is also used in agriculture, crafts, evaporative coolers, firefighting, toothpaste, and cosmetics.

An unpleasant (odiferous), drippy experience has been changed into something much more tolerable. Baby caregivers of the world are grateful for this chemical advance.

### ASSESSING THE OBJECTIVES FOR SECTION 12-7

**EXERCISE 12-7(a) KNOWLEDGE:** Liquid A is a pure compound and liquid B contains a solute dissolved in liquid A.

- Which boils at the higher temperature?
- Which freezes at the higher temperature?
- Which has the higher osmotic pressure?

**EXERCISE 12-7(b) ANALYSIS:** Calculate the molality if 15.0 g of  $\text{NaNO}_3$  is dissolved in 50.0 g of  $\text{H}_2\text{O}$ .

**EXERCISE 12-7(c) ANALYSIS:** What is the freezing point of a solution if 0.750 mol of a nonelectrolyte solute is dissolved in 250.0 g of  $\text{H}_2\text{O}$ ? What is the freezing point if it's 0.750 mol of  $\text{CaCl}_2$  that's dissolved?

**EXERCISE 12-7(d) SYNTHESIS:** Acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) is a weak electrolyte. What would be the effect on the boiling point of water by adding one mole of acetic acid compared to 1 mole of some nonelectrolyte molecular solute? What would be the effect compared to adding 1 mole of  $\text{NaCl}$ ?

For additional practice, work chapter problems 12-56, 12-58, 12-60, 12-64, and 12-67.



PART B  
SUMMARY

## KEY TERMS

- 12-6.1** A medium that conducts electricity is known as a **conductor**, whereas a medium that does not is an **insulator** (or **nonconductor**). p. 382
- 12-6.2** A solute that does not change water to a conductor is a **nonelectrolyte**, whereas an **electrolyte** allows the solution to become a conductor. p. 382
- 12-6.2** A **strong electrolyte** makes water a good conductor, whereas a **weak electrolyte** makes water a weak conductor. p. 382
- 12-7** A **colligative property** of a solution depends only on the amount of solute present. p. 384
- 12-7.1** A nonvolatile solute causes a **vapor pressure lowering** compared to the pure solvent. p. 384
- 12-7.2** A nonvolatile solute causes **boiling-point elevation**, the amount of which depends on the **molality** of the solution. p. 385
- 12-7.3** A solute causes a **freezing-point lowering**. p. 386
- 12-7.4** The presence of a solute allows **osmosis** to occur, which causes **osmotic pressure**. pp. 388–389

## SUMMARY CHART

| Colligative Properties |         |  |
|------------------------|---------|--|
| Property of Solution   | Effect  | Result   |
| Vapor pressure         | lowered | Solutions evaporate slower than pure solvents.   |
| Boiling point          | raised  | Solutions boil at higher temperatures than pure solvents.  |
| Freezing point         | lowered | Solutions freeze at lower temperatures than pure solvents.   |
| Osmotic pressure       | raised  | Solvent from dilute solutions diffuses through a semipermeable membrane into concentrated solutions. |

## CHAPTER SUMMARY

Water acts as an effective solvent, dispersing solutes into a homogeneous mixture known as a solution. When two liquids are **miscible**, they form a solution, but if they are **immiscible**, they remain a heterogeneous mixture. Some ionic compounds may dissolve in water because the ion–water forces (**ion–dipole**) overcome the forces holding the crystal together. Polar covalent molecular compounds may dissolve in water as discrete molecules, or they may undergo **ionization**. Although many ionic compounds are considered soluble, others are said to be insoluble since a very limited amount dissolves. The amount that dissolves—the **solubility** of a compound—is indicated by some convenient unit of **concentration**.

How much of a compound can dissolve at a certain temperature to make a **saturated** solution varies from compound to compound. **Unsaturated** solutions contain less than the maximum amount of a compound so that more of the compound may dissolve. **Supersaturated** solutions are unstable solutions containing more of a compound than the solubility would indicate. A precipitate often forms in such a solution. Solid compounds are generally more soluble at higher temperatures, whereas gaseous compounds are less soluble at higher temperatures. This property can be used to purify solids in a process called **recrystallization**. External pressure

does not affect the solubility of solids but does affect gases, which illustrates **Henry's Law**.

Besides mass of solute per 100 g of solvent, which was used to illustrate comparative solubilities, other units of concentration are **percent by mass**, **molarity (M)**, and **molality**. **Parts per million (ppm)** and **parts per billion (ppb)** are used for very small concentrations.

Since molarity relates volume of a solution to moles of solute, it can be incorporated into the general scheme for stoichiometry problems along with the mass of a compound (Chapter 9) and the volume of a gas (Chapter 10) (see Figure 12-6). **Titration**s are examples of solution stoichiometry.

We also studied the physical properties of solutions. In the first property mentioned, we found that certain solutes act as **nonelectrolytes** or as either **weak** or **strong electrolytes**. **Electrolytes** change water from a **nonconductor (insulator)** to a **conductor** of electricity. Electrolytes produce ions in solution, which allows water to become a conductor of electricity.

There are also four **colligative properties** of solutions. These are **vapor pressure lowering**, **boiling-point elevation**, and **freezing-point lowering**. The magnitude of the latter two properties relate to the **molality** of the solution. The process of **osmosis** leads to **osmotic pressure elevation**, the fourth colligative property.

| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES            | OBJECTIVES     |                            |
|---------|---|---------------------|----------------|----------------------------|
|         |   |                     | EXERCISES      | CHAPTER PROBLEMS           |
| 12-1    | Describe the role of water in the formation of aqueous solutions of ionic compounds, strong acids, and polar molecules. |                     | 1a, 1b, 1c, 1d | 1, 5, 6, 7                 |
| 12-2    | Define terms associated with solubility.  |                     | 1d, 2a, 2c     | 2, 3                       |
|         | Predict the effects of temperature and pressure on solubility.  |                     | 2b, 2c, 2d     | 9, 10, 11                  |
| 12-3    | Perform calculations of concentration involving percent by mass.  | 12-1, 12-2, 12-3    | 3a, 3b, 3c, 3d | 14, 15, 16, 20, 22         |
| 12-4    | Perform calculations of concentration involving molarity.   | 12-4, 12-5, 12-6    | 4a, 4c, 4e     | 23, 24, 25, 26, 27         |
|         | Perform calculations involving the dilution of concentrated solutions.  | 12-7, 12-8          | 4b, 4d, 4e     | 34, 35, 37, 40, 42         |
| 12-5    | Perform calculations involving titrations and other solution stoichiometry.   | 12-9, 12-10, 12-11  | 5a, 5b, 5c     | 44, 45, 47, 49, 50, 51, 53 |
| 12-6    | Explain the differences between nonelectrolytes, strong electrolytes, and weak electrolytes.                            |                     | 6a, 6b         | 56, 57                     |
| 12-7    | Explain how the presence of a solute in water affects its physical properties.  |                     | 7a, 7d         | 60, 62, 66, 67             |
|         | Calculate the boiling and melting points of aqueous solutions of nonelectrolytes and electrolytes.                      | 12-12, 12-13, 12-14 | 7b, 7c         | 64, 71, 72, 73, 74, 75, 80 |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

12-1(a) (a) yes (b) yes (c) no (d) yes (e) yes

## 12-1(b)

(a)  $2\text{NH}_4^+(aq) + \text{Cr}_2\text{O}_7^{2-}(aq)$  (b)  $\text{H}^+(aq) + \text{NO}_3^-(aq)$   
 (c)  $\text{CH}_3\text{COCH}_3(aq)$  (d)  $\text{Zn}^{2+}(aq) + 2\text{Br}^-(aq)$

12-1(c) (a) ion-dipole (b) hydrogen bonding (c) London force (the only force between nonpolar molecules)

12-1(d) The term *dissociates* here means “to break apart.” The chemical is already ionic, so the water merely separates the positive ion from the negative ion. In the case of  $\text{HNO}_3$ , the compound was originally molecular in nature. But due to the strong interaction with water, the water was able to *ionize* the acid, or form ions out of the individual particles, so that what ends up dissolved is  $\text{H}^+$  and  $\text{NO}_3^-$ .

12-2(a) If a soluble compound dissolves to the limit of its solubility at a given temperature, the solution is saturated; if the solute is not dissolved to the limit, the solution is unsaturated. If more solute is present than indicated by its solubility, the solution is supersaturated and the excess solute may eventually form a precipitate. Solids generally become more soluble at higher temperatures, whereas gases become less soluble. An increase in partial pressure of a gas above a liquid increases its solubility.

12-2(b) (a)  $\text{Cl}_2$  is a gas. It is more soluble at low temperature and high pressures. (b)  $\text{Na}_2\text{SO}_4$  is an ionic solid, it is more soluble at high temperatures but pressure has no effect.

12-2(c) (a) supersaturated (b) unsaturated (c) saturated (d) unsaturated

12-2(d) Something that large should be ground up into smaller particles to increase the surface area. Since it's an ionic solid, the solvent can be gently heated to help dissolve the solid. Stirring or swirling the flask usually helps as well.

12-3(a) 8.0 g KBr/100 g solution, 8.0 g KBr/92 g  $\text{H}_2\text{O}$ , and 92 g  $\text{H}_2\text{O}$ /100 g solution

12-3(b)  $15.0 \text{ g}/60.0 \text{ g} = 25.0\%$  by mass

12-3(c) 154 g of solvent

12-3(d) (a)  $2.5 \times 10^{-5}\%$  (b) 0.25 ppm (c) 250 ppb

Based on the size of the numbers, the ppb gives the most appropriately sized value.

12-4(a) 2.00 M

12-4(b) 0.200 M

12-4(c) 6.23 g KI

12-4(d) 16.7 mL of 6.00 M  $\text{H}_2\text{SO}_4$

**12-4(e)** (a) Using a 250-mL volumetric flask, measure out 7.31 g of NaCl. Transfer the solid into the flask. Fill the flask halfway with water and swirl until all the solid is dissolved. Fill the flask the rest of the way, using a dropper at the end to get the volume to the volumetric line. Cap and invert several times. (b) Using a buret, dispense 41.7 mL of 3.00 M NaCl solution into a 250-mL volumetric flask. Fill the rest of the way with water, swirling to ensure thorough mixing. Use a dropper at the end to get the volume to the volumetric line. Cap and invert several times.

**12-5(a)** 13.5 mL of 0.125 M Ca(OH)<sub>2</sub>

**12-5(b)** 1.26 M HCl

**12-5(c)**  $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$   
6.25 M HCl

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Aqueous Solutions (SECTION 12-1)

**12-1.** When an ionic compound dissolves in water, what forces in the crystal resist the solution process? What forces between water molecules and the crystal remove the ions from the lattice?

**12-2.** When a sample of KOH is placed in water, a homogeneous mixture of KOH is formed. Which is the solute, which is the solvent, and which is the solution?

**12-3.** Calcium bromide readily dissolves in water, but lead(II) bromide does not. Liquid benzene and water form a heterogeneous mixture, but liquid isopropyl alcohol and water mix thoroughly. Which of the above is said to be miscible, which immiscible, which insoluble, and which soluble?

**12-4.** Write equations illustrating the solution of each of the following ionic compounds in water.

- |   |  |
|---|--|
| (a) LiF   | (c) Na <sub>2</sub> CO <sub>3</sub>                                |
| (b) (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> | (d) Ca(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> |

**12-5.** Write equations illustrating the solution of each of the following ionic compounds in water.

- |   |  |
|---|--|
| (a) BaCl <sub>2</sub>                               | (c) Cr(NO <sub>3</sub> ) <sub>3</sub>  |
| (b) Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | (d) Mg(ClO <sub>4</sub> ) <sub>2</sub> |

**12-6.** Formaldehyde (H<sub>2</sub>CO) dissolves in water without formation of ions. Write the Lewis structure of formaldehyde and show what types of interactions between solute and solvent are involved.

**12-7.** Nitric acid is a covalent compound that dissolves in water to form ions, as does HCl. Write the equation illustrating its solution in water.

### Temperature and Solubility (SECTION 12-2)

**12-8.** Referring to Figure 12-5, determine which of the following compounds is most soluble at 10°C: NaCl, KCl, or Li<sub>2</sub>SO<sub>4</sub>. Which is most soluble at 70°C?

## PART B

### EXERCISES

**12-6(a)** (a) strong electrolytes (b) weak electrolytes (c) nonelectrolytes (d) strong electrolytes (e) nonelectrolytes (f) weak electrolytes

**12-6(b)** (a) weak electrolyte (b) strong electrolyte (c) nonelectrolyte

**12-7(a)** (a) liquid B (b) liquid A (c) liquid B

**12-7(b)** 3.53 m

**12-7(c)** -5.58°C for the nonelectrolyte solute; -16.7°C for CaCl<sub>2</sub>

**12-7(d)** The effect of acetic acid would be somewhere between a nonelectrolyte solute, which produces one particle per mole, and NaCl, which produces two particles per mole. Acetic acid is a weak electrolyte, which means only a small percent of the molecules are ionized. In fact, its effect would be only slightly greater than that of a nonelectrolyte.

**12-9.** Referring to Figure 12-5, determine what mass of each of the following dissolves in 250 g of H<sub>2</sub>O at 60°C: KBr, KCl, and Li<sub>2</sub>SO<sub>4</sub>.

**12-10.** Referring to Figure 12-5, determine whether each of the following solutions is saturated, unsaturated, or supersaturated. (All are in 100 g of H<sub>2</sub>O.)

- |                                      |                          |
|--------------------------------------|--------------------------|
| (a) 40 g of KNO <sub>3</sub> at 40°C | (c) 75 g of KBr at 80°C  |
| (b) 40 g of KNO <sub>3</sub> at 20°C | (d) 20 g of NaCl at 40°C |

**12-11.** A 200-g sample of water is saturated with KNO<sub>3</sub> at 50°C. What mass of KNO<sub>3</sub> forms as a precipitate if the solution is cooled to the freezing point of water? (Refer to Figure 12-5.)

**12-12.** A 500-mL portion of water is saturated with Li<sub>2</sub>SO<sub>4</sub> at 0°C. What happens if the solution is heated to 100°C? (Refer to Figure 12-5.)

### Percent by Mass (SECTION 12-3)

**12-13.** What is the percent by mass of solute in a solution made by dissolving 9.85 g of Ca(NO<sub>3</sub>)<sub>2</sub> in 650 g of water?

**12-14.** What is the percent by mass of solute if 14.15 g of NaI is mixed with 75.55 g of water?

**12-15.** A solution is 10.0% by mass NaOH. How many moles of NaOH are dissolved in 150 g of solution?

**12-16.** A solution contains 15.0 g of NH<sub>4</sub>Cl in water and is 8.50% NH<sub>4</sub>Cl. What is the mass of water present?

**12-17.** A solution is 23.2% by mass KNO<sub>3</sub>. What mass of KNO<sub>3</sub> is present in each 100 g of H<sub>2</sub>O?

**12-18.** A solution contains 1 mol of NaOH dissolved in 9 mol of ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH). What is the percent by mass NaOH?

**12-19.** Blood contains 10 mg of calcium ions in 100 g of blood serum (solution). What is this concentration in ppm?

**12-20.** A high concentration of mercury in fish is 0.5 ppm. What mass of mercury is present in each kilogram of fish? What is this concentration in ppb?

**12-21.** Seawater contains  $1.2 \times 10^{-2}$  ppb of gold ions. If all the gold could be extracted, what volume in liters of seawater is needed to produce 1.00 g of gold? (Assume the density of seawater is the same as that of pure water.)

**12-22.** The maximum allowable level of lead in drinking water is 50 ppb. What mass of lead in milligrams is contained in a small swimming pool containing 5000 gallons of water? (Assume that the density of the water is the same as that of pure water.)

### Molarity (SECTION 12-4)

**12-23.** What is the molarity of a solution made by dissolving 2.44 mol of NaCl in enough water to make 4.50 L of solution?

**12-24.** Fill in the blanks.

| Solute           | M     | Amount of Solute | Volume of Solution |
|------------------|-------|------------------|--------------------|
| (a) KI           | _____ | 2.40 mol         | 2.75 L             |
| (b) $C_2H_5OH$   | _____ | 26.5 g           | 410 mL             |
| (c) $Na_2C_2O_4$ | 0.255 | 3.15 mol         | _____ L            |
| (d) $LiNO_2$     | 0.625 | _____ g          | 1.25 L             |
| (e) $BaCl_2$     | _____ | 0.250 mol        | 850 mL             |
| (f) $Na_2SO_3$   | 0.054 | _____ mol        | 0.45 L             |
| (g) $K_2CO_3$    | 0.345 | 14.7 g           | _____ mL           |
| (h) LiOH         | 1.24  | _____ g          | 1650 mL            |
| (i) $H_2SO_4$    | 0.905 | 0.178 g          | _____ mL           |

**12-25.** What is the molarity of a solution of 345 g of Epsom salts ( $MgSO_4 \cdot 7H_2O$ ) in 7.50 L of solution?

**12-26.** What mass of  $CaCl_2$  is in 2.58 L of a solution with a concentration of 0.0784 M?

**12-27.** What volume in liters of a 0.250 M solution contains 37.5 g of KOH?

**12-28.** What is the molarity of a solution made by dissolving  $2.50 \times 10^{-4}$  g of baking soda ( $NaHCO_3$ ) in enough water to make 2.54 mL of solution?

**12-29.** What are the molarities of the hydroxide ion and the barium ion if 13.5 g of  $Ba(OH)_2$  is dissolved in enough water to make 475 mL of solution?

**12-30.** What is the molarity of each ion present if 25.0 g of  $Al_2(SO_4)_3$  is present in 250 mL of solution?

**\*12-31.** A solution is 25.0% by mass calcium nitrate and has a density of 1.21 g/mL. What is its molarity?

**\*12-32.** A solution of concentrated NaOH is 16.4 M. If the density of the solution is 1.43 g/mL, what is the percent by mass NaOH?

**\*12-33.** Concentrated nitric acid is 70.0%  $HNO_3$  and 14.7 M. What is the density of the solution?

### Dilution (SECTION 12-4)

**12-34.** What volume of 4.50 M  $H_2SO_4$  should be diluted with water to form 2.50 L of 1.50 M acid?

**12-35.** If 450 mL of a certain solution is diluted to 950 mL with water to form a 0.600 M solution, what was the molarity of the original solution?

**12-36.** One liter of a 0.250 M solution of NaOH is needed. The only available solution of NaOH is a 0.800 M solution. Describe how to make the desired solution.

**12-37.** What is the volume in liters of a 0.440 M solution if it was made by dilution of 250 mL of a 1.25 M solution?

**12-38.** What is the molarity of a solution made by diluting 3.50 L of a 0.200 M solution to a volume of 5.00 L?

**12-39.** What volume of water in milliliters should be added to 1.25 L of 0.860 M HCl so that its molarity will be 0.545?

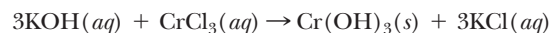
**12-40.** What volume of water in milliliters should be added to 400 mL of a solution containing 35.0 g of KBr to make a 0.100 M KBr solution?

**\*12-41.** What volume in milliliters of pure acetic acid should be used to make 250 mL of 0.200 M  $HC_2H_3O_2$ ? (The density of the pure acid is 1.05 g/mL.)

**\*12-42.** What would be the molarity of a solution made by mixing 150 mL of 0.250 M HCl with 450 mL of 0.375 M HCl?

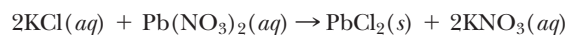
### Stoichiometry and Titrations (SECTION 12-5)

**12-43.** Given the reaction



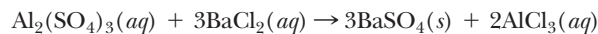
what mass of  $Cr(OH)_3$  would be produced if 500 mL of 0.250 M KOH were added to a solution containing excess  $CrCl_3$ ?

**12-44.** Given the reaction



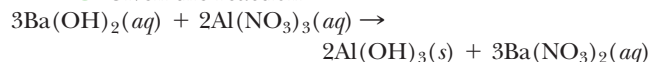
what mass of  $Pb(NO_3)_2$  is required to react with 1.25 L of 0.550 M KCl?

**12-45.** Given the reaction



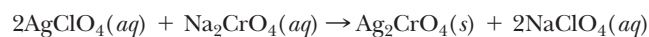
what mass of  $BaSO_4$  is produced from 650 mL of 0.320 M  $Al_2(SO_4)_3$ ?

**12-46.** Given the reaction



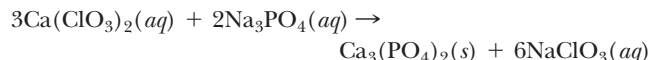
what volume of 1.25 M  $Ba(OH)_2$  is required to produce 265 g of  $Al(OH)_3$ ?

**12-47.** Given the reaction



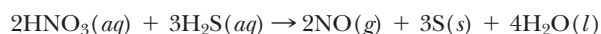
what volume of a 0.600 M solution of  $AgClO_4$  is needed to produce 160 g of  $Ag_2CrO_4$ ?

**12-48.** Given the reaction



what volume of a 2.22 M solution of  $Na_3PO_4$  is needed to react with 580 mL of a 3.75 M solution of  $Ca(ClO_3)_2$ ?

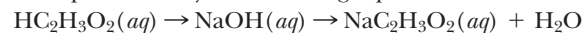
**12-49.** Consider the reaction



(a) What volume of 0.350 M  $HNO_3$  will completely react with 275 mL of 0.100 M  $H_2S$ ?

(b) What volume of NO gas measured at 27°C and 720 torr will be produced from 650 mL of 0.100 M  $H_2S$  solution?

**12-50.** The concentration of acetic acid in vinegar can be determined by titration with sodium hydroxide. This reaction is represented by the following equation.

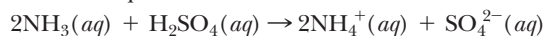


What is the concentration of acetic acid in 10.0 mL of vinegar if it takes 28.8 mL of 0.300 M NaOH to reach the end point?



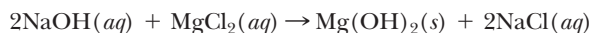
**12-51.** A household antibacterial cleanser is made from a solution of sodium hydroxide. What is its concentration of NaOH if it takes 42.5 mL of 0.0500 M HCl to titrate 25.0 mL of the cleanser to the end point?

**12-52.** Dilute aqueous solutions of ammonia are used as cleansers, especially for grease stains. What is the concentration of the ammonia in the cleanser if 22.6 mL of 0.220 M sulfuric acid is needed to titrate 10.0 mL of the ammonia solution? The equation for neutralization is



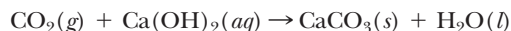
**12-53.** What is the molarity of 1.00 L of HNO<sub>3</sub> solution if it reacts completely with 25.0 g of Ca(OH)<sub>2</sub>?

**\*12-54.** Given the reaction



what mass of Mg(OH)<sub>2</sub> would be produced by mixing 250 mL of 0.240 M NaOH with 400 mL of 0.100 M MgCl<sub>2</sub>?

**\*12-55.** Given the reaction



what is the molarity of a 1.00 L solution of Ca(OH)<sub>2</sub> that would completely react with 10.0 L of CO<sub>2</sub> measured at 25°C and 0.950 atm?

### Properties of Solutions (SECTIONS 12-6 AND 12-7)

**12-56.** Three hypothetical binary compounds dissolve in water. AB is a strong electrolyte, AC is a weak electrolyte, and AD is a nonelectrolyte. Describe the extent to which each of these solutions conducts electricity and how each compound exists in solution.

**12-57.** Chlorous acid (HClO<sub>2</sub>) is a weak electrolyte, and perchloric acid (HClO<sub>4</sub>) is a strong electrolyte. Write equations illustrating the different behaviors of these two polar covalent molecules in water.

**12-58.** Explain the difference in the following three terms: 1 mole NaBr, 1 molar NaBr, and 1 molal NaBr.

**12-59.** What is the molality of a solution made by dissolving 25.0 g of NaOH in (a) 250 g of water and (b) 250 g of alcohol (C<sub>2</sub>H<sub>5</sub>OH)?

**12-60.** What is the molality of a solution made by dissolving 1.50 kg of KCl in 2.85 kg of water?

**12-61.** What mass of NaOH is in 550 g of water if the concentration is 0.720 *m*?

**12-62.** What mass of water is in a 0.430 *m* solution containing 2.58 g of CH<sub>3</sub>OH?

**12-63.** What is the freezing point of a 0.20 *m* aqueous solution of a nonelectrolyte?

**12-64.** What is the boiling point of a 0.45 *m* aqueous solution of a nonelectrolyte?

**12-65.** When immersed in salty ocean water for an extended period, a person gets very thirsty. Explain.

**12-66.** Dehydrated fruit is wrinkled and shriveled up. When put in water, the fruit expands and becomes smooth again. Explain.

**12-67.** Explain how pure water can be obtained from a solution without boiling.

**12-68.** In industrial processes, it is often necessary to concentrate a dilute solution (much more difficult than diluting a concentrated solution). Explain how the principle of reverse osmosis can be applied.

**\*12-69.** What is the molality of an aqueous solution that is 10.0% by mass CaCl<sub>2</sub>?

**\*12-70.** A 1.00 *m* KBr solution has a mass of 1.00 kg. What is the mass of the water?

**\*12-71.** Ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) is used as an antifreeze. What mass of ethylene glycol should be added to 5.00 kg of water to lower the freezing point to -5.0°C? (Ethylene glycol is a nonelectrolyte.)

**\*12-72.** What is the boiling point of the solution in problem 12-71?

**\*12-73.** Methyl alcohol can also be used as an antifreeze. What mass of methyl alcohol (CH<sub>3</sub>OH) must be added to 5.00 kg of water to lower its freezing point to -5.0°C?

**12-74.** What is the molality of an aqueous solution that boils at 101.5°C?

**12-75.** What is the boiling point of a 0.15 *m* solution of a solute in liquid benzene? (For benzene, *K*<sub>b</sub> = 2.53, and the boiling point of pure benzene is 80.1°C.)

**12-76.** What is the boiling point of a solution of 75.0 g of naphthalene (C<sub>10</sub>H<sub>8</sub>) in 250 g of benzene? (See problem 12-75.)

**12-77.** What is the freezing point of a solution of 100 g of CH<sub>3</sub>OH in 800 g of benzene? (For benzene, *K*<sub>f</sub> = 5.12, and the freezing point of pure benzene is 5.5°C.)

**12-78.** What is the freezing point of a 10.0% by mass solution of CH<sub>3</sub>OH in benzene? (See problem 12-77.)

**12-79.** A 1 *m* solution of HCl lowers the freezing point of water almost twice as much as a 1 *m* solution of HF. Explain.

**12-80.** What is the freezing point of automobile antifreeze if it is 40.0% by mass ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) in water? (Ethylene glycol is a nonelectrolyte.)

**12-81.** In especially cold climates, methyl alcohol (CH<sub>3</sub>OH) may be used as an automobile antifreeze. Would a 40.0% by mass of an aqueous solution of methyl alcohol remain a liquid at 40°C? (Methyl alcohol is a nonelectrolyte.)

**\*12-82.** Give the freezing point of each of the following in 100 g of water.

(a) 10.0 g of CH<sub>3</sub>OH (b) 10.0 g of NaCl (c) 10.0 g of CaCl<sub>2</sub>

### General Problems

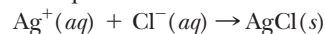
**12-83.** A mixture is composed of 10 g of KNO<sub>3</sub> and 50 g of KCl. What is the approximate amount of KCl that can be separated using the difference in solubility shown in Figure 12-5.

**12-84.** KBr and KNO<sub>3</sub> have equal solubilities at about 42°C. What is the composition of the precipitate if 100 g of H<sub>2</sub>O saturated with these two salts at 42°C is then cooled to 0°C? (Refer to Figure 12-5.)

**12-85.** What is the percent composition by mass of a solution made by dissolving 10.0 g of sugar and 5.0 g of table salt in 150 mL of water?

**12-86.** What is the molarity of each ion in a solution that is 0.15 M CaCl<sub>2</sub>, 0.22 M Ca(ClO<sub>4</sub>)<sub>2</sub>, and 0.18 M NaCl?

**\*12-87.** 500 mL of 0.20 M AgNO<sub>3</sub> is mixed with 500 mL of 0.30 M NaCl. What is the concentration of Cl<sup>-</sup> ion in the solution? The net ionic equation of the reaction that occurs is



**\*12-88.** 400 mL of 0.15 M Ca(NO<sub>3</sub>)<sub>2</sub> is mixed with 500 mL of 0.20 M Na<sub>2</sub>SO<sub>4</sub>. Write the net ionic equation of the precipitation reaction that occurs. Of the two anions involved,



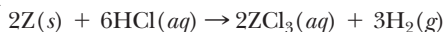
which remains in solution after precipitation? What is its concentration?

**\*12-89.** A certain metal (M) reacts with HCl according to the equation



1.44 g of the metal reacts with 225 mL of 0.196 M HCl. What is the metal?

**\*12-90.** Another metal (Z) also reacts with HCl according to the equation



24.0 g of Z reacts with 0.545 L of 2.54 M HCl. What is the metal? What volume of  $H_2$  measured at STP is produced?

**\*12-91.** A certain compound dissolves in a solvent known as nitrobenzene. For nitrobenzene,  $K_f = 8.10$ . A solution with 3.07 g of the compound dissolved in 120 g of nitrobenzene freezes at  $2.22^\circ\text{C}$ . The freezing point of pure nitrobenzene is  $5.67^\circ\text{C}$ . Analysis of the compound shows it to be 40.0% C, 13.3% H, and 46.7% N. What is the formula of the compound?

**12-92.** Given 1.00 *m* aqueous solutions of (a)  $\text{Na}_3\text{PO}_4$ , (b)  $\text{CaCl}_2$ , (c) urea (a nonelectrolyte), (d)  $\text{Al}_2(\text{SO}_4)_3$ , and (e) LiBr. Order these solutions from highest to lowest freezing points and explain.

**12-93.** Order the following solutions from lowest to highest boiling points.

- (a) 0.30 *m* sugar (a nonelectrolyte)    (d) 0.12 *m* KCl  
 (b) pure water    (e) 0.05 *m*  $\text{CrCl}_3$   
 (c) 0.05 *m*  $\text{K}_2\text{CO}_3$

**\*12-94.** One mole of an electrolyte dissolves in water to form three moles of ions. A 9.21-g quantity of this compound is dissolved in 175 g of water. The freezing point of this solution is  $-1.77^\circ\text{C}$ . The compound is 47.1% K, 14.5% C, and 38.6% O. What is the formula of this compound?

**\*12-95.** A sample of a metal reacts with water to form 487 mL of a 0.120 M solution of the metal hydroxide along with 753 mL of hydrogen gas measured at  $25^\circ\text{C}$  and 0.650 atm. Is the metal Na or Ca?

**12-96.** What volume of  $\text{NH}_3$  measured at 0.951 atm and  $25^\circ\text{C}$  is needed to form 250 mL of 0.450 M aqueous ammonia?

**12-97.** A 1.82-L volume of gaseous  $\text{H}_2\text{S}$  measured at 1.08 atm and  $20^\circ\text{C}$  is dissolved in water. What is the molarity of the aqueous  $\text{H}_2\text{S}$  if the volume of the solution is 2.00 L?

**12-98.** Sodium bicarbonate reacts with hydrochloric acid to form water, sodium chloride, and carbon dioxide gas. What volume of  $\text{CO}_2$  measured at  $35^\circ\text{C}$  and 1.00 atm could be released by the reaction of 1.00 L of a 0.340 M solution of sodium bicarbonate with excess hydrochloric acid solution?

**12-99.** Aqueous calcium hydroxide solutions absorb gaseous carbon dioxide to form calcium bicarbonate solutions. What mass of calcium bicarbonate would be formed by reaction of 25.0 mL of 0.150 M calcium hydroxide with 450 mL of gaseous carbon dioxide measured at STP?

**\*12-100.** The molecules of a compound are composed of one phosphorus and multiple chlorine atoms. A molecule of the compound is described as a trigonal pyramid. This gaseous compound dissolves in water to form a hydrochloric acid solution and phosphoric acid ( $\text{H}_3\text{PO}_3$ ). What is the molarity of the hydrochloric acid if 750 mL of the gas, measured at STP, dissolves in 250 mL of water?

**\*12-101.** A phosphorus–oxygen compound is 43.7% phosphorus. When the compound dissolves in water, it forms one compound, phosphoric acid. If 0.100 mol of the phosphorus–oxygen compound dissolves in 4.00 L of water to form a 0.100 M solution of phosphoric acid, what is the formula of the original compound?

**\*12-102.** A 10.0-g quantity of a compound is dissolved in 100 g of water. The solution formed has a melting point of  $-7.14^\circ\text{C}$ . Is the compound KCl,  $\text{Na}_2\text{S}$ , or  $\text{CaCl}_2$ ?

**12-103.** An aqueous solution has a freezing point of  $-2.50^\circ\text{C}$ . What is its boiling point?

**\*12-104.** An aqueous solution of a nonelectrolyte is made by dissolving the solute in 1.00 L of water. The solution has a freezing point of  $-1.50^\circ\text{C}$ . What volume of water must be added to change the freezing point to  $-1.15^\circ\text{C}$ ?

**\*12-105.** An aqueous solution of a nonelectrolyte in 500 mL of water has a boiling point of  $100.86^\circ\text{C}$ . How many moles of solute must be added so that the solution freezes at  $-2.06^\circ\text{C}$ ?

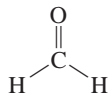
## STUDENT WORKSHOP

### Determining the Dipole of Planar Molecules

**Purpose:** To estimate the dipole moment of several simple molecules based on molecular shape and bond polarity. (Work in groups of three or four. Estimated time: 25 min.)

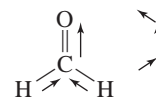
As we have seen in this chapter, polarity plays a major role in determining what compounds will dissolve in what solvents. “Like dissolves like” is a saying that indicates that polar solutes dissolve in polar solvents and nonpolar solutes dissolve in nonpolar solvents. Slightly polar solutes might dissolve in either, but certainly slightly polar solvents would be our first choice. The degree of polarity of a molecule can be estimated by the following activity. We will use only linear and planar molecules for simplicity. As an example, we will evaluate the polarity of formaldehyde,  $\text{CH}_2\text{O}$ .

1. Draw the Lewis structure of the molecule, attempting to be faithful to the bond angles predicted by VSEPR theory.



2. Draw arrows next to each bond, pointing in the direction of the more electronegative atom.

The length of the arrow should be proportional to the difference in electronegativity between the two atoms. In this case, oxygen is significantly more electronegative than carbon, which is slightly more electronegative than hydrogen.



3. Next to the structure on the paper, redraw the arrows, tail to tip, in any order, maintaining their exact orientation.

4. Connect the tail of the first arrow to the tip of the last with another arrow. This last arrow represents the dipole of the molecule. The longer it is, the more polar the molecule, and it points toward the molecule's negative end. If the tail and tip are exactly in the same place, then there is no dipole, and the molecule is nonpolar.

Using the above procedure, evaluate the dipoles of the following molecules or ions:

- $\text{H}_2\text{O}$     •  $\text{SO}_2$     • HCN    •  $\text{CO}_2$     •  $\text{COCl}_2$     •  $\text{NO}_3^-$

CHAPTER  
13

# Acids, Bases, and Salts



**T**he lemon is known for its sour taste, which is caused by citric acid.

Acids are a unique class of compounds that are discussed in this chapter.

**PART A**  
**ACIDS, BASES, AND THE**  
**FORMATION OF SALTS**

**13-1** Properties of Acids and Bases

**13-2** Brønsted–Lowry Acids and Bases

**13-3** Strengths of Acids and Bases

**13-4** Neutralization and the Formation  
of Salts



**MAKING IT REAL**

*Salts and Fingerprint Imaging*

**PART B**  
**THE MEASUREMENT**  
**OF ACID STRENGTH**

**13-5** Equilibrium of Water

**13-6** The pH Scale

**PART C**  
**SALTS AND OXIDES AS**  
**ACIDS AND BASES**

**13-7** The Effect of Salts on pH—  
Hydrolysis

**13-8** Control of pH—Buffer Solutions



**MAKING IT REAL**

*The pH Balance in the Blood*

**13-9** Oxides as Acids and Bases



**MAKING IT REAL**

*Acid Rain—The Price of Progress?*

**SETTING THE STAGE** It can make your mouth pucker, your body shudder, and your eyes water. That's the reaction one gets from taking a bite of a fresh lemon. A taste of vinegar has the same effect. Even carbonated beverages produce a subtle sour taste that peeps up the drink. All these substances have a similar effect because of the presence of a compound that produces a sour taste (but to different degrees). These compounds, known as acids, were characterized over 500 years ago, during the Middle Ages, in the chemical laboratories of alchemists. Substances were classified as acids because of their common properties (such as sourness) rather than a certain chemical composition. Acids are well known to the general population. They are very common in foods and drugs, such as citric acid in lemons, acetic acid in vinegar, lactic acid in sour milk, or acetylsalicylic acid in aspirin. Some must be handled with caution, such as sulfuric acid used in car batteries, or hydrochloric acid, used to clean concrete. We also relate the word *acid* to the serious environmental hazard of acid rain. When rain is acidic, reactions characteristic of acids lead to the degradation of stone used in buildings and the liberation of poisonous metal ions locked in soil.

We briefly introduced acids, bases, and the reaction between them in Section 5-6.2. At that time we restricted our discussion to strong acids and bases. We have covered quite a bit of chemistry since Chapter 5, so we will reexamine this important topic in more detail. We can expand on our discussion of these compounds by including weak acids and bases.

In Part A of this chapter, we will review and expand on the concept of acids and bases introduced in earlier chapters. How acidity is measured and reported is the emphasis of Part B. Finally, we expand the concept of acids and bases even further to include salts, buffers, and oxides in Part C.

## PART A ACIDS, BASES, AND THE FORMATION OF SALTS

### SETTING A GOAL

- You will expand your knowledge of acids and bases with more general definitions that allow us to examine their comparative strengths.

### OBJECTIVES

- 13-1** List the general properties of acids and bases.
- 13-2 (a)** Identify the Brønsted acids and bases in a proton exchange reaction. **(b)** Identify conjugate acid–base pairs.
- 13-3** Calculate the hydronium ion concentration in a solution of a strong acid and a weak acid given the initial concentration of the acid and the percent ionization of the weak acid.
- 13-4** Write the molecular, total ionic, and net ionic equations for neutralization reactions.

### ▶ OBJECTIVE FOR SECTION 13-1

List the general properties of acids and bases.



**FIGURE 13-1** Zinc and Limestone in Acid Zinc (top) reacts with acid to liberate hydrogen; limestone ( $\text{CaCO}_3$ , bottom) reacts with acid to liberate carbon dioxide.

## 13-1 PROPERTIES OF ACIDS AND BASES



**LOOKING AHEAD!** Historically, well before scientists knew much about their compositions, acids and bases were classified as such based on their common properties. These common properties relate to a specific “active ingredient.” The nature of these properties and the active ingredients are the topics of this section. ■

The sour taste of acids accounts for the origin of the word itself. The word *acid* originates from the Latin *acidus*, meaning “sour,” or the closely related Latin *acetum*, meaning “vinegar.” This ancient class of compounds has several characteristic chemical properties. Acids are compounds that do the following:

- Taste sour (of course, one *never* tastes laboratory chemicals)
- React with certain metals (e.g., Zn and Fe), with the liberation of hydrogen gas (see Figure 13-1)
- Cause certain organic dyes to change color (e.g., litmus paper turns from blue to red in acids)
- React with limestone ( $\text{CaCO}_3$ ), with the liberation of carbon dioxide gas (see Figure 13-1)
- React with bases to form salts and water

Some familiar acids, their common names, and their formulas are shown below.

| CHEMICAL NAME     | COMMON NAME                  | FORMULA                           |
|-------------------|------------------------------|-----------------------------------|
| hydrochloric acid | muratic acid                 | HCl                               |
| sulfuric acid     | oil of vitriol, battery acid | $\text{H}_2\text{SO}_4$           |
| acetic acid       | vinegar (sour ingredient)    | $\text{HC}_2\text{H}_3\text{O}_2$ |
| carbonic acid     | carbonated water             | $\text{H}_2\text{CO}_3$           |

The counterparts to acids are bases. Bases are compounds that do the following:

- Taste bitter
- Feel slippery or soapy
- Dissolve oils and grease
- Cause certain organic dyes to change color (e.g., litmus paper turns from red to blue in bases)
- React with acids to form salts and water

### 13-1.1 Arrhenius Acids and Bases

The properties listed above relate to what acids and bases do, not to their chemical composition. It was not until 1884 that a Swedish chemist, Svante Arrhenius, suggested that the particular composition of these compounds determined their behavior. *He proposed that acids produced  $H^+$  ions and bases produced  $OH^-$  ions in water.*

### 13-1.2 Strong Acids in Water

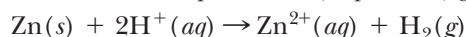
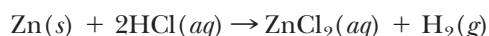
The ionization process of acids in water was illustrated in Figure 12-3 in the previous chapter. To illustrate the importance of water in the ionization process, the reaction of an acid with water can be represented as



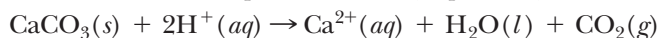
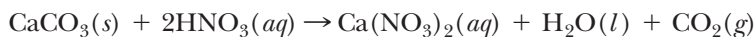
*Instead of  $H^+$ , the acid species is often represented as  $H_3O^+$ , which is known as the hydronium ion.* The hydronium ion is simply a representation of the  $H^+$  ion in a hydrated form. The acid species is represented as  $H_3O^+$  rather than  $H^+$  because it is somewhat closer to what is believed to be the actual species. In fact, the nature of  $H^+$  in aqueous solution is even more complex than  $H_3O^+$  (i.e.,  $H_5O_2^+$ ,  $H_7O_3^+$ , etc.). In any case, the acid species can be represented as  $H^+(aq)$  or  $H_3O^+(aq)$ , depending on the convenience of the particular situation. *Just remember that both refer to the same species in aqueous solution.* If  $H^+(aq)$  is used, it should be understood that it is not just a bare proton in aqueous solution but is associated with water molecules. (It is hydrated.)

It is the current practice to list on the label the active ingredient in medicines or drugs. In this regard, the active ingredient of acids is the  $H^+(aq)$  ion. We can now see how this ion accounts for some of the behavior of acids listed previously. Equation 1 in the list below illustrates the reaction of an acid with a metal. In equation 2, the reaction of an acid with limestone is illustrated. And in equation 3, we show a neutralization reaction. The net ionic equations of these reactions are also shown, which emphasizes the role of the  $H^+(aq)$  ion in each case.

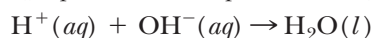
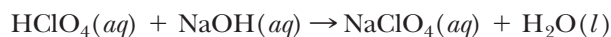
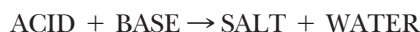
1. Acids react with metals (e.g., Zn) and give off hydrogen gas.



2. Acids react with limestone to give off carbon dioxide gas.



3. Acids react with bases.



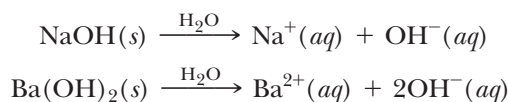
The last reaction is of prime importance and is discussed in more detail in section 13-4.

### 13-1.3 Strong Bases in Water

Now let's turn our attention to bases. Bases are compounds that produce  $OH^-$  ions in water, forming what are known as basic solutions, sometimes referred to as *alkaline* or *caustic* solutions. Some of the commonly known bases are sodium hydroxide (also known as caustic soda, or lye), potassium hydroxide (caustic potash), calcium hydroxide (slaked lime), and ammonia. Except for ammonia, these compounds are



all solid ionic compounds. Forming a solution in water simply releases the  $\text{OH}^-$  ion into the aqueous medium.



The action of ammonia ( $\text{NH}_3$ ) as a base is somewhat different from that of the ionic hydroxides and is better described by a more detailed look at acids and bases in the following section.

**ASSESSING THE  
OBJECTIVE FOR  
SECTION 13-1**

**EXERCISE 13-1(a) KNOWLEDGE:** Fill in the blanks.

An acid is a compound that produces the \_\_\_\_\_ ion in solution, which is also written as the hydronium ion (\_\_\_\_\_). A base is a compound that produces an ion with the formula \_\_\_\_\_ and the name \_\_\_\_\_ ion.

**EXERCISE 13-1(b) ANALYSIS:** Write the formula and name of the acid or base formed from the following ions.

- (a)  $\text{ClO}_4^-$       (b)  $\text{Fe}^{2+}$       (c)  $\text{S}^{2-}$       (d)  $\text{Li}^+$

**EXERCISE 13-1(c) ANALYSIS:** Write a formula of the reaction that occurs when the following compounds are placed in water:

- (a) HI      (b) LiOH

**EXERCISE 13-1(d) SYNTHESIS:** Based on the list of properties of acids and bases, which of the two do the following most likely contain?

- (a) drain cleaner      (d) dishwashing detergent  
(b) orange juice      (e) bleach  
(c) salad dressing      (f) antacid

For additional practice, work chapter problems 13-1, 13-3, 13-5, and 13-6.

**▶ OBJECTIVES FOR  
SECTION 13-2**

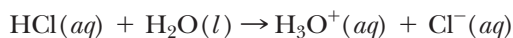
- (a) Identify the Brønsted acids and bases in a proton exchange reaction.  
(b) Identify conjugate acid–base pairs.

## 13-2 BRØNSTED-LOWRY ACIDS AND BASES



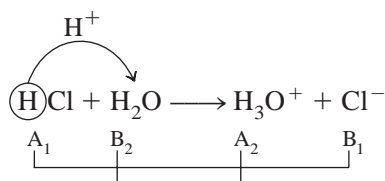
**LOOKING AHEAD!** Besides neutral compounds that act as acids or bases in water, certain ions have acid or base behavior. However, to better describe the action of ions in water, we need a more inclusive definition of acids and bases. We do this in the following discussion. ■

Limestone ( $\text{CaCO}_3$ ) is quite a versatile compound. We can use it as solid rock in the construction of huge buildings or we can use it as a powder in chalk. It is also the major ingredient of many antacids, which are consumed to neutralize excess stomach acid. In this reaction, the carbonate ion ( $\text{CO}_3^{2-}$ ) is the ingredient that reacts as a base (i.e., an antacid). From our previous definition of acids and bases, it is not immediately obvious how an anion such as  $\text{CO}_3^{2-}$  behaves as a base. In order to include anions as bases, we need a broader, more inclusive definition than that of Arrhenius, which focused mainly on molecular compounds. We will now focus on the role of the  $\text{H}^+$  ion in solution. In the **Brønsted-Lowry** definition, an **acid** is a proton ( $\text{H}^+$ ) donor and a **base** is a proton acceptor. To illustrate this definition, we again look at the reaction of HCl as an acid to form the  $\text{H}_3\text{O}^+$  ion.

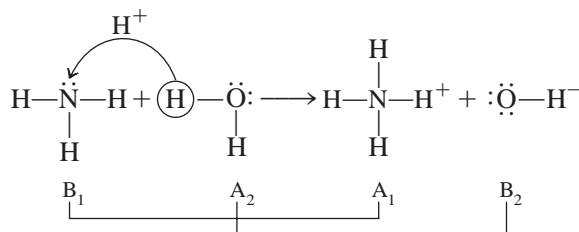


### 13-2.1 Conjugate Acid–Base Pairs

HCl is an acid by the Arrhenius definition because it produces the  $\text{H}_3\text{O}^+$  ion. It is also an acid by the Brønsted–Lowry definition because *it donates an  $\text{H}^+$  to  $\text{H}_2\text{O}$* . In this definition, however, the  $\text{H}_2\text{O}$  molecule also takes on the role of a base because it accepts an  $\text{H}^+$  from the HCl. The reaction of an acid and a base in water can be considered as an exchange of the proton. The species accepting the proton could then conceivably pass it on to another base, and so is itself an acid. In addition, the species losing the proton could potentially accept one from something else and could therefore behave as a base. So, in our example, an acid (HCl) reacts with a base ( $\text{H}_2\text{O}$ ) to form another acid ( $\text{H}_3\text{O}^+$ ) and base ( $\text{Cl}^-$ ). *The base that remains when an acid donates a proton is known as the **conjugate base** of the acid. Likewise, the acid that is formed when the base accepts a proton is known as the **conjugate acid** of the base.* Thus  $\text{HCl} - \text{Cl}^-$  and  $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$  are known as *conjugate acid–base pairs*. The exchange of  $\text{H}^+$  is illustrated below, where  $\text{A}_1$  and  $\text{B}_1$  refer to a specific conjugate acid–base pair and  $\text{A}_2$  and  $\text{B}_2$  refer to the other acid–base pair.



Now consider the reaction of ammonia ( $\text{NH}_3$ ) in water. Ammonia is a base in the Arrhenius definition because it forms  $\text{OH}^-$  in aqueous solution even though the ammonia molecule itself does not contain the  $\text{OH}^-$  ion. If we examine its behavior in water as a Brønsted–Lowry base, however, it becomes more obvious how  $\text{OH}^-$  ions are produced.

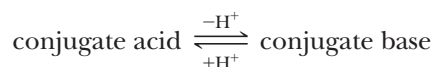


In the Brønsted–Lowry sense, the reaction can be viewed as simply an exchange of an  $\text{H}^+$ . When the base ( $\text{NH}_3$ ) reacts, it adds  $\text{H}^+$  to form its conjugate acid ( $\text{NH}_4^+$ ). When the acid ( $\text{H}_2\text{O}$ ) reacts, it loses an  $\text{H}^+$  to form its base ( $\text{OH}^-$ ). The  $\text{NH}_3$ ,  $\text{NH}_4^+$  ( $\text{B}_1$  and  $\text{A}_1$ ) and the  $\text{H}_2\text{O}$ ,  $\text{OH}^-$  ( $\text{A}_2$  and  $\text{B}_2$ ) pairs are conjugate acid–base pairs.

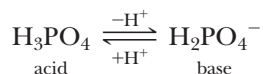
### 13-2.2 Amphiprotic Ions

In the previous reaction,  $\text{H}_2\text{O}$  is an acid since it donates an  $\text{H}^+$  to form  $\text{NH}_4^+$ . Recall that  $\text{H}_2\text{O}$  acts as a base when HCl is present. *A compound or ion that can both donate and accept  $\text{H}^+$  ions is called **amphiprotic**.* Water is amphiprotic since it can accept  $\text{H}^+$  ions when an acid is present or donate  $\text{H}^+$  when a base is present. An amphiprotic substance has both a conjugate acid and a conjugate base. Examples of other amphiprotic substances include  $\text{HS}^-$  and  $\text{H}_2\text{PO}_4^-$ .

Before we look at other examples of Brønsted–Lowry acid–base reactions, we should emphasize the identification of conjugate acids and bases. *The conjugate base of a compound or ion results from removal of an  $\text{H}^+$ . The conjugate acid of a compound or ion results from the addition of an  $\text{H}^+$ .*

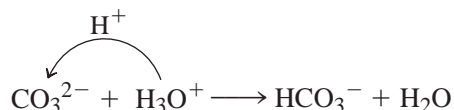


For example,



Notice that in the formation of a conjugate base, the base species ( $\text{H}_2\text{PO}_4^-$ ) has one less hydrogen and the charge decreases by 1 from the acid ( $\text{H}_3\text{PO}_4$ ). The reverse is true for formation of a conjugate acid from a base. That is, the acid has one more hydrogen and the charge increases by 1.

We are now ready to examine how the carbonate ion in calcium carbonate behaves as a base in antacid tablets. The  $\text{CO}_3^{2-}$  ion relieves acidic stomachs (containing excess  $\text{H}_3\text{O}^+$ ) as illustrated by the following proton exchange reaction.



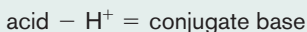
Notice that the carbonate ion acts as a base by accepting the proton from  $\text{H}_3\text{O}^+$  to form its conjugate acid ( $\text{HCO}_3^-$ ), while the  $\text{H}_3\text{O}^+$  ion forms its conjugate base ( $\text{H}_2\text{O}$ ). Decreasing the hydronium ion concentration in the stomach is what is meant by “relief of stomach distress.”

### EXAMPLE 13-1

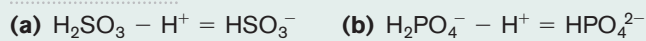
#### Determining Conjugate Bases of Compounds

What are the conjugate bases of (a)  $\text{H}_2\text{SO}_3$  and (b)  $\text{H}_2\text{PO}_4^-$ ?

#### PROCEDURE



#### SOLUTION

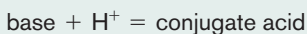


### EXAMPLE 13-2

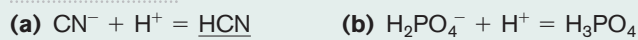
#### Determining Conjugate Acids of Compounds

What are the conjugate acids of (a)  $\text{CN}^-$  and (b)  $\text{H}_2\text{PO}_4^-$ ?

#### PROCEDURE



#### SOLUTION



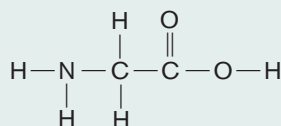
#### ANALYSIS

Notice that in this example the conjugate bases have negative charges and the conjugate acids are neutral. Another example of a conjugate acid–base pair is  $\text{NH}_4^+ - \text{NH}_3$ , where the acid is positively charged and the base is neutral. This illustrates a fairly consistent pattern found in acids and bases. Acids are usually neutral or positively charged species. Bases are usually neutral or negatively charged species. In the case of amphiprotic anions, however, the anion can act as an acid because it contains an acidic hydrogen (e.g.,  $\text{H}_2\text{PO}_4^-$ ).

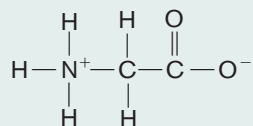
#### SYNTHESIS

Proteins consist of long chains of amino acids. Amino acids are interesting compounds in regards to acid–base pairs and amphiprotism. Just from the name, you might suspect that something is unique. *Amino* is similar to the name *ammonia*, which we know to

be a base, and the term *acid* is unambiguous. Amino acids are well-known amphiprotic compounds. What makes them unique is that the acid–base reaction they undergo can be with themselves! The neutral structure of a simple amino acid is



But in most natural conditions, the acid part on the right of the molecule donates a proton to the base part on the left. This produces the conjugate acid and base on each end of the molecule.



Amino acids thus have properties more typical of ionic compounds (i.e., high melting points). Can you identify the structural regions in the amino acid that form the conjugate acid–base pairs?

### EXAMPLE 13-3

#### Writing Acid–Base Reactions

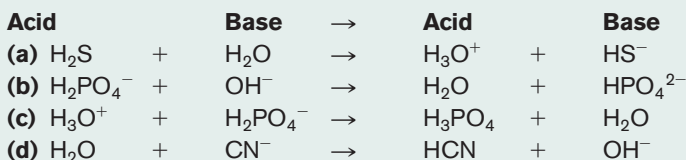
Write the equations illustrating the following Brønsted–Lowry acid–base reactions.

- a.  $\text{H}_2\text{S}$  as an acid with  $\text{H}_2\text{O}$                       c.  $\text{H}_2\text{PO}_4^-$  as a base with  $\text{H}_3\text{O}^+$   
 b.  $\text{H}_2\text{PO}_4^-$  as an acid with  $\text{OH}^-$                       d.  $\text{CN}^-$  as a base with  $\text{H}_2\text{O}$

#### PROCEDURE

A Brønsted–Lowry acid–base reaction produces a conjugate acid and base. Remove an  $\text{H}^+$  from the acid and transfer it to the base to form the products.

#### SOLUTION



#### ANALYSIS

Acid–base reactions always move from the stronger acid–base pair to the weaker pair. So we can examine reactions that work well to help rank acids and bases relative to each other. For instance,  $\text{H}_3\text{O}^+$  reacts completely with  $\text{H}_2\text{PO}_4^-$  to produce the conjugate acid  $\text{H}_3\text{PO}_4$  [part (c)]. This tells us that the hydronium cation is a stronger acid than phosphoric acid. It's also not that surprising that a cation is more acidic than a neutral molecule. We will discuss the relative strengths of acids and bases in more detail in the next section.

#### SYNTHESIS

Note that equations (b) and (c) indicate that the  $\text{H}_2\text{PO}_4^-$  is amphiprotic. Another question that could be asked, especially in equation (a), is what makes  $\text{H}_2\text{S}$  the acid and  $\text{H}_2\text{O}$  the base. Both are neutral, and they're very similar, with sulfur and oxygen both in the Group VIA column. Further, in (b), both species are negative. Why is either an acid? This becomes a question of relative acidic or basic strength of the two species involved, and is explored in the next section.

### ASSESSING THE OBJECTIVES FOR SECTION 13-2

**EXERCISE 13-2(a) KNOWLEDGE:** Fill in the blanks.

In the Brønsted–Lowry definition, acids are \_\_\_\_\_ donors and bases are \_\_\_\_\_ acceptors. A conjugate acid of a compound or ion results from the \_\_\_\_\_ of an \_\_\_\_\_ ion. A substance that has both a conjugate acid and a conjugate base is said to be \_\_\_\_\_.

**EXERCISE 13-2(b) ANALYSIS:** Write the conjugate acid and the conjugate base of the  $\text{HC}_2\text{O}_4^-$  ion.

**EXERCISE 13-2(c) ANALYSIS:** Write the reaction of the  $\text{HCO}_3^-$  ion with water (a) where water acts as a base and (b) where water acts as an acid.

**EXERCISE 13-2(d) SYNTHESIS:** Complete the following reaction of a Brønsted–Lowry proton exchange. What are the two sets of conjugate acid/base pairs?



For additional practice, work chapter problems 13-7, 13-9, 13-11, and 13-13.

**▶ OBJECTIVE FOR SECTION 13-3**

Calculate the hydronium ion concentration in a solution of a strong acid and a weak acid given the initial concentration of the acid and the percent ionization of the weak acid.

## 13-3 STRENGTHS OF ACIDS AND BASES



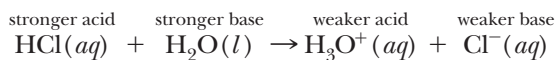
**LOOKING AHEAD!** The properties of acids and bases described in Section 13-1 are mostly associated with strong acids and bases. Other substances display these properties but in less dramatic fashion. For example, dilute acetic acid is sour but tame enough to use on a salad, and ammonia dissolves grease but is mild enough to clean oil stains from floors. There is a wide range of behavior that we regard as acidic or basic. This is the subject of this section. ■

Ammonia as a base would do a poor job of unclogging a stopped-up drain, yet we certainly wouldn't want to use lye to clean an oil spot from a carpet. In the former case, the base is too weak; in the latter, it is much too strong. Strong acids and bases are difficult and dangerous to handle and store. Weak acids and bases are quite easy and safe to have around. The large difference in acid or base behavior relates to the concentration of the active ingredient ( $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ ) produced by the acid or base in water. This depends on its strength. First, we will consider the strength of acids.

### 13-3.1 The Strength of Acids

In Chapter 5, we indicated that strong acids were 100% dissociated into ions in solution. Actually, there are only six common strong acids. In addition to hydrochloric (HCl), which we have already discussed, there are two other binary acids, hydrobromic acid (HBr) and hydroiodic acid (HI). The other strong acids are sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), and perchloric acid ( $\text{HClO}_4$ ). Sulfuric acid is a somewhat more complex case but will be considered shortly.

We have been using the 100% ionization criteria to describe a strong acid, but we still haven't formally answered the question "strong compared to what?" In the Brønsted–Lowry definition, the reaction of a molecular acid with water is considered a proton ( $\text{H}^+$ ) exchange reaction. In fact, there is a competition between the proton-donating abilities of two acids (e.g., HCl and  $\text{H}_3\text{O}^+$ ) and, like other competitions, the stronger prevails. *The stronger acid reacts with the stronger base to produce a weaker conjugate acid and conjugate base. In the case of a strong acid in water, the molecular acid (e.g., HCl) is a stronger proton donor than  $\text{H}_3\text{O}^+$ .* Therefore, the reaction proceeds essentially 100% to the right.

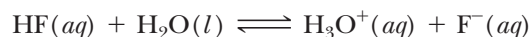


Most acids that we may be familiar with, such as acetic acid, ascorbic acid (vitamin C), and citric acid, are all considered weak acids. The weak acids that we will discuss in this section are also neutral molecular acids. A **weak molecular acid** is *partially ionized (usually less than 5% at typical molar concentrations)*.

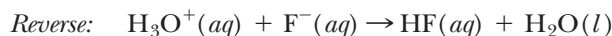
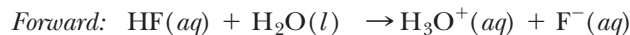
The ionization of a weak acid appears to be limited because it is a reversible reaction. Such a reaction was briefly mentioned in Section 12-6.1, since weak acids are examples of weak electrolytes. We will discuss the concept of reversible reactions and equilibrium in detail in Chapter 15, but a basic understanding of these concepts will



help us understand the action of weak acids and bases in water. The ionization of HF, a weak acid, is as follows.



This is an example of a chemical reaction that reaches a state of equilibrium, which is represented by a double arrow ( $\rightleftharpoons$ ). (A single arrow represents a reaction that essentially goes to completion.) *In a reaction at equilibrium, two reactions are occurring simultaneously.* In the ionization of HF, a forward reaction occurs to the right, producing ions ( $\text{H}_3\text{O}^+$  and  $\text{F}^-$ ), and a reverse reaction occurs to the left, producing the original reactants, which are the molecular compounds HF and  $\text{H}_2\text{O}$ .



*At equilibrium, the forward and reverse reactions occur at the same rate and the concentrations of all species remain constant.* However, the identities of the individual molecules and ions do change. The reaction thus *appears* to have gone to a certain extent and then stopped. In fact, at equilibrium, a *dynamic (constantly changing)* situation exists in which two reactions going in opposite directions at the same rate keep the concentrations of all species constant.

For weak acids, the point of equilibrium lies far to the left side of the original ionization equation. This is because the  $\text{H}_3\text{O}^+$  ion is a stronger proton donor than the HF molecular acid, opposite the case for strong acids. Thus, reactants (the molecular compounds on the left) are favored over the ionic products on the right. In other words, most of the fluorine is present in the form of molecular HF rather than fluoride ions. In a weak acid solution the concentration of the active ingredient,  $\text{H}_3\text{O}^+$ , and the anion is comparatively small (See Figure 13-2.)

In the following discussions and examples we will refer to the percent ionization of the weak acid.

Like all percent problems, the actual amount or concentration of ions present is found by multiplying the total amount of acid initially present by the percent expressed in decimal form, which is obtained by dividing the percent ionization by 100%. Thus, if the original concentration of an acid is 0.20 M and it is 5.0% ionized, the concentration of each ion (the  $\text{H}_3\text{O}^+$  cation and the specific anion) is

$$0.20 \text{ M} \times \frac{5.0\%}{100\%} = 0.20 \text{ M} \times 0.050 = 0.010 \text{ M}$$

The following examples illustrate the difference in acidity (the difference in  $\text{H}_3\text{O}^+$  concentration) between a strong acid and a weak acid. In these examples, *the appearance of a species in brackets (e.g.,  $[\text{H}_3\text{O}^+]$ ) represents the numerical value of the concentration of that species in moles per liter (M).*

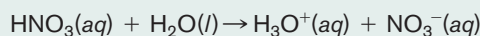
#### EXAMPLE 13-4

##### Calculating the $\text{H}_3\text{O}^+$ Concentration in a Strong Acid Solution

What is  $[\text{H}_3\text{O}^+]$  in a 0.100 M  $\text{HNO}_3$  solution?

##### PROCEDURE

$\text{HNO}_3$  is a strong acid, so the following reaction goes 100% to the right.



**FIGURE 13-2 Strong Acids and Weak Acids** Strong acids are completely ionized in water; weak acids are only partially ionized.

As in other stoichiometry problems involving complete reactions, the amount (or concentration) of a product is found from the amount (or concentration) of a reactant using a mole ratio conversion factor from the balanced equation.

### SOLUTION

$$0.100 \text{ mol/L HNO}_3 \times \frac{1 \text{ mol/L H}_3\text{O}^+}{1 \text{ mol/L HNO}_3} = 0.100 \text{ mol/L H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = \underline{\underline{0.100 \text{ M}}}$$

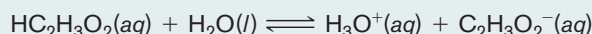
### EXAMPLE 13-5

#### Calculating the $\text{H}_3\text{O}^+$ Concentration in a Weak Acid Solution

What is  $[\text{H}_3\text{O}^+]$  in a 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$  solution that is 1.34% ionized?

### PROCEDURE

Calculate the concentration of  $\text{H}_3\text{O}^+$  from the percent ionization and the initial concentration. Since  $\text{HC}_2\text{H}_3\text{O}_2$  is a weak acid, the following ionization reaches equilibrium when 1.34% of the initial  $\text{HC}_2\text{H}_3\text{O}_2$  is ionized.



The  $[\text{H}_3\text{O}^+]$  is calculated by multiplying the original concentration of acid by the percent expressed in fraction form.

$$[\text{H}_3\text{O}^+] = [\text{original concentration of acid}] \times \frac{\% \text{ ionization}}{100\%}$$

### SOLUTION

In this case,

$$[\text{H}_3\text{O}^+] = [0.100] \times \frac{1.34\%}{100\%} = \underline{\underline{1.34 \times 10^{-3} \text{ M}}}$$

### ANALYSIS

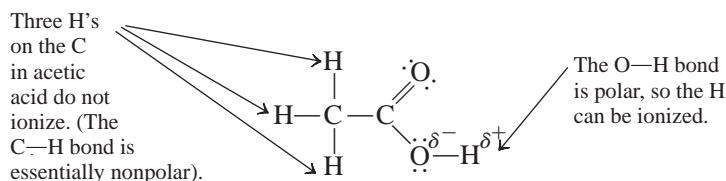
So which is more dangerous or reactive, a dilute strong acid or a concentrated weak acid? Of course the terms are vague, and we'd have to know the exact concentrations and the exact percent ionization of the weak acid. Clearly, though, both factors play a role. We will have to come up with some convenient way of measuring the relative strength of such solutions, based on a common component of both. We'll take this up in Section 13-5.

### SYNTHESIS

A 0.100 M solution seems to us to be relatively dilute. Furthermore, if it is less than 2% ionized, it would appear that the solution in question has very little acid in it at all. As it turns out, a little acid goes a long way. The solution described above is about as acidic as orange juice and more acidic than acid rain. Acid rain kills fish and trees, and eats away at marble buildings and structures. So, even at  $1.34 \times 10^{-3}$  M, there's still plenty of hydronium to do the damage associated with acids.

In the two preceding examples, we found that the concentration of  $\text{H}_3\text{O}^+$  is about 100 times greater in the strong acid solution, although both were at the same original concentration. Only in the case of strong acids does the original concentration of the acid equal the concentration of  $\text{H}_3\text{O}^+$  ions.

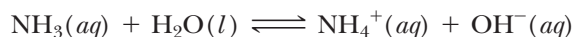
In Example 13-5 we used acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) as a typical weak acid. Perhaps one wonders why it is written that way, not as  $\text{H}_4\text{C}_2\text{O}_3$ . However, if we look at the Lewis representation of acetic acid, we notice that there are two types of hydrogen atoms. The one attached to the oxygen is polar and is potentially acidic. It is ionized (to a limited extent) by the water molecules, as illustrated in Figure 12-3 in the previous chapter. In the case of acetic acid, the three hydrogen atoms attached to the carbon are essentially nonpolar and do not interact with polar water molecules when placed in aqueous solution. Thus, the three hydrogen atoms attached to carbon are not affected by proton exchange and remain as part of the acetate ion.



### 13-3.2 The Strength of Bases

Now we consider the case of bases. They also exhibit a range of strengths depending on the concentration of  $\text{OH}^-$  produced by the base. Strong bases are ionic compounds that dissolve in water to form  $\text{OH}^-$  anions. All alkali metal hydroxides are strong bases and are quite soluble in water. The alkaline earth hydroxides [except  $\text{Be}(\text{OH})_2$ ] also completely dissociate into ions in solution. However,  $\text{Mg}(\text{OH})_2$  has a very low solubility in water and so produces a very small concentration of aqueous  $\text{OH}^-$ . Because of its low solubility, it can be taken internally, as a solid suspension, to combat excess stomach acid (milk of magnesia).

The most familiar example of a weak molecular base and the one we will emphasize is ammonia ( $\text{NH}_3$ ), whose reaction as a base was discussed in Section 13-2. A **weak molecular base** is a base that is only partially converted into ions in solution. The reaction of ammonia as a base is shown by the equation



The tip-off that ammonia is a weak base is found in the equilibrium arrows rather than the single arrow that implies a complete reaction. As in the case of weak acids, the position of equilibrium lies far to the left. The vast majority of dissolved  $\text{NH}_3$  molecules remain in the molecular form shown on the left of the double arrows rather than as ions, shown on the right. In the Brønsted–Lowry sense, we note that  $\text{NH}_4^+$  is a stronger proton donor than  $\text{H}_2\text{O}$  and  $\text{OH}^-$  is a stronger proton acceptor than  $\text{NH}_3$ . Several other neutral nitrogen-containing compounds, such as methylamine ( $\text{CH}_3\text{NH}_2$ ) and pyridine ( $\text{C}_5\text{H}_5\text{N}$ ), also react with water in a similar manner to produce weakly basic solutions.



Milk of magnesia is a base taken for indigestion.

#### ASSESSING THE OBJECTIVE FOR SECTION 13-3

**EXERCISE 13-3(a) KNOWLEDGE:** Fill in the blanks.

Strong acids are essentially \_\_\_\_\_% ionized in aqueous solution, whereas weak acids are \_\_\_\_\_ ionized. Sodium hydroxide is a strong base, but ammonia is a \_\_\_\_\_. When a weak acid reacts with water, the reaction is said to be at \_\_\_\_\_.

**EXERCISE 13-3(b) ANALYSIS:** A certain 0.10 M solution of an acid is 2.50% ionized. Is this a strong or a weak acid? What is the  $[\text{H}_3\text{O}^+]$  in this solution?

**EXERCISE 13-3(c) ANALYSIS:** An acid with a concentration of 0.25 M contains a hydronium concentration of 0.0050 M. What percent of the acid is ionized? Is it strong or weak?

**EXERCISE 13-3(d) SYNTHESIS:** Write the equation for each of the following reacting with water. Be sure to include the proper arrow ( $\rightarrow$  or  $\rightleftharpoons$ ) as appropriate.

- (a)  $\text{HNO}_3$       (b)  $\text{HNO}_2$       (c)  $\text{HClO}_2$       (d)  $\text{HClO}_4$

For additional practice, work chapter problems 13-18, 13-21, 13-23, 13-24 and 13-25.

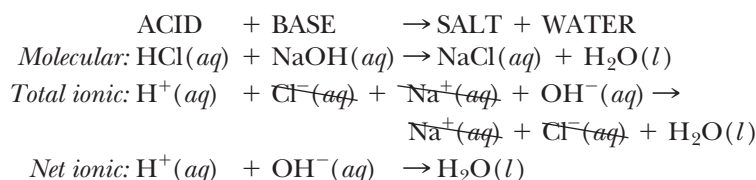
**▶ OBJECTIVE FOR SECTION 13-4**

Write the molecular, total ionic, and net ionic equations for neutralization reactions.

**13-4 NEUTRALIZATION AND THE FORMATION OF SALTS**

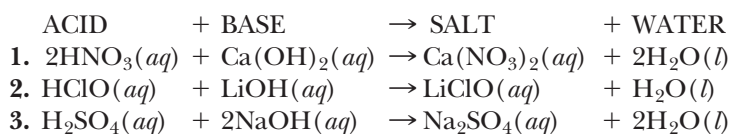
**LOOKING AHEAD!** Molecules or ions that act as acids in water have characteristic properties, as do molecules or ions that act as bases. When solutions of acids and bases are mixed in the proper amounts, the characteristic properties are destroyed or neutralized. The products of such a reaction are a salt and water. We will look at the interactions of solutions of acids with solutions of bases next. ■

In Chapter 5 we described a type of double-displacement reaction between acids and bases known as *neutralization*. If we mix the acid and base in stoichiometric amounts, the products are simply water and a salt. We will begin our discussion of neutralization reactions with a review of the reaction between a strong acid (hydrochloric acid) and a strong base (sodium hydroxide) as described in Chapter 5 and then move on to other cases. The molecular, total ionic, and net ionic equations are shown below. In this case, it is more convenient to represent the acid species as simply  $\text{H}^+(aq)$  rather than  $\text{H}_3\text{O}^+$ .

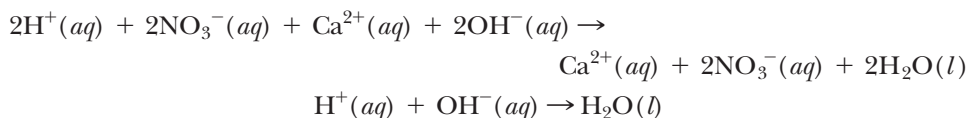


The key to what drives neutralization reactions is found in the net ionic equation. The active ingredient from the acid [ $\text{H}^+(aq)$ ] reacts with the active ingredient from the base [ $\text{OH}^-(aq)$ ] to form the molecular compound water. A salt is what is left over—usually present as spectator ions if the salt is soluble.

As a vital mineral needed to maintain good health, “salt” refers to just one substance, sodium chloride, as formed in the preceding reaction. Actually, salts can result from many different combinations of anions and cations from a variety of neutralizations. The following neutralization reactions, written in molecular form, illustrate the formation of some other salts.

**13-4.1 Neutralization of a Strong Acid with a Strong Base**

Each of these three neutralization reactions represents somewhat different situations, so we will look at these reactions one at a time in ionic form. Reaction 1 in the above list again represents the neutralization of a strong acid with a strong base. In this case, however, the base,  $\text{Ca}(\text{OH})_2$ , dissolves in water to produce two  $\text{OH}^-$  ions per formula unit. Thus two moles of acid are needed per mole of base for complete neutralization. The total ionic and net ionic equations for reaction 1 are as follows.



Notice that the net ionic equation is identical to the reaction illustrated at the beginning of this section.

### 13-4.2 Neutralization of a Weak Acid with a Strong Base

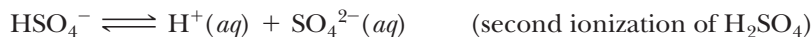
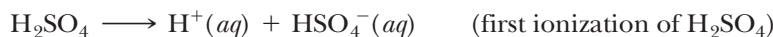
Reaction 2 illustrates a neutralization of hypochlorous acid ( $\text{HClO}$ ), a weak acid, with a strong base. Recall that in the case of most weak acids, the overwhelming majority of molecules are present in solution in the molecular form [i.e.,  $\text{HClO}(aq)$ ] rather than as ions [i.e.,  $\text{H}^+(aq)$  and  $\text{ClO}^-(aq)$ ]. Thus, when we write the total ionic and net ionic equations, the acid is displayed in the predominant molecular form. These two equations for reaction 2 are shown as follows.



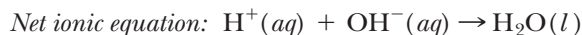
### 13-4.3 Neutralization of a Polyprotic Acid with a Strong Base

Acids are sometimes designated by the number of  $\text{H}^+$  ions that are available from each molecule. Thus,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HClO}$  are known as **monoprotic acids**, since only one  $\text{H}^+$  is produced per molecule. Those acids that can produce more than one  $\text{H}^+$  are known as **polyprotic acids**. More specifically, polyprotic acids may be **diprotic** (two  $\text{H}^+$ 's) such as  $\text{H}_2\text{SO}_4$  or **triprotic** (three  $\text{H}^+$ 's) in the case of  $\text{H}_3\text{PO}_4$ .

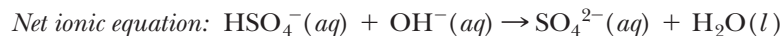
Reaction 3 represents the neutralization of the strong diprotic acid  $\text{H}_2\text{SO}_4$ . In Chapter 7 we represented the ionization of  $\text{H}_2\text{SO}_4$  as being complete, but that is not exactly the case. The first ionization is indeed complete (100%), typical of a strong acid, but the second is not. This ionization reaches an equilibrium typical of weak acids. This later reaction is thus represented by a double arrow.



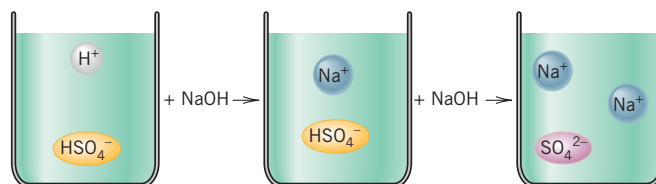
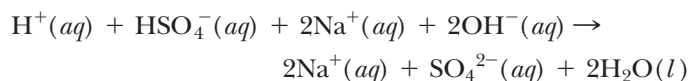
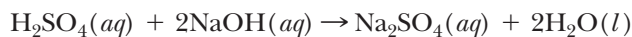
Addition of one mole of  $\text{NaOH}$  to  $\text{H}_2\text{SO}_4$  results in a partial neutralization, forming water and  $\text{NaHSO}_4$  (sodium bisulfate). Sodium bisulfate (or sodium hydrogen sulfate) is an example of an acid salt. An **acid salt** is an ionic compound containing an anion with one or more acidic hydrogens that can be neutralized by a base. Such anions are, by nature, amphoteric.



This reaction is typical of strong acid–strong base neutralizations where the  $\text{HSO}_4^-$  and the  $\text{Na}^+$  ions are subtracted out to produce the net ionic equation. A second mole of  $\text{NaOH}$  added to the  $\text{NaHSO}_4$  solution completes the neutralization. The net ionic equation for this reaction is typical of a weak acid–strong base neutralization where the anion acts as the acid.



The complete neutralization (3) can now be represented by the molecular, total ionic, and net ionic equations as follows. The overall net ionic equation is just the sum of the two individual net ionic equations for the two separate neutralizations after the common ions are eliminated from both sides. (See Figure 13-3.)



**FIGURE 13-3**  
**Neutralization of  $\text{H}_2\text{SO}_4$**  The hydrogens of  $\text{H}_2\text{SO}_4$  can be neutralized one at a time.

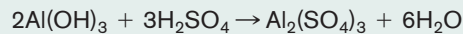


**EXAMPLE 13-6****Writing a Complete Neutralization Reaction**

Write the balanced equation in molecular form illustrating the complete neutralization of  $\text{Al}(\text{OH})_3$  with  $\text{H}_2\text{SO}_4$ .

**PROCEDURE**

Complete neutralization requires one  $\text{H}^+$  for each  $\text{OH}^-$ . Since  $\text{Al}(\text{OH})_3$  has three available  $\text{OH}^-$  ions and  $\text{H}_2\text{SO}_4$  can only provide two  $\text{H}^+$  ions, the reaction requires two moles of  $\text{Al}(\text{OH})_3$  for three moles of  $\text{H}_2\text{SO}_4$ .

**SOLUTION****ANALYSIS**

When the goal is complete neutralization, it is easy to determine the mole ratio between acid and base without having to write out the balanced reaction. Just use the procedure above to match up the  $\text{H}^+$ 's produced by the acid with the  $\text{OH}^-$ 's available from the base. What would the mole ratio for complete neutralization be for the reaction between  $\text{NaOH}$  and  $\text{H}_3\text{PO}_4$ ? It would take three bases for each acid.

**SYNTHESIS**

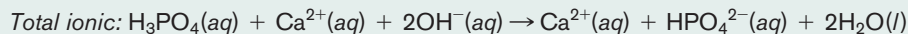
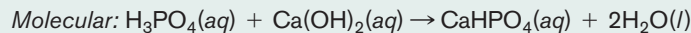
The experimental procedure used to neutralize an acid and a base is called a *titration*, as discussed in the previous chapter. Here, base solution of a known molarity is slowly added to a known amount of acid using a *buret*, an accurately calibrated glass tube with a stopcock at its base. A chemical indicator added to the original acid solution changes color when there is an excess of base present. Typically one drop of indicator solution indicates visually when the solution changes from acidic to basic. A commonly used indicator is phenolphthalein. It is colorless when the solution is acidic but changes abruptly to pink when even a slight excess of base is present. The stoichiometric equivalence point is the point where the solution just changes color.

**EXAMPLE 13-7****Writing a Partial Neutralization Reaction**

Write the balanced molecular, total ionic, and net ionic equations illustrating the reaction of 1 mol of  $\text{H}_3\text{PO}_4$  with 1 mol of  $\text{Ca}(\text{OH})_2$ .

**PROCEDURE**

Although 1 mol of  $\text{H}_3\text{PO}_4$  has three available  $\text{H}^+$  ions to neutralize, 1 mol of  $\text{Ca}(\text{OH})_2$  can react with only two of them. This would leave the  $\text{HPO}_4^{2-}$  ion in solution.

**SOLUTION****ANALYSIS**

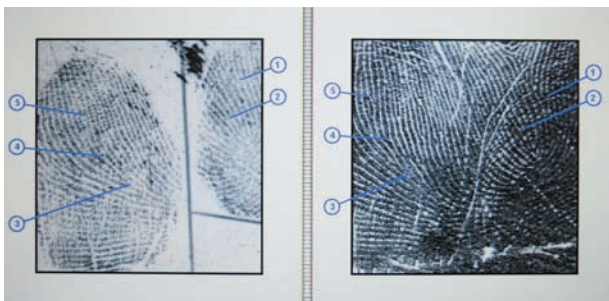
In most cases, the strength of the first acidic hydrogen in a polyprotic acid is several thousand times greater than the second acidic hydrogen, and if there is a third, the second is several thousand times greater than the second. As a result, when we neutralize acids with bases, we can do so one hydrogen at a time. It would not be the case that two moles of  $\text{OH}^-$  would form some  $\text{PO}_4^{3-}$ , and an equal amount of  $\text{H}_2\text{PO}_4^-$  would not react. Instead, the reaction essentially takes place one step at a time.

**SYNTHESIS**

We can apply some common chemical sense to understand why it gets progressively harder to remove each successive  $\text{H}^+$  from a polyprotic acid and its acid salt. Covalent bonds hold the hydrogens onto the molecule. These bonds must be broken, which requires energy. The first  $\text{H}^+$  is removed from a neutral molecule. But the second  $\text{H}^+$  must be removed from a negative ion. It is harder to remove a positive ion from a negative ion than from a neutral molecule. After it is removed, the resulting conjugate base is even more negative. Energetically, it takes progressively more and more energy to remove the next  $\text{H}^+$ . The weaker the acid, the harder it is to remove an  $\text{H}^+$ .



## Salts and Fingerprint Imaging



A latent fingerprint (left) is matched with one in a file (right).

The use of fingerprints to identify individuals has been in practice for over 2000 years. In the second century B.C., the Chinese used the imprint of a finger in a wax seal to identify the sender of a document. For over 400 years it has been known that the pattern of a fingerprint is unique to each individual. In modern times, fingerprints can be matched by comparing certain characteristics of the print called loops, whorls, and arches. There are about 20 to 30 characteristics of a fingerprint that are usually classified. Chances are less than one in a billion that two individuals would have more than eight of these characteristics the same.

There are three types of prints that are found at a crime scene. *Visible* prints are obvious when they are in a colored material such as blood, paint, or ink. *Plastic* prints are also obvious when they occur in wax, soap, or even dust. The most difficult to detect are *latent* prints, which are invisible and made by the transfer of perspiration or body oils to the material in question. Detection of latent prints is very difficult and requires special techniques depending on the surface where the print is suspected.

A crime scene that has latent prints is first “dusted for prints.” Special powders are used that can be applied with a

brush and will contrast with the surface. The powder adheres to the perspiration or body oil of the print and results in an image. Charcoal and aluminum powder are often used in dusting.

The use of ultraviolet light is also used to detect prints without the use of powders. Ultraviolet light is directed at the surface and reflected back. A sensor detects the difference in reflected light from the surface and the print. The sensor also converts the ultraviolet light to visible light, which can then be recorded or made into a photographic print.

The use of chemicals is also important for some prints that are very hard to detect by other methods. A procedure usually performed in a laboratory in an enclosed container involves subjecting the object containing the print to vapors of an organic compound called cyanoacrylate ester (the major component of *super glue*). Fumes from the chemical adhere to the fingerprint, and eventually it becomes visible.

Lasers that emit an intense beam of light with a specific wavelength are also used to detect fingerprints. The laser causes compounds in the print to fluoresce, or give off light of a different specific wavelength. The investigator wears goggles, which protect the eyes from the laser light and transmit only the light from the print.

So what does all of this have to do with salts? Perspiration contains several salts, mainly sodium chloride and potassium chloride. Even after the perspiration dries, the solid salts are left behind. Recently, at an American Chemical Society Convention in 2005, scientists at Los Alamos National Laboratory reported that a type of X-rays called micro X-rays cause the elements in the two salts to fluoresce. The light that is given off from the salts can be analyzed by a computer and converted into a print. It is hoped that this technique, combined with others, will provide yet another weapon in the identification of a hard-to-detect latent fingerprint that may be weeks or even months old.

### EXERCISE 13-4(a) KNOWLEDGE: Fill in the blanks.

The reaction between an acid and a base is known as a \_\_\_\_\_ reaction. The net ionic equation of this reaction always has \_\_\_\_\_ as a product. The spectator ions of the reaction form a \_\_\_\_\_. The partial neutralization of polyprotic acids produces an \_\_\_\_\_ and water.

**EXERCISE 13-4(b) ANALYSIS:** Write the balanced molecular, total ionic, and net ionic equations illustrating the neutralization of  $\text{HNO}_3$  with  $\text{Sr}(\text{OH})_2$ .

**EXERCISE 13-4(c) ANALYSIS:** Write the balanced molecular, total ionic, and net ionic equations illustrating the reaction of 1 mol of  $\text{H}_2\text{C}_2\text{O}_4$  (oxalic acid) and 1 mol of  $\text{CsOH}$ .

**ASSESSING THE  
OBJECTIVE FOR  
SECTION 13-4**

**EXERCISE 13-4(d) SYNTHESIS:** What acid and base react together to form the following?

- (a)  $\text{K}_2\text{SO}_4$     (b)  $\text{KHSO}_4$     (c)  $\text{NH}_4\text{Cl}$

For additional practice, work chapter problems 13-35, 13-36, 13-41, and 13-45.

## PART A SUMMARY

### KEY TERMS

- 13-1.2** The **hydronium ion** represents the proton in hydrated form. p. 399
- 13-2** In the **Brønsted–Lowry** definition, an **acid** is a proton donor and a **base** is a proton acceptor. p. 400
- 13-2.1** A proton exchange reaction produces **conjugate acid** and **conjugate base** pairs. p. 401
- 13-2.2** An **amphiprotic** substance can act as either a proton acceptor or donor. p. 401
- 13-3.1** **Weak molecular acids** produce limited amounts of hydronium ion in solution. p. 404
- 13-3.2** **Weak molecular bases** produce limited amounts of hydroxide ion in solution. p. 407
- 13-4.3** A **monoprotic acid** can donate one proton. A **diprotic** (two protons) and **triprotic** (three protons) are **polyprotic** acids. p. 409
- 13-4.3** An **acid salt** is produced by the partial neutralization of a polyprotic acid. p. 409

### SUMMARY CHARTS

| Acids and Bases |   |                 |  |
|-----------------|---|-----------------|--|
| Substance       | Arrhenius                                       | Brønsted–Lowry  | Comments   |
| Acid            | Increases $\text{H}^+(\text{aq})$ concentration | Proton donor    | Strong—100% ionized<br>weak—usually less than 10% ionized. |
| Base            | Increases $\text{OH}^-$ concentration.          | Proton acceptor | Strong—100% ionized<br>weak—usually less than 10% ionized. |

| Neutralization and Partial Neutralization Reactions |                                      |                                      |                                  |
|---|--------------------------------------|--------------------------------------|----------------------------------|
| Acid  | + Base                               | → Salt                               | + Water                          |
| 1. $\text{HX}(\text{aq})$                           | + $\text{M}^+\text{OH}^-(\text{aq})$ | → $\text{M}^+\text{X}^-(\text{aq})$  | + $\text{H}_2\text{O}(\text{l})$ |
| 2. $\text{H}_2\text{Y}(\text{aq})$                  | + $\text{M}^+\text{OH}^-(\text{aq})$ | → $\text{M}^+\text{HY}^-(\text{aq})$ | + $\text{H}_2\text{O}(\text{l})$ |

## PART B THE MEASUREMENT OF ACID STRENGTH

### SETTING A GOAL

- You will learn about how the relative acidities of aqueous solutions are expressed.

### OBJECTIVES

- 13-5** Using the ion product of water, relate the hydroxide ion and the hydronium ion concentrations.
- 13-6** Given the hydronium or hydroxide ion concentration, calculate the pH and pOH.

### ▶ OBJECTIVE FOR SECTION 13-5

Using the ion product of water, relate the hydroxide ion and the hydronium ion concentrations.

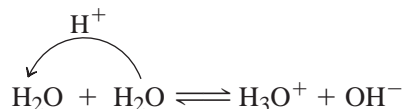
## 13-5 EQUILIBRIUM OF WATER



**LOOKING AHEAD!** We still need a convenient way to express the acidity of a solution, which relates to the concentration of  $\text{H}_3\text{O}^+$  ions. To do this we need to take a closer look at water itself. As we will see in this section, there is more going on in pure water than we originally indicated. ■

### 13-5.1 Autoionization

In the previous chapter, pure water was classified as a nonconductor of electricity. This implied that no ions were present. This isn't exactly true, however. With more sensitive instruments, we find that there actually are very small and equal concentrations of hydronium and hydroxide ions in pure water. The presence of ions in pure water is due to a process known as autoionization. **Autoionization** produces positive and negative ions from the dissociation of the molecules of the liquid. For water, this is represented as follows, the double arrow again indicating that the reaction is reversible and reaches a state of equilibrium.



Although this equilibrium lies very far to the left, a small but important amount of  $\text{H}_3\text{O}^+$  ions and  $\text{OH}^-$  ions coexist in pure water. It is this small concentration that we will focus on as a means of expressing acid and base behaviors and their relative strengths.

The concentration of each ion at  $25^\circ\text{C}$  has been found by experiment to be  $1.0 \times 10^{-7}$  mol/L. This means that only about one out of every 100 million water molecules is actually ionized at any one time. Other experimental results tell us that the product of the ion concentrations is a constant. This phenomenon will be explained in more detail in Chapter 15, but for now we accept it as fact. Therefore, at  $25^\circ\text{C}$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (\text{a constant})$$

Substituting the actual concentrations of the ions, we can now find the numerical value of the constant.

$$[1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

### 13-5.2 The Ion Product of Water

$K_w(1.0 \times 10^{-14})$  is known as the **ion product of water** at  $25^\circ\text{C}$ . The importance of this constant is that it tells us the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  not only in pure water but also in acidic and basic solutions. The following example illustrates this relationship. In Figure 13-4, the ion product of water is illustrated. Notice that there is an inverse relationship between the two ion concentrations. That is, the larger the concentration of  $\text{H}_3\text{O}^+$ , the smaller the concentration of  $\text{OH}^-$ . In pure water or a neutral solution, the concentrations are both equal to  $1.0 \times 10^{-7}$  M. If an acid is added to pure water, the balance is tipped toward the  $\text{H}_3\text{O}^+$  side and the solution becomes acidic to some degree. This means that the concentration of  $\text{H}_3\text{O}^+$  rises above  $10^{-7}$  M, while the concentration of  $\text{OH}^-$  drops below  $10^{-7}$  M. It is analogous to the action of a teeter-totter. As one side goes up, the other goes down.

|         | $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$ | $[\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 10^{-14}$ |
|---------|--------------------------|-----------------|---|
| Acidic  | $10^{-3}$                | $10^{-11}$      | $10^{-3} \cdot 10^{-11} = 10^{-14}$                     |
|         | $10^{-5}$                | $10^{-9}$       | $10^{-5} \cdot 10^{-9} = 10^{-14}$                      |
| Neutral | $10^{-7}$                | $10^{-7}$       | $10^{-7} \cdot 10^{-7} = 10^{-14}$                      |
| Basic   | $10^{-9}$                | $10^{-5}$       | $10^{-9} \cdot 10^{-5} = 10^{-14}$                      |
|         | $10^{-11}$               | $10^{-3}$       | $10^{-11} \cdot 10^{-3} = 10^{-14}$                     |

**FIGURE 13-4** The Relationship Between  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in Water A large concentration of  $\text{H}_3\text{O}^+$  corresponds to a low concentration of  $\text{OH}^-$  in a solution, and vice versa.

In summary, an acidic, basic, or neutral solution can now be defined in terms of concentrations of ions.

$$\text{Neutral: } [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$$

$$\text{Acidic: } [\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \quad \text{and} \quad [\text{OH}^-] < 1.0 \times 10^{-7}$$

$$\text{Basic: } [\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \quad \text{and} \quad [\text{OH}^-] > 1.0 \times 10^{-7}$$

We should now incorporate this information into our understanding of acids and bases. In the Arrhenius definition, an acid is a substance that produces  $\text{H}_3\text{O}^+$  ions in aqueous solution. But now we see that  $\text{H}_3\text{O}^+$  is present in neutral and even basic solutions as well. A slight modification of the definition solves this problem. *An acid is any substance that increases  $[\text{H}_3\text{O}^+]$  in water, and a base is any substance that increases  $[\text{OH}^-]$  in water.* With our new understanding of the equilibrium, we can see that a substance can be an acid by directly donating  $\text{H}^+$  (aq) to the solution (e.g., HCl,  $\text{H}_2\text{S}$ ), or a substance can be an acid by reacting with  $\text{OH}^-$  ions, thus removing them from the solution.

**EXAMPLE 13-8****Calculating  $[\text{OH}^-]$  from  $[\text{H}_3\text{O}^+]$** 

In a certain solution,  $[\text{H}_3\text{O}^+] = 1.5 \times 10^{-2}$  M. What is  $[\text{OH}^-]$  in this solution?

**PROCEDURE**

Use the relationship for  $K_w$ ,  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ , and solve for  $[\text{OH}^-]$ .

**SOLUTION**

$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= 1.0 \times 10^{-14} \\ [\text{OH}^-] &= \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-2}} \\ &= \underline{\underline{6.7 \times 10^{-13} \text{ M}}} \end{aligned}$$

**ANALYSIS**

Notice that any concentration of acid or base above 1.0 M will lead to the other concentration being below  $1.0 \times 10^{-14}$ . This is perfectly acceptable, both mathematically and in practice. In the next section, we'll see that it leads to some calculations that many students initially assume are impossible.

**SYNTHESIS**

When the hydronium concentration is high, it requires large amounts of acid or base to change the relative values of the two. When the hydroxide concentration is high, the same situation occurs. However, in the middle range, where both concentrations are around  $10^{-7}$ , it only takes small amounts of acid or base to dramatically alter the relative concentrations. What's the lesson here? In our typically neutral, or close-to-neutral, world, it doesn't take a lot of acidic or basic substances released into the environment to dramatically change things. Acid rain doesn't have to be very acidic to kill plants or fish. Small amounts will raise the concentration above a level that is toxic.

**ASSESSING THE OBJECTIVE FOR SECTION 13-5**

**EXERCISE 13-5(a) KNOWLEDGE:** Fill in the blanks.

Pure water contains a small but important concentration of \_\_\_\_\_ and \_\_\_\_\_ ions. The product of the concentrations of these two ions, known as the \_\_\_\_\_ of water, is symbolized by \_\_\_\_\_ and has a value of \_\_\_\_\_ at 25°C. As the concentration of \_\_\_\_\_ increases in water, the concentration of  $\text{H}_3\text{O}^+$  \_\_\_\_\_.

**EXERCISE 13-5(b) ANALYSIS:** What is the  $[\text{H}_3\text{O}^+]$  in a solution that has  $[\text{OH}^-] = 7.2 \times 10^{-5}$ ?

**EXERCISE 13-5(c) SYNTHESIS:** Is the solution in Exercise 13-5(b) acidic or basic? Is it strongly or weakly acidic or basic? What is an example of a compound that could produce a hydronium concentration at that level?

*For additional practice, work chapter problems 13-51, 13-53, and 13-57.*



## 13-6 THE pH SCALE



**LOOKING AHEAD!** The concentration of hydronium or hydroxide ions in aqueous solution is usually quite small. While scientific notation is a great help in expressing these very small numbers, it is still awkward in this case. There is another way. This involves expressing the numbers as logarithms, which then gives us a three- or four-digit number that tells us the same thing. The expression of these numbers in this manner is discussed in this section. ■

### OBJECTIVE FOR SECTION 13-6

Given the hydronium or hydroxide ion concentration, calculate the pH and pOH.

### 13-6.1 The Definition of pH

The producers of commercial television advertising assume that the general population is aware not only of the importance of acidity but also of how it is scientifically expressed. For example, we often hear references to controlled pH in hair shampoo commercials and other products. In fact, pH is an important and convenient method for expressing acid strength. For example, in a typical acidic solution, assume  $[\text{H}_3\text{O}^+]$  is equal to  $1 \times 10^{-5}$  M. Scientific notation is certainly better than using a string of nonsignificant zeros (i.e., 0.00001 M), but expressed as pH, the number is simply 5.0. The pH scale represents the negative exponent of 10 as a positive number. The exponent of 10 in a number is the number's common logarithm or, simply, log. **pH** is a logarithmic expression of  $[\text{H}_3\text{O}^+]$ .

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Therefore, a solution of  $\text{pH} = 1.00$  has  $[\text{H}_3\text{O}^+]$  equal to  $1.0 \times 10^{-1}$  M, and pure water has  $\text{pH} = 7.00$  ( $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$  M). In expressing pH, the number to the right of the decimal place should have the same number of significant figures as the original coefficient or number. That is,

$$\text{if } [\text{H}_3\text{O}^+] = \frac{1.00}{\uparrow} \times 10^{-4} \text{ M, } \text{pH} = \frac{4.000}{\uparrow}$$

3 significant figures                      3 places to the right of the decimal

A much less popular but valid way of expressing  $[\text{OH}^-]$  is **pOH**.

$$\text{pOH} = -\log [\text{OH}^-]$$

A simple relationship between pH and pOH can be derived from the ion product of water.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

If we now take  $-\log$  of both sides of the equation, we have

$$-\log[\text{H}_3\text{O}^+][\text{OH}^-] = -\log(1.0 \times 10^{-14})$$

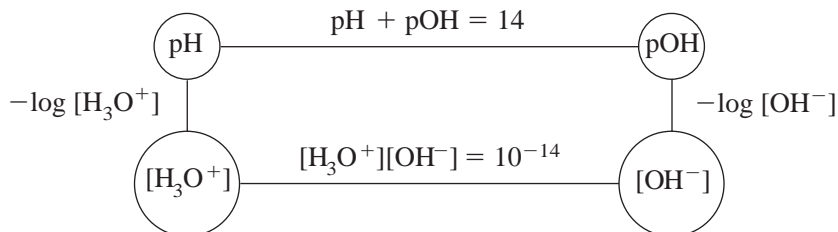
Since  $\log(A \times B) = \log A + \log B$ , the equation can be written as

$$-\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] = -\log 1.0 - \log 10^{-14}$$

Since  $\log 1.0 = 0.00$  and  $\log 10^{-14} = -14$ , the equation is

$$\text{pH} + \text{pOH} = 14.00$$

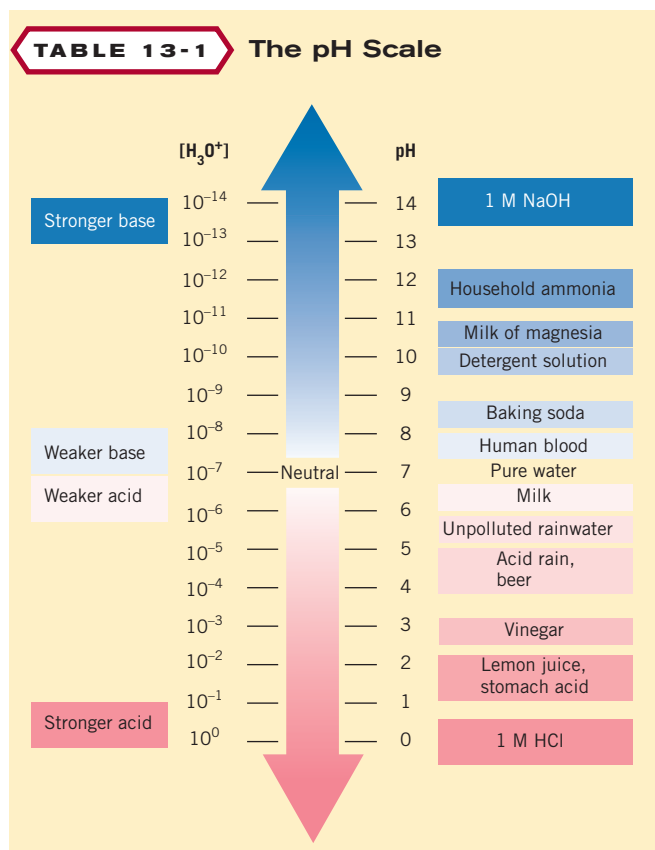
Generally, pOH is not used extensively since pH relates to the  $\text{OH}^-$  concentration as well as the  $\text{H}_3\text{O}^+$  concentration. The relationships among  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH and pOH are summarized as follows.



This shampoo is supposedly desirable because it is "pH balanced."

|         | $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$ | pH | pOH |
|---------|--------------------------|-----------------|----|-----|
| Acidic  | $10^{-3}$                | $10^{-11}$      | 3  | 11  |
|         | $10^{-5}$                | $10^{-9}$       | 5  | 9   |
| Neutral | $10^{-7}$                | $10^{-7}$       | 7  | 7   |
| Basic   | $10^{-9}$                | $10^{-5}$       | 9  | 5   |
|         | $10^{-11}$               | $10^{-3}$       | 11 | 3   |

**FIGURE 13-5**  
Concentrations of Ions, pH, and pOH A low pH in a solution corresponds to a high pOH.



Although most of us are tempted to go straight to our calculators to change from scientific notation to logarithms, it is helpful to review the *meaning* of common logs and some of the rules of their use. You are encouraged to read Appendix C, which contains a brief discussion of common logarithms.

In Figure 13-5 we have included the pH and pOH in addition to the ion concentrations shown in Figure 13-4. Acidic, basic, and neutral solutions can now be defined in terms of pH and pOH.

$$\text{Neutral: } \text{pH} = \text{pOH} = 7.00$$

$$\text{Acidic: } \text{pH} < 7.00 \text{ and } \text{pOH} > 7.00$$

$$\text{Basic: } \text{pH} > 7.00 \text{ and } \text{pOH} < 7.00$$

### 13-6.2 pH and the Acidity of Solutions

In the use of pH, one must remember that the *lower* the value for pH, the *higher* the concentration of  $\text{H}_3\text{O}^+$ . Also, a change in one unit in the pH (e.g., from 4 to 3) corresponds to a 10-fold change in concentration (e.g., from  $10^{-4}$  to  $10^{-3}$  M). Another scientific scale that is logarithmic is the Richter scale for measuring earthquakes. This scale measures the amplitude of seismic waves set off by the tremor. An earthquake with a reading of 7.0 on this scale indicates the waves are 10 times larger than an earthquake of magnitude 6.0.

In Table 13-1, we have listed the pH of some common chemicals, foods, or products. A 1.0 M HCl solution is the most acidic solution listed. Solutions of pH 1 or less are considered *strongly acidic*. Solutions with pH less than 7 but greater than 1 are considered *weakly acidic*. Even then what we refer to as a weakly acidic solution still covers quite a range. A solution of pH 6 is 100,000 times less acidic than a solution of pH 1. On the other side of the scale, we have a 1 M solution of NaOH, which has a pH of 14. Solutions of pH 13 or greater are considered *strongly basic*. Solutions with pH greater than 7 but less than 13 are considered *weakly basic*.

#### EXAMPLE 13-9

##### Expressing the pH and pOH of a Solution

What is the pH of a solution with  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-8}$  M? What is the pOH?

##### PROCEDURE

A calculator is not needed for calculations of pH where the coefficient is exactly 1. Understanding the definition is sufficient. The pH is simply the negative of the exponent of 10.

**SOLUTION**

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log(1.0 \times 10^{-8}) = \underline{\underline{8.00}}$$

(Since there are two significant figures, there should be two places to the right of the decimal.)

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pOH} = 14.00 - \text{pH}$$

$$\text{pOH} = 14.00 - 8.00 = \underline{\underline{6.00}}$$

**ANALYSIS**

The pOH could have been calculated in another way as well. Knowing the inverse relationship of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , we determine that a  $1.0 \times 10^{-8} \text{ M}$  hydronium solution would be  $1.0 \times 10^{-14}/1.0 \times 10^{-8} = 1.0 \times 10^{-6} \text{ M}$  hydroxide. The pOH is equal to  $-\log(1.0 \times 10^{-6})$ , which is 6.00.

**SYNTHESIS**

What is the pH of a 10.0 M solution of  $\text{H}_3\text{O}^+$ ? 10.0 in scientific notation is  $1.00 \times 10^1$ . The pH equals  $-1.000$ , since the negative of the exponent in this case is  $-1$ . This solution has a pH of less than zero, as would any hydronium concentration greater than 1.0 M. Conversely, the pH scale can range higher than 14 as well, for particularly concentrated hydroxide solutions.

**EXAMPLE 13-10****Calculating the  $[\text{H}_3\text{O}^+]$  from the pH**

What is the  $[\text{H}_3\text{O}^+]$  of a solution with a pH = 3.00? What is the pOH? What is  $[\text{OH}^-]$ ?

**PROCEDURE**

Again, a calculator is not needed for calculations if the pH is a whole number. The  $[\text{H}_3\text{O}^+]$  is simply the antilog (or inverse log) of the minus value of pH.

**SOLUTION**

$$\text{pH} = 3.00$$

$$3.00 = -\log [\text{H}_3\text{O}^+]$$

$$-3.00 = \log [\text{H}_3\text{O}^+]$$

This means that the exponent of 10 is  $-3$  and the coefficient should be expressed to two significant figures.

$$[\text{H}_3\text{O}^+] = \underline{\underline{1.0 \times 10^{-3}}}$$

$$\text{pOH} = 14.00 - 3.00 = \underline{\underline{11.00}}$$

$$[\text{OH}^-] = -\text{antilog}[11.00] = \underline{\underline{1.0 \times 10^{-11}}}$$

**ANALYSIS**

You must be careful of what you are expressing with pH. You are not necessarily calculating the concentration of the acid itself but only the  $\text{H}_3\text{O}^+$  concentration produced by the specific acid. Whether this translates into the concentration of the acid producing the hydronium depends on whether the acid is strong or weak and therefore on how much of its original concentration is converted into hydronium.

**SYNTHESIS**

Occasionally advertisers will play on the general public's lack of scientific literacy by using terms associated with pH to mislead. Speaking of a substance's pH as being "higher" than normal has opposite meanings when the substance is an acid or a base. Acids with a higher pH are weaker, whereas bases with a higher pH are stronger. Not knowing which an advertiser is referring to can lead a consumer to believe that a chemical in question is more dangerous when in fact it is more benign. When advertisers say that the pH of a woman's sweat is higher than a man's in order to sell a product, what they are really saying is that it is weaker, as sweat is mildly acidic. But it sells the antiperspirant.



pH is read directly with this common laboratory instrument.

**EXAMPLE 13-11****Calculating the pH and pOH of a Strong Acid Solution**

What is the pH of a  $1.5 \times 10^{-2}$  M solution of  $\text{HClO}_4$ ? What is the pOH of this solution?

**PROCEDURE**

$\text{HClO}_4$  is a strong acid, which means that it is 100% ionized in solution. Therefore,  $[\text{H}_3\text{O}^+]$  is equal to the original  $\text{HClO}_4$  concentration. In cases where the coefficient is not exactly 1, a calculator is needed. The following instructions are for a nongraphing calculator.

1. Enter the number. First enter "1.5," then push the exponent key, **[EXP]** or **[EE]**, and enter "2." Push the **[+/-]** key to change the exponent to  $-2$ .
2. Push the **[log]** key.
3. The display reads  $-1.82$ , which is the log of the number you entered.
4. Change the reading to  $1.82$ , since the pH is the negative of the log.

**SOLUTION**

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 1.5 \times 10^{-2} \text{ M} \\ \log(1.5 \times 10^{-2}) &= -1.82 \\ \text{pH} &= -\log(1.5 \times 10^{-2}) = \underline{1.82} \\ \text{pH} + \text{pOH} &= 14.00 \\ \text{pOH} &= 14.00 - 1.82 = \underline{12.18}\end{aligned}$$

**ANALYSIS**

If this were a KOH solution of the same concentration, what would be the pH? The only difference in the solutions, as far as pH is concerned, is that the concentration is hydroxide. So it would be the pOH that would be calculated directly from the starting concentration and the pH that would be determined by subtracting from 14.00.  $\text{pOH} = 1.82$  and  $\text{pH} = 12.18$ . This makes sense. KOH is a base, and therefore its solutions should have pH's greater than 7.0.

**SYNTHESIS**

The calculation above holds true only for a strong acid (or base, with the appropriate changes for pOH). If the acid in question were weak, you would have to know the % ionization to figure out what the concentration of  $\text{H}_3\text{O}^+$  was. There are alternate methods, which can be used, that are discussed in Chapter 15.

**EXAMPLE 13-12****Converting pH to  $[\text{H}_3\text{O}^+]$** 

In a given weakly basic solution,  $\text{pH} = 9.62$ . What is  $[\text{H}_3\text{O}^+]$ ?

**PROCEDURE**

In this case, it is necessary to take the antilog (or the inverse log on a calculator).

1. Enter the 9.62 on the calculator.
2. Change the sign (**[+/-]** key).
3. Press the **[inv]**, **[shift]**, or **[2<sup>nd</sup>]** key, then the **[log]** key. Consult the instructions for your calculator if these keys are different or not available.
4. The number displayed should be rounded off to two significant figures since there are two numbers to the right of the decimal place in the original number.

**SOLUTION**

$$\begin{aligned}-\log[\text{H}_3\text{O}^+] &= 9.62 & \log[\text{H}_3\text{O}^+] &= -9.62 \\ [\text{H}_3\text{O}^+] &= \underline{2.4 \times 10^{-10} \text{ M}}\end{aligned}$$

**ANALYSIS**

Remember to make sure that your answers make mathematical and chemical sense. Failure to convert the sign to negative gives a concentration of 4 billion molar. That number can be rejected immediately. Furthermore, if you forget the shift or 2<sup>nd</sup>

key, and simply take the log of a negative number, you'll get an error message. It is mathematically meaningless. Typically, acid concentrations will range from 1.0 M down to  $10^{-5}$  M for chemically relevant acids. Those represent a pH range from 0 to 5. Bases have the same concentration range, and the pH generally ranges from 14 down to 9. A pH in the middle range, 6–8, tends to be very dilute, and the actual pH is affected by the dissociation of water itself, thus boosting the hydronium or hydroxide concentrations higher than you might expect.

### SYNTHESIS

The more deeply you get into science, the more prevalent you'll find logarithmic scales. Along with the Richter scale, and, of course, pH, logarithmic scales are used to measure all sorts of phenomena whose values are spread out over several orders of magnitude. Stellar brightness is measured on a logarithmic scale (though not  $\log_{10}$ , like pH), as is the decibel in acoustics. In spectroscopy, light absorbance, which is a direct function of concentration, is related logarithmically to the transmittance, or the percentage of light passing through the sample. The voltage of a battery depends on the log of the concentration of the chemicals in the battery. These are just a few examples, but they illustrate the importance of the use of logarithms in the study of science.

### ASSESSING THE OBJECTIVE FOR SECTION 13-6

**EXERCISE 13-6(a) KNOWLEDGE:** Fill in the blanks.

The pH of a solution is defined as \_\_\_\_\_. An acidic solution is one that has an  $[\text{H}_3\text{O}^+]$  greater than \_\_\_\_\_ and a pH \_\_\_\_\_ than 7. A basic solution is one that has an  $[\text{OH}^-]$  greater than \_\_\_\_\_ and a pH \_\_\_\_\_ than 7.

**EXERCISE 13-6(b) ANALYSIS:** What is the pH of the solution where  $[\text{OH}^-] = 7.2 \times 10^{-5}$ ?

**EXERCISE 13-6(c) ANALYSIS:** What is the concentration of an LiOH solution where the pH is 13.40?

**EXERCISE 13-6(d) ANALYSIS:** For a solution of NaOH that is 0.075 M, what are the following?

(a) hydronium concentration (b) hydroxide concentration (c) pH (d) pOH

**EXERCISE 13-6(e) SYNTHESIS:** Which has the higher  $[\text{H}_3\text{O}^+]$ , a 0.005 M solution of HCl or a 0.2 M solution of  $\text{HC}_2\text{H}_3\text{O}_2$ , which is only 0.4% ionized?

*For additional practice, work chapter problems 13-61, 13-63, 13-69, and 13-71.*

### PART B SUMMARY

#### KEY TERMS

- 13-5.1** The ionization of the molecules of a solvent into positive and negative ions is known as **autoionization**. p. 413
- 13-5.2** The **ion product** of water ( $K_w$ ) is the quantitative relationship between the hydronium and hydroxide ions. p. 413
- 13-6.1** **pH** is the logarithmic measurement of the hydronium ion concentration. **pOH** is the same measurement of the hydroxide ion concentration. p. 415

#### SUMMARY CHART

Relative Acidity of Solutions

| Solution        | $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$ | pH       | pOH      |
|-----------------|--------------------------|-----------------|----------|----------|
| Strongly acidic | $> 10^{-1}$              | $< 10^{-13}$    | $< 1.0$  | $> 13.0$ |
| Weakly acidic   | $10^{-4}$                | $10^{-10}$      | 4.0      | 10.0     |
| Neutral         | $10^{-7}$                | $10^{-7}$       | 7.0      | 7.0      |
| Weakly basic    | $10^{-10}$               | $10^{-4}$       | 10.0     | 4.0      |
| Strongly basic  | $< 10^{-13}$             | $> 10^{-1}$     | $> 13.0$ | $< 1.0$  |



**PART C**  
**SALTS AND OXIDES AS**  
**ACIDS AND BASES**

**SETTING A GOAL**

- You will learn how salts and oxides can also affect the pH of aqueous solutions.

**OBJECTIVES**

- 13-7** Identify a salt solution as neutral, acidic, or basic.
- 13-8 (a)** Describe how a buffer solution works. **(b)** Write equations illustrating the fate of hydronium or hydroxide added to such a solution.
- 13-9** Determine, if possible, whether a specific oxide is acidic or basic.

► **OBJECTIVE FOR**  
**SECTION 13-7**

Identify a salt solution as neutral, acidic, or basic.

## 13-7 THE EFFECT OF SALTS ON pH—HYDROLYSIS



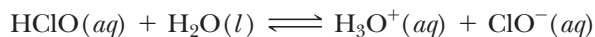
**LOOKING AHEAD!** Solutions of some salts are neutral, some basic, and some acidic. Why this is so is the subject of this section. ■

When a salt dissolves in water, both a cation and an anion are produced. The cation has the potential to act as an acid and the anion as a base. *The reaction of a cation as an acid or an anion as a base is known as a hydrolysis reaction.* To understand this, we will first consider ions that do not undergo hydrolysis, which means that they have no acid or base character in water and will not change the pH of pure water from 7.0.

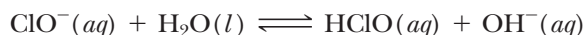
First, consider the  $\text{Cl}^-$  ion, which is the anion or conjugate base of the strong acid HCl. Recall that in the ionization process of HCl, the forward reaction is essentially 100% complete, so the reverse reaction does not occur in water. Thus we notice that the  $\text{Cl}^-$  ion, although formally known as a conjugate base, in fact does not exhibit proton-accepting ability in water to form an HCl molecule. *Therefore, the  $\text{Cl}^-$  ion does not undergo hydrolysis. In fact, other anions of strong acids (i.e.,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) do not undergo hydrolysis reactions.* (The  $\text{HSO}_4^-$  ion is an exception and is weakly acidic in water, as we indicated previously.) The same is true for the cations of strong bases (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  and other alkali metal and alkaline earth metal ions). They all exist as independent, hydrated ions in aqueous solution and so do not undergo hydrolysis.

### 13-7.1 Anion Hydrolysis

Now consider again the ionization equilibrium for the weak acid HClO.



Since this reaction reaches a point of equilibrium favoring the reactants on the left, the  $\text{ClO}^-$  does demonstrate proton-accepting ability in water. Now consider what happens when this anion is added to water as part of a salt. It exhibits its weakly basic nature by producing a small concentration of hydroxide ion. The following equation represents the hydrolysis reaction of the hypochlorite ion.

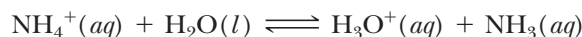


The extent of hydrolysis of anions is generally quite small, however, so the equilibrium lies far to the left. We can now make a general statement. *The anions of weak acids (i.e., their conjugate bases) undergo hydrolysis in aqueous solution, producing weakly basic solutions.* We can make another generalization: the weaker the acid, the stronger is its conjugate base. In fact, the anions (conjugate bases) of strong acids are so weak

they don't act as bases at all in water. The anions (conjugate bases) of weak acids, however, are strong enough to exhibit proton-accepting ability in water.

### 13-7.2 Cation Hydrolysis

Now consider the weak base ammonia. As indicated in Section 13-3, its reaction with water produces small concentrations of  $\text{NH}_4^+$  and  $\text{OH}^-$  ions. Since this is also an equilibrium situation, we can conclude that the  $\text{NH}_4^+$  ion demonstrates proton-donating properties in the reverse reaction. When the ammonium ion is placed in water as part of a salt, it exhibits a weakly acidic nature by producing a small concentration of hydronium ion. The hydrolysis of the ammonium ion is illustrated by the following equation.



We can generalize this behavior also. *Cations (conjugate acids) of weak bases undergo hydrolysis in aqueous solution, producing weakly acidic solutions.*

We are now ready to predict how the solutions of various salts in water affect the pH. To do this, we must look at the cation and the anion individually and determine whether neither, one, or both undergo hydrolysis. We will consider four representative cases.

### 13-7.3 Aqueous Solutions of Salts

- 1. Neutral solutions of salts.** When neither the cation nor the anion undergoes a hydrolysis reaction, solutions of these salts do not affect the pH. They remain the same as that of pure water, which is 7.0. In such salts, the anions originate from strong acids and the cations originate from strong bases [i.e., the alkali and alkaline earth metals (except  $\text{Be}^{2+}$ )]. Examples of neutral salts are  $\text{NaCl}$ ,  $\text{Ba}(\text{ClO}_4)_2$ , and  $\text{KNO}_3$ .
- 2. Basic solutions of salts.** When the salt forms from the cation of a strong base and the anion of a weak acid, the cation does not affect the pH but the anion does. In the anion hydrolysis reaction, a small equilibrium concentration of  $\text{OH}^-$  makes the solution basic. Examples of basic salts are  $\text{NaOCl}$ ,  $\text{Ca}(\text{NO}_2)_2$ , and  $\text{NaF}$ . The pH of solutions of these salts will be greater than 7.0.
- 3. Acidic solutions of salts.** When a salt forms from the cation of a weak base and the anion of a strong acid, the anion does not affect the pH but the cation does. The primary example of a cation that undergoes hydrolysis is  $\text{NH}_4^+$ . Since the anions do not undergo hydrolysis, solutions of salts such as  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{NO}_3$  are weakly acidic. The pH of such solutions will be less than 7.0. Other examples of acidic cations include transition metal cations and  $\text{Al}^{3+}$ . The neutral hydroxides of these cations are also weak bases but generally insoluble in water. For example, solutions of  $\text{FeCl}_3$  and  $\text{Cu}(\text{NO}_3)_2$ , which produce the  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions, respectively, are weakly acidic solutions.
- 4. Complex cases.** There are other salt solutions that are not easy to predict without quantitative data. For example, in a solution of the salt  $\text{NH}_4\text{NO}_2$ , both anion and cation undergo hydrolysis, but not to the same extent. In other cases, it is not immediately obvious whether solutions of acid salts are acidic or basic. For example, the  $\text{HCO}_3^-$  ion is amphoteric, which means that it is potentially an acid since it has a hydrogen that can react with a base. However, it is also the conjugate base of the weak acid  $\text{H}_2\text{CO}_3$ , so it can act as a base by undergoing hydrolysis. Sodium bicarbonate solutions are actually weakly basic and for that reason are sometimes used as an antacid to treat upset stomachs. On the other hand, solutions of the acid salts  $\text{NaHSO}_3$  and  $\text{NaHSO}_4$  are acidic. Quantitative information, which is discussed in Chapter 15, would be needed, however, for us to have predicted these facts.



Solutions of ordinary bleach ( $\text{NaClO}$ ) are weakly basic.

The discussion of the effect on pH when salts dissolve in water is summarized as follows.

| ORIGIN OF CATION | ORIGIN OF ANION | PH OF SOLUTION          | EXAMPLES   |
|------------------|-----------------|-------------------------|--|
| strong base      | strong acid     | 7.0                     | KI, Sr(ClO <sub>4</sub> ) <sub>2</sub>                               |
| strong base      | weak acid       | >7.0                    | KNO <sub>2</sub> , BaS   |
| weak base        | strong acid     | <7.0                    | NH <sub>4</sub> ClO <sub>4</sub> , AlCl <sub>3</sub>                 |
| weak base        | weak acid       | more information needed | NH <sub>4</sub> ClO, N <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>   |
| strong base      | acid salt       | more information needed | KH <sub>2</sub> PO <sub>4</sub> , Ca(HSO <sub>3</sub> ) <sub>2</sub> |

### EXAMPLE 13-13

#### Predicting the Acidity of Salt Solutions

Indicate whether the following solutions are acidic, basic, or neutral. If the solution is acidic or basic, write the equation illustrating the appropriate reaction.

- (a) KCN      (b) Ca(NO<sub>3</sub>)<sub>2</sub>      (c) (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>Br<sup>-</sup> [(CH<sub>3</sub>)<sub>2</sub>NH is a weak base like NH<sub>3</sub>.]

#### PROCEDURE

Identify the ions formed by the solution of each salt. Determine whether the anion originates from a weak or strong acid and the cation from a weak or strong base.

#### SOLUTION

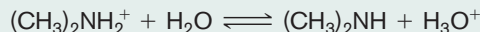
- (a) KCN: K<sup>+</sup> is the cation of the strong base KOH and does not hydrolyze. The CN<sup>-</sup> ion, however, is the conjugate base of the weak acid HCN and hydrolyzes as follows.



Since OH<sup>-</sup> is formed in this solution, the solution is basic.

- (b) Ca(NO<sub>3</sub>)<sub>2</sub>: Ca<sup>2+</sup> is the cation of the strong base Ca(OH)<sub>2</sub> and does not hydrolyze. NO<sub>3</sub><sup>-</sup> is the conjugate base of the strong acid HNO<sub>3</sub> and also does not hydrolyze. Since neither ion hydrolyzes, the solution is neutral.

- (c) (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>Br<sup>-</sup>: (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup> is the conjugate acid of the weak base (CH<sub>3</sub>)<sub>2</sub>NH. It undergoes hydrolysis according to the equation



The Br<sup>-</sup> ion is the conjugate base of the strong acid HBr and does not hydrolyze. Since only the cation undergoes hydrolysis, the solution is acidic.

#### ANALYSIS

Another way of evaluating the pH of a salt solution is to think about what compounds would have to be mixed together to make the salt. Consider KCN in (a). It is formed from the neutralization of the strong base KOH with the weak acid HCN. Intuitive sense indicates that a mixture of a *strong* base and a *weak* acid would form a solution that is more basic than acidic, so we'd predict a basic salt. A salt like NH<sub>4</sub>NO<sub>3</sub> works as the exact opposite. The *weak* base, NH<sub>3</sub>, neutralized with the *strong* acid, HNO<sub>3</sub>, should give an acidic salt. Note that this line of reasoning doesn't *explain* where the excess acid or base is coming from, unlike the equations above, but it is a quick way to arrive at the correct answer.

#### SYNTHESIS

A good example of how we take advantage of acidic and basic salts is by using them to alter soil pH. Typically, plants grow better in slightly acidic soils, although a few do better at a higher pH. Ammonium salts lower the pH of soils nicely, while also adding critical nitrogen. Aluminum sulfate is another product used to lower the pH of soils. Calcium, another critical mineral, tends to wash out of acidic soils, so basic calcium carbonate, or lime, is used to treat acidic soil and to increase the calcium content.

### ASSESSING THE OBJECTIVE FOR SECTION 13-7

**EXERCISE 13-7(a) KNOWLEDGE:** What type of salt (acidic, basic, or neutral) will the following produce?

- (a) cation of a weak base with anion of a strong acid  
 (b) cation of a strong base with anion of a strong acid

(c) cation of a strong base with anion of a weak acid

(d) cation of a weak base with anion of a weak acid

**EXERCISE 13-7(b) ANALYSIS:** Identify the following as forming acidic, basic, or neutral solutions when dissolved in water.

(a)  $\text{Li}_3\text{PO}_4$     (b)  $\text{NH}_4\text{ClO}_4$     (c)  $\text{CaBr}_2$     (d)  $\text{K}_2\text{SO}_3$

**EXERCISE 13-7(c) ANALYSIS:** Write the hydrolysis reaction (if any) of the following salts.

(a)  $\text{Na}_2\text{CO}_3$     (b)  $\text{BaBr}_2$     (c)  $\text{N}_2\text{H}_5\text{NO}_3$  ( $\text{N}_2\text{H}_4$  is a weak base like ammonia.)

**EXERCISE 13-7(d) SYNTHESIS:** What are two examples of compounds you could add to  $\text{NaOH}$  in order to form a basic salt?

**EXERCISE 13-7(e) SYNTHESIS:** What are two examples of compounds you could add to ammonia in order to form an acidic salt?

For additional practice, work chapter problems 13-78, 13-79, 13-83, and 13-87.

## 13-8 CONTROL OF pH—BUFFER SOLUTIONS

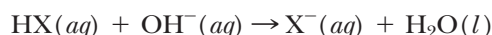


**LOOKING AHEAD!** Perhaps the most important chemical system involves the blood coursing through our veins. Our blood has a pH of about 7.4, but a variation of as little as 0.2 pH unit causes coma or even death. How is the pH of the blood so rigidly controlled despite all the acidic and basic substances we ingest? The control of pH is the job of buffers, which are discussed next. ■

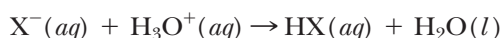
### 13-8.1 The Function of a Buffer

The word *buffer* is usually used in the context of “absorbing a shock.” For example, a car bumper serves as a buffer for the passengers by absorbing the energy of an impact. A buffer solution has a similar effect on the pH of a solution. A **buffer solution resists changes in pH caused by the addition of limited amounts of a strong acid or a strong base.** Commercial products tell us that buffered solutions are important in items such as hair shampoo and aspirin. But to us it is most important because many chemical reactions in our bodies, including those that give us life’s energy, must take place in a controlled pH environment.

A buffer works by having a substance in solution that is available to react with any added  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ . The most logical candidates for this duty are weak bases and weak acids, respectively. Consider how a hypothetical monoprotic weak acid (HX) reacts with added  $\text{OH}^-$ .



In the previous section we found that the conjugate base of the weak acid ( $\text{X}^-$ ) can act as a base in water. In fact, it reacts with  $\text{H}_3\text{O}^+$  as follows



Both of these reactions are essentially complete. So, if we have a solution that contains a significant concentration of both the weak acid and its conjugate weak base, we have a solution that reacts with either added  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ . One may think that just the weak acid alone would be a buffer because the ionization produces some of its anion. However, the amount from ionization is very small, so we need additional anion concentration from another source such as a salt.

### OBJECTIVES FOR SECTION 13-8

(a) Describe how a buffer solution works. (b) Write equations illustrating the fate of hydronium or hydroxide added to such a solution.

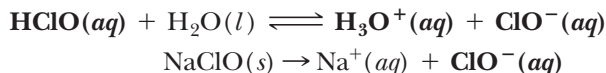


The buffer in this product controls the pH.

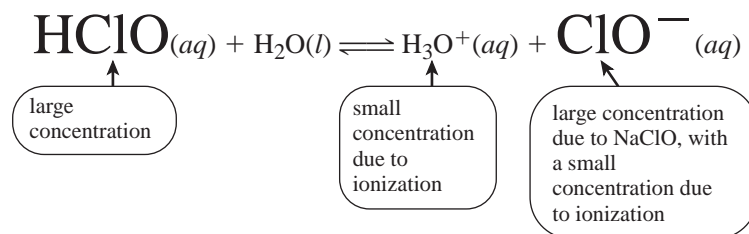
### 13-8.2 The Composition of a Buffer

Buffer solutions are made from (a) a solution of a weak acid that also contains a salt of its conjugate base or (b) a solution of a weak base that also contains a salt of its conjugate acid.

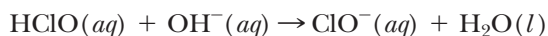
A typical buffer solution is put to use in swimming pools. To keep bacteria at bay, we use ordinary household bleach ( $\text{NaClO}$ ). However, it also has another important function as it keeps the pH at a comfortable 7.5. If the pH gets too low (acidic), the water can sting the eyes and cause corrosion. If it gets too high (alkaline), the water can become cloudy and algae may thrive. In fact, the swimming pool has a significant concentration of both  $\text{ClO}^-$  and  $\text{HClO}$ , which together act as a buffer. The solution of these two compounds, one a weak acid and the other a strong electrolyte, is illustrated by the following two equations.



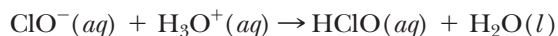
Notice that a mixture of these two compounds in water produces a solution containing three ions,  $\text{H}_3\text{O}^+$ ,  $\text{Na}^+$ , and  $\text{ClO}^-$ , and one molecular compound,  $\text{HClO}$ . The  $\text{Na}^+$  is the cation of a strong base that is a spectator ion and can be neglected. It does not affect the pH. Our main focus, then, is on the comparatively large concentration of molecular  $\text{HClO}$  and  $\text{ClO}^-$  ion, along with the small concentration of  $\text{H}_3\text{O}^+$ , which are shown in bold above. The relevant equilibrium is illustrated as



The  $\text{HClO}$  and the  $\text{ClO}^-$  ion (from the salt) are available to react with any  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  added to the system. When  $\text{OH}^-$  is added to the system, the molecular  $\text{HClO}$  removes it as follows:



Should some  $\text{H}_3\text{O}^+$  be added to the system, the  $\text{ClO}^-$  is available to remove it.



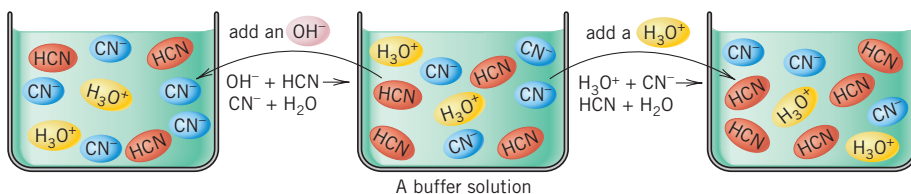
The addition of a limited amount of acid or base is thus counteracted by species present in the buffer solution, and the pH changes very little. (See Figure 13-6.)

A strong acid and its salt (e.g.,  $\text{HCl}$  and  $\text{NaCl}$ ) cannot act as a buffer because the acid is not present in solution in molecular form—it is completely ionized in water. Therefore, there is no reservoir of  $\text{HCl}$  molecules that can react with added  $\text{OH}^-$  ions, nor can the very weak conjugate base ( $\text{Cl}^-$ ) react with  $\text{H}_3\text{O}^+$  ions.

Consider the following analogy. One person has \$20 in his pocket with no savings in the bank; another person has \$20 in her pocket in addition to \$100 in the bank. A \$12 expense will change the first person's pocket money drastically, as it will decrease to \$8. On the other hand, the second person is "buffered" from this expense and can replenish the loss with the bank savings; this person can then maintain the same amount of pocket money.

The molecular  $\text{HClO}$  is like "money in the bank." It is available to react with added  $\text{OH}^-$ , leaving the original concentration of  $\text{H}_3\text{O}^+$ , which is analogous to "money in the pocket," essentially unchanged. The person who keeps

**FIGURE 13-6 A Buffer Solution** A buffer can react with added  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ .





all his money in his pocket is analogous to a strong acid solution in which there is no molecular acid in reserve. In this case, since all the acid ionizes to  $\text{H}_3\text{O}^+$ , any added  $\text{OH}^-$  decreases the  $\text{H}_3\text{O}^+$  concentration and thus increases the pH.

Solutions of weak bases and salts containing their conjugate acids (e.g.,  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ ) also serve as buffers. The two relevant reactions in this case are



The pH of the buffer solution depends on the strength of the acid or base chosen. In Chapter 15, actual pH values of buffer solutions are calculated from quantitative information related to acid strength.

We began this section by mentioning the importance of the buffer system of our blood. The carbonic acid–bicarbonate buffer system is our main protection and is discussed in Making It Real, “The pH Balance in the Blood.” However, another buffer system is at work in the cells of our bodies. This is the  $\text{H}_2\text{PO}_4^-$ – $\text{HPO}_4^{2-}$  buffer system. In this system the dihydrogen phosphate ion ( $\text{H}_2\text{PO}_4^-$ ) acts as the acid species and the hydrogen phosphate ion ( $\text{HPO}_4^{2-}$ ) acts as the base species. These two ions can remove  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions produced in the cells as follows.



### The pH Balance in the Blood



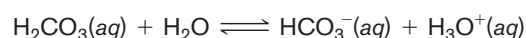
The pH of the blood is an important measurement.

our body but they function only in a very narrow pH range. Deviations of only 0.2 pH unit either way can cause coma or even be fatal. If the pH drops below 7.20, a condition known as *acidosis* results. If the pH rises to above 7.60, the opposite condition is called *alkalosis*. Either situation seriously upsets our body chemistry.

Perhaps one of the most amazing properties of blood is its ability to maintain a nearly constant pH despite the fact that acids and bases find their way into the bloodstream. The pH of our blood is held constant by two buffering systems. We will look closely at the more important system, which is the carbonic acid–bicarbonate buffer. This system is represented by the equation

The chemistry of the blood is a science unto itself. It is our river of life, delivering fuel and oxygen for the muscles, removing waste products, and keeping our body temperature steady. The pH of the blood is 7.40, just barely alkaline. As

mentioned in an earlier Making It Real, enzymes un-



The carbonic acid ( $\text{H}_2\text{CO}_3$ ) part of the buffer reacts with any extra  $\text{OH}^-$  ion that enters our blood, and the  $\text{HCO}_3^-$  ion reacts with any added  $\text{H}_3\text{O}^+$ . For example, exercise produces extra  $\text{H}_3\text{O}^+$  from the lactic acid formed in the muscles. The  $\text{H}_3\text{O}^+$  reacts with  $\text{HCO}_3^-$  to form carbonic acid. This is transported to the lungs where it decomposes to  $\text{CO}_2$  gas and  $\text{H}_2\text{O}$ , which is then exhaled. Our bodies respond to exercise by faster breathing and faster release of carbon dioxide.

If extra  $\text{OH}^-$  enters the blood, it reacts with  $\text{H}_2\text{CO}_3$  and more bicarbonate is formed, which is eventually excreted by the kidneys. Sometimes when people get nervous, they breathe too fast, which is called *hyperventilation*. This causes too much carbon dioxide to be exhaled, and the pH of the blood rises above 7.4. If the person faints, the breathing rate decreases and the pH quickly comes back into balance. Actually, the concentration of bicarbonate is about 10 times the concentration of carbonic acid, so we are more protected against extra acid than extra base, which works out well.

Health problems such as diabetes and kidney disease may disturb the buffers of the blood. Generally, however, we couldn't have a better system to maintain pH and with it the smooth functioning of our body.

### 13-8.3 Buffer Capacity

There is a limit to how much a buffer system can resist change. If the added amount of  $\text{OH}^-$  exceeds the reserve of  $\text{HClO}$  (referred to as the *buffer capacity*), then the pH will rise. This is analogous to a \$110 expense for the person with the \$100 savings. It is more than she can cover with bank savings, so the amount in her pocket decreases. The buffer capacity also relates to the original amount of the salt ( $\text{NaClO}$ ) present.

#### ASSESSING THE OBJECTIVES FOR SECTION 13-8

**EXERCISE 13-8(a) KNOWLEDGE:** Fill in the blanks.

A buffer solution consists of a weak acid and a salt of its \_\_\_\_\_. Buffer solutions resist a change in \_\_\_\_\_ because any hydronium is neutralized with the \_\_\_\_\_ and any hydroxide is neutralized with the \_\_\_\_\_. The \_\_\_\_\_ is a measure of how much strong acid or strong base the buffer can absorb.

**EXERCISE 13-8(b) KNOWLEDGE:** Which of these would form a buffer solution?

- (a)  $\text{HNO}_3 + \text{KNO}_3$       (c)  $\text{HF} + \text{NaF}$   
 (b)  $\text{HNO}_2 + \text{KNO}_2$       (d)  $\text{HBr} + \text{NaBr}$

**EXERCISE 13-8(c) ANALYSIS:** What salt could you add in order to make a buffer solution from each of the following aqueous solutions:

- (a)  $\text{NH}_3$       (b)  $\text{Na}_2\text{SO}_3$       (c)  $\text{HClO}_2$

**EXERCISE 13-8(d) ANALYSIS:** A mixture of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  can act as a buffer. (a) Write the reaction that occurs when  $\text{H}_3\text{O}^+$  is added to the solution. (b) Write the reaction when  $\text{OH}^-$  is added to the solution.

**EXERCISE 13-8(e) SYNTHESIS:** The addition of  $\text{HCl}$  to the weak base  $\text{C}_5\text{H}_4\text{N}$  can create a buffer solution if the number of moles of  $\text{HCl}$  added is less than the number of moles of  $\text{C}_5\text{H}_5\text{N}$  present. What two species make up that buffer?

*For additional practice, work chapter problems 13-29, 13-95, and 13-97.*

#### ▶ OBJECTIVE FOR SECTION 13-9

Determine, if possible, whether a specific oxide is acidic or basic.

## 13-9 OXIDES AS ACIDS AND BASES

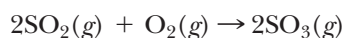


**LOOKING AHEAD!** We have one more important question concerning acids. How do they get into the atmosphere so as to make rain acidic? The question of acid rain is a matter of international consequence. ■

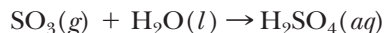
### 13-9.1 Acid Anhydrides

One of the more important consequences of the human race's progress is acid rain. Tall industrial smokestacks disperse exhaust gases high into the atmosphere, where prevailing winds may carry pollutants hundreds of miles before they return to the earth in the form of acid rain. Since acid rain passes over the boundaries of many countries, it can be a touchy subject between nations. Its effect on lakes and forests can be devastating, and there is little doubt that the problem must be faced and solved. To understand the origin of acid rain, we will examine how the oxides of the elements also leads to acid-base behavior.

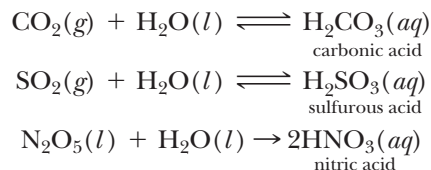
Most acid rain originates from the combustion of coal or other fossil fuels that contain sulfur as an impurity. Combustion of sulfur or sulfur compounds produces sulfur dioxide ( $\text{SO}_2$ ). In the atmosphere, sulfur dioxide reacts with oxygen to form sulfur trioxide ( $\text{SO}_3$ ).



The sulfur trioxide reacts with water in the atmosphere to form sulfuric acid.



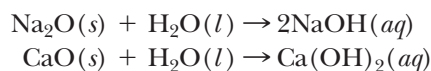
The sulfuric acid solution that comes down in the rain is a strong acid, which is corrosive and destructive. As mentioned earlier, acids react with metals and limestone, which are both used externally in buildings. (See Figure 13-7.) In the above reaction, sulfur trioxide can be considered as simply the dehydrated form of sulfuric acid. It is thus known as an **acid anhydride**, which means *acid without water*. Many nonmetal oxides are acid anhydrides. When dissolved in water, they form acids. Three other reactions of nonmetal oxides to form acids follow.



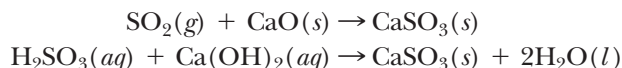
We have previously mentioned that carbon dioxide, the acid anhydride of carbonic acid, is responsible for the fizz and the tangy taste in carbonated soft drinks and beer. When all the carbon dioxide escapes, the beverage goes flat. Carbon dioxide is also present in the atmosphere and dissolves in rainwater to make rain naturally acidic. Carbon dioxide by itself lowers the pH of rain to about 5.7. Oxides of sulfur and nitrogen, however, lower the pH to 4.0 or even lower.\* The oxides of nitrogen originate mainly from engines in automobiles. The high temperature in the engine causes the two elements of air, nitrogen and oxygen, to combine to form nitrogen oxides. In eastern North America and western Europe, the acidity in rain is about two-thirds due to sulfuric acid and the remainder due to nitric acid. There is also a small amount of hydrochloric acid in acid rain.

### 13-9.2 Base Anhydrides

*Ionic metal oxides dissolve in water to form bases and thus are known as base anhydrides.* Some examples of these reactions are



Salt is formed by the reaction between an acid anhydride and a base anhydride. For example, the following reaction and the neutralization of  $\text{H}_2\text{SO}_3$  with  $\text{Ca}(\text{OH})_2$  in aqueous solution produce the same salt.



The first reaction represents a way of removing  $\text{SO}_2$  from the combustion products of an industrial plant so that some of our abundant high-sulfur coal can be used without harming the environment.



**FIGURE 13-7** The Effect of Acid Rain The deterioration of the statue is due to acid rain.

**EXERCISE 13-9(a) KNOWLEDGE:** Fill in the blanks.

Most nonmetal oxides react with water to form \_\_\_\_\_ solutions, and ionic metal oxides react with water to form \_\_\_\_\_ solutions. Compounds like  $\text{K}_2\text{O}$  or  $\text{Cl}_2\text{O}$  are called base or acid \_\_\_\_\_ because they contain no water.

**EXERCISE 13-9(b) KNOWLEDGE:** Do you expect the following to be acidic or basic?

- (a)  $\text{P}_4\text{O}_{10}$     (b)  $\text{NO}_2$     (c)  $\text{MgO}$     (d)  $\text{B}_2\text{O}_3$

\*On April 10, 1974, a rain fell on Piloehry, Scotland that had a pH of 2.4, which is about the same as that of vinegar. This is the most acidic rain ever recorded.

**EXERCISE 13-9(c) ANALYSIS:** What acid could form directly from  $\text{SO}_2$ ?

**EXERCISE 13-9(d) ANALYSIS:** What base could form directly from  $\text{Li}_2\text{O}$ ?

**EXERCISE 13-9(e) SYNTHESIS:** What is the problem with burning high-sulfur coal? Why would we want to do it? What can we do to remove the sulfur from the exhaust?

For additional practice, work chapter problems 13-99 and 13-101.

MAKING

IT

REAL

### Acid Rain—The Price of Progress?



Acid rain has had a harmful effect on the environment.

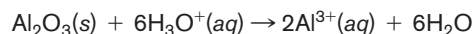
A century ago, it was inconceivable that we could actually change our planet. The human population was less than 2 billion and the world seemed vast and the environment forgiving. Now we know better. Greenhouse gases, ozone holes, and polluted water are serious problems created by people. One problem that we are doing something about is *acid rain*. Acid rain results from the presence of nonmetal oxides in the atmosphere as industrial or automobile by-products.

In Canada and Scandinavia some lakes have been seriously affected. The pH of these lakes has become progressively lower as a result of acid rain. Fish and any other aquatic creatures have completely disappeared. In these areas of the world, the soil and rocks contain little of the types of minerals that neutralize acids, such as limestone ( $\text{CaCO}_3$ , the active ingredient in many antacids).

In other situations, the vulnerability of  $\text{CaCO}_3$  to acid rain causes problems. Marble statues and mortar that have survived for centuries are rapidly deteriorating in the industrialized world. Various attempts are being made to protect these treasures with coatings, but so far nothing completely effective has been found.

The fertility of the soil is being affected by acid rain. Metal oxides are an integral part of the soil. These oxides

are insoluble in water but become more soluble at low pH, as illustrated by the following equation.



Some forests in the world seem to be seriously stressed. Acid rain is the suspected culprit. In addition to oxides, many exposed metals that are not affected by ordinary rain are corroded by acid rain.

There is progress, however. There are strict limits on sulfur emissions from power plants. Catalytic converters on automobiles are reducing the nitrogen emissions. Laws are on the books and more are coming as we attempt to reverse this serious problem. These solutions do not come cheaply, however. We are all paying the billions of dollars necessary to prevent these oxides from entering the atmosphere.

Another concern about the buildup of  $\text{CO}_2$  in the atmosphere is its effect on the acidity of the oceans. As the partial pressure of  $\text{CO}_2$  increases in the atmosphere, more dissolves in the ocean (recall Henry's law), decreasing its pH. In fact, it has recently been reported that in the past 200 years the pH of the surface of the ocean has decreased from 8.3 to 8.2. That may not seem like much, but considering that pH is a logarithmic scale, the change represents a 20% increase in  $\text{H}_3\text{O}^+$  concentration (i.e., from  $5 \times 10^{-9}$  mol/L to  $6 \times 10^{-9}$  mol/L). It is projected that the pH could fall to 7.7 (a 400% increase) by 2100 if the  $\text{CO}_2$  concentration in the atmosphere increases as projected. It is not possible, at this time, to predict how the increased acidity of the oceans will affect the ocean's ecology or Earth's temperature. But it is a matter of concern.

## PART C SUMMARY

### KEY TERMS

- 13-7** The reaction of an ion as an acid or base in water is known as a **hydrolysis** reaction. p. 420
- 13-8.1** A **buffer** is a solution that resists changes in pH and contains both a weak acid and a weak base. p. 423
- 13-9.1** An **acid anhydride** is a nonmetal oxide that forms an acid in water. p. 427
- 13-9.2** A **base anhydride** is a metal oxide that forms a base in water. p. 427

## SUMMARY CHART

| The Identity of Acids and Bases                |              |  |
|--|--------------|--|
| Type   | Example      | Reaction   |
| ACIDS  |              |  |
| 1. Molecular hydrogen compounds ( $H^+$ + ion) | $HClO_4$     | $HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$                                       |
| 2. Cations (conjugate acids of weak bases)     | $NH_4^+$     | $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$                                   |
| 3. Nonmetal oxides                             | $SO_3$       | $SO_3 + H_2O \rightarrow H_2SO_4$<br>$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ |
| BASES  |              |  |
| 1. Ionic hydroxides                            | $Ca(OH)_2$   | $Ca(OH)_2 \xrightarrow{H_2O} Ca^{2+} + 2OH^-$                                      |
| 2. Molecular nitrogen compounds                | $(CH_3)_2NH$ | $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$                       |
| 3. Anions (conjugate bases of weak acids)      | $CN^-$       | $CN^- + H_2O \rightleftharpoons HCN + OH^-$  |
| 4. Metal oxides                                | $K_2O$       | $K_2O + H_2O \rightarrow 2KOH$<br>$KOH \xrightarrow{H_2O} K^+OH^-$                 |

## CHAPTER SUMMARY

Compounds have been classified as acids or bases for hundreds of years on the basis of common sets of chemical characteristics. In the twentieth century, however, acid character was attributed to formation of  $H^+$  [also represented as the **hydronium ion** ( $H_3O^+$ )] in aqueous solution. Base character is due to the formation of  $OH^-$  in solution.

Our understanding of acid–base behavior can be broadened somewhat by use of the **Brønsted–Lowry** definition, which defines **acids** as proton ( $H^+$ ) donors and **bases** as proton acceptors. **Amphiprotic** substances can either donate or accept a proton. An acid–base reaction constitutes an  $H^+$  exchange between an acid and a base to form a **conjugate base** and **conjugate acid**, respectively.

Acids and bases can also be classified according to strength. Strong acids and strong bases are 100% ionized in water, whereas **weak molecular acids** and **weak molecular bases** are only partially ionized. Partial ionization of a molecular acid occurs when a reaction reaches a point of equilibrium in which both molecules (on the left of the equation) and ions (on the right) are present. For weak molecular acids and bases, the point of equilibrium favors the left, or molecular, side of the equation. Therefore, the  $H_3O^+$  concentration in a weak acid solution is considerably lower than in a strong acid solution at the same initial concentration of acid.

When acidic and basic solutions are mixed, the two active ions combine in a neutralization reaction to form water. Complete neutralization of a **monoprotic acid** results in a salt and water. Incomplete neutralization of

a **polyprotic acid** (either **diprotic** or **triprotic**) produces an **acid salt** and water.

Even in pure water, there is a very small equilibrium concentration of  $H_3O^+$  and  $OH^-$  ( $1.0 \times 10^{-7} M$ ) due to the **autoionization** of water. The product of these concentrations is a constant known as the **ion product** ( $K_w$ ) of water. The ion product can be used to calculate the concentration of one ion from that of the other in any aqueous solution. A convenient method to express the  $H_3O^+$  or  $OH^-$  concentrations of solutions involves the use of the logarithmic expressions **pH** and **pOH**.

The ions of a salt may or may not interact with water as acids or bases. If such a reaction of an ion does occur, it is known as **hydrolysis**. To predict the effect of the solution of a salt on the pH, possible hydrolysis reactions of both the cation and the anion must be examined. The resulting solution may be neutral, weakly basic, or weakly acidic, depending on the ion undergoing hydrolysis.

When a solution of a weak acid is mixed with a solution of a salt, providing its conjugate base, a **buffer** solution is formed. Buffer solutions resist changes in pH from addition of limited amounts of a strong acid or base. In a buffer, the reservoir of nonionized acid (e.g.,  $HC_2H_3O_2$ ) reacts with added  $OH^-$ , while the reservoir of the conjugate base (e.g.,  $C_2H_3O_2^-$ ) reacts with added  $H_3O^+$ . Weak bases and salts providing their conjugate acids also act as buffers (e.g.,  $NH_3$  and  $NH_4^+Cl^-$ ).

Finally, the list of acids and bases was expanded to include oxides, which can be classified as **acid anhydrides** or **base anhydrides**.



## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES                  | EXERCISES          | CHAPTER PROBLEMS                       |
|---------|---|---------------------------|--------------------|--|
| 13-1    | List the general properties of acids and bases.   |                           | 1a, 1b, 1c, 1d     | 5, 6                                   |
| 13-2    | Identify the Brønsted acids and bases in a proton exchange reaction.  | 13-3                      | 2a, 2b, 2c, 3d     | 1, 2, 11, 14                           |
|         | Identify conjugate acid – base pairs.   | 13-1, 13-2                | 2d                 | 7, 8, 9, 10                            |
| 13-3    | Calculate the hydronium ion concentration in a solution of a strong acid and a weak acid given the initial concentration of the acid and the percent ionization of the weak acid. | 13-4, 13-5                | 3a, 3b, 3c         | 17, 23, 24, 26, 29                     |
| 13-4    | Write the molecular, total ionic, and net ionic equations for neutralization reactions.   | 13-6, 13-7                | 4a, 4b, 4c, 4d     | 18, 19, 21, 33, 34, 35, 36, 40, 42, 45 |
| 13-5    | Using the ion product of water, relate the hydroxide ion and the hydronium ion concentrations.  | 13-8                      | 5a, 5b, 5c         | 52, 53, 54, 56                         |
| 13-6    | Given the hydronium or hydroxide ion concentration, calculate the pH and pOH.   | 13-9, 13-10, 13-11, 13-12 | 6a, 6b, 6c         | 60, 62, 64, 66, 67, 70, 73             |
| 13-7    | Identify a salt solution as neutral, acidic, or basic.  | 13-13                     | 7a, 7b, 7c, 7d, 7c | 31, 79, 82, 84, 86, 87, 88             |
| 13-8    | Describe how a buffer solution works.   |                           | 8a, 8b             | 92, 98                                 |
|         | Write equations illustrating the fate of hydronium or hydroxide added to such a solution.   |                           | 8c, 8d, 8e         | 94, 95, 97                             |
| 13-9    | Determine, if possible, whether a specific oxide is acidic or basic.  |                           | 9a, 9b, 9c, 9d, 9e | 99, 100                                |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**13-1(a)** An acid is a compound that produces the hydrogen ion in solution, which is also written as the hydronium ion ( $\text{H}_3\text{O}^+$ ). A base is a compound that produces an ion with the formula  $\text{OH}^-$  and the name hydroxide ion.

**13-1(b)** (a)  $\text{HClO}_4$ , perchloric acid (b)  $\text{Fe}(\text{OH})_2$ , iron(II) hydroxide (c)  $\text{H}_2\text{S}$ , hydrosulfuric acid (d)  $\text{LiOH}$ , lithium hydroxide

**13-1(c)** (a)  $\text{HI} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{I}^-$

(b)  $\text{LiOH} + \text{H}_2\text{O} \rightarrow \text{Li}^+(\text{aq}) + \text{OH}^-(\text{aq})$

**13-1(d)** (a) base (b) acid (c) acid (d) base (e) base (f) base

**13-2(a)** In the Brønsted–Lowry definition, acids are proton donors and bases are proton acceptors. A conjugate acid of a compound or ion results from the exchange of an  $\text{H}^+$  ion. A substance that has both a conjugate acid and a conjugate base is said to be amphiprotic.

**13-2(b)** acid:  $\text{H}_2\text{C}_2\text{O}_4$ ; base:  $\text{C}_2\text{O}_4^{2-}$

**13-2(c)** (a)  $\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$

(b)  $\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{OH}^-$

**13-2(d)**  $\text{CH}_3\text{COOH} + (\text{CH}_3)_3\text{N} \rightarrow \text{CH}_3\text{COO}^- + (\text{CH}_3)_3\text{NH}^+$ . The two sets of conjugate acid–base pairs are  $\text{CH}_3\text{COOH} - \text{CH}_3\text{COO}^-$  and  $(\text{CH}_3)_3\text{NH}^+ - (\text{CH}_3)_3\text{N}$

**13-3(a)** Strong acids are essentially 100 % ionized in aqueous solution, whereas weak acids are partially ionized. Sodium hydroxide is a strong base, but ammonia is a weak base. When a weak acid reacts with water, the reaction is said to be at equilibrium.

**13-3(b)** This is a weak acid.  $[\text{H}_3\text{O}^+] = 0.10 \times 0.025 = 0.0025 \text{ M}$ .

**13-3(c)** Since the hydronium concentration is less than the original acid concentration, this is a weak acid. The percent ionization =  $0.0050 \times 100 / .25 = 2.0\%$ .

**13-3(d)** (a)  $\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$

(b)  $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$

(c)  $\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_2^-$

(d)  $\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$

**13-4(a)** The reaction between an acid and a base is known as a neutralization reaction. The net ionic equation of this reaction always has  $\text{H}_2\text{O}$  as a product. The spectator ions of the reaction form a salt. The partial neutralization of polyprotic acids produces an acid salt and water.

**13-4(b)**

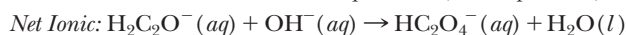
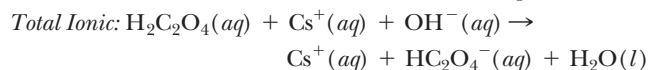
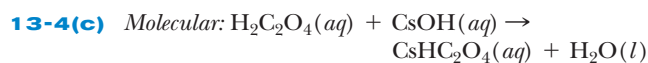
*Molecular:*  $2\text{HNO}_3(\text{aq}) + \text{Sr}(\text{OH})_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

+  $\text{Sr}(\text{NO}_3)_2(\text{aq})$

*Total Ionic:*  $2\text{H}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + \text{Sr}^{2+}(\text{aq})$

+  $2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{Sr}^{2+} + 2\text{NO}_3^-(\text{aq})$

*Net Ionic:*  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$



## PART B

## EXERCISES

**13-5(a)** Pure water contains a small but important concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. The product of the concentrations of these two ions, known as the ion product of water, is symbolized by  $K_w$  and has a value of  $1 \times 10^{-14}$  at  $25^\circ\text{C}$ . As the concentration of  $\text{OH}^-$  increases in water, the concentration of  $\text{H}_3\text{O}^+$  decreases.

**13-5(b)**  $(1.0 \times 10^{-14}) / (7.2 \times 10^{-5}) = 1.4 \times 10^{-10}$

**13-5(c)**  $[\text{OH}^-]$  is larger than  $1.0 \times 10^{-7}$ , so the solution is basic. It would need to be close to  $10^{-1}$  to be considered strongly basic, so this is weakly basic. A common weak base that could produce that solution would be  $\text{NH}_3$ .

**13-6(a)** The pH of a solution is defined as  $-\log[\text{H}_3\text{O}^+]$ . An acidic solution is one that has an  $[\text{H}_3\text{O}^+]$  greater than  $1 \times 10^{-7}$  and a pH less than 7. A basic solution is one that has an  $[\text{OH}^-]$  greater than  $1 \times 10^{-7}$  and a pH greater than 7.

**13-6(b)**  $\text{pH} = 9.86$

**13-6(c)**  $[\text{LiOH}] = 0.25$

**13-6(d)** (a)  $1.3 \times 10^{-13}$  (b)  $0.075 \text{ M OH}^-$

(c)  $\text{pH} = 12.88$  (d)  $\text{pOH} = 1.12$

**13-6(e)** The HCl is a strong acid and the  $\text{H}_3\text{O}^+$  is determined directly from the concentration of acid. It is  $0.005 \text{ M}$ , and the pH is 2.3. The acetic acid's  $\text{H}_3\text{O}^+$  comes only from the part that is ionized, or  $0.0008 \text{ M}$ , which is about six times less than the HCl solution. The pH of the second solution is 3.1.

## PART C

## EXERCISES

**13-7(a)** (a) acidic (b) neutral (c) basic (d) more information is needed

**13-7(b)** (a) basic (b) acidic (c) neutral (d) basic

**13-7(c)** (a)  $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$

(b) No hydrolysis is occurring.

(c)  $\text{N}_2\text{H}_5^+ + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_4 + \text{H}_3\text{O}^+$

**13-7(d)** Any weak acid would work, such as  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{HClO}_2$ ,  $\text{HNO}_2$  or HF.

**13-7(e)** Any strong acid would work, such as HCl,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$ .

**13-8(a)** A buffer solutions consist of a weak acid and a salt of its conjugate base. Buffer solutions resist a change in pH because any hydronium is neutralized with the base and any hydroxide is neutralized with the acid. The buffer capacity is a measure of how much strong acid or strong base the buffer can absorb.

**13-8(b)** Possible buffers include (b) and (c).

**13-8(c)** (a)  $\text{NH}_4\text{Cl}$  (b)  $\text{NaHSO}_3$  (c)  $\text{KClO}_2$

**13-8(d)** (a)  $\text{H}_3\text{O}^+ + \text{HC}_2\text{O}_4^- \rightarrow \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$

(b)  $\text{OH}^- + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{O}$

**13-8(e)**  $\text{C}_5\text{H}_4\text{NH}^+\text{Cl}^-$  (the weakly acidic salt) and  $\text{C}_5\text{H}_4\text{N}$  (the weak base)

**13-9(a)** Most nonmetal oxides react with water to form acidic solutions, and ionic metal oxides react with water to form basic solutions. Chemicals like  $\text{K}_2\text{O}$  or  $\text{Cl}_2\text{O}$  are called base or acid anhydrides because they contain no water.

**13-9(b)** (a) acidic (b) acidic (c) basic (d) acidic

**13-9(c)**  $\text{H}_2\text{SO}_3$

**13-9(d)** LiOH

**13-9(e)** High-sulfur coal releases  $\text{SO}_2$  into the environment, which can lead to the formation of acid rain. High-sulfur coal, though, is abundant and therefore costs less. To keep the  $\text{SO}_2$  out of the environment, we can use scrubbers that react the acid anhydride  $\text{SO}_2$  with the base anhydride CaO to form the insoluble salt  $\text{CaSO}_3$ .

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## Acids and Bases (SECTION 13-1)

**13-1.** Give the formulas and names of the acid compounds derived from the following anions.

(a)  $\text{NO}_3^-$  (b)  $\text{NO}_2^-$  (c)  $\text{ClO}_3^-$  (d)  $\text{SO}_3^{2-}$

**13-2.** Give the formulas and names of the acid compounds derived from the following anions.

(a)  $\text{CN}^-$  (b)  $\text{CrO}_4^{2-}$  (c)  $\text{ClO}_4^-$  (d)  $\text{Br}^-$

**13-3.** Give the formulas and names of the base compounds derived from the following cations.

(a)  $\text{Cs}^+$  (b)  $\text{Sr}^{2+}$  (c)  $\text{Al}^{3+}$  (d)  $\text{Mn}^{3+}$

**13-4.** Give the formulas and names of the acid or base compounds derived from the following anions.

(a)  $\text{Ba}^{2+}$  (c)  $\text{Pb}^{2+}$  (e)  $\text{H}_2\text{PO}_4^-$

(b)  $\text{Se}^{2-}$  (d)  $\text{ClO}^-$  (f)  $\text{Fe}^{3+}$

**13-5.** Write reactions illustrating the acid or base behavior in water for the following.

(a)  $\text{HNO}_3$  (b)  $\text{CsOH}$  (c)  $\text{Ba}(\text{OH})_2$  (d)  $\text{HBr}$

**13-6.** Write reactions illustrating the acid or base behavior in water for the following.

(a) HI (b)  $\text{Sr}(\text{OH})_2$  (c)  $\text{RbOH}$  (d)  $\text{HClO}_4$

## Brønsted-Lowry Acids and Bases (SECTION 13-2)

**13-7.** What is the conjugate base of each of the following?

(a)  $\text{HNO}_3$  (c)  $\text{HPO}_4^{2-}$  (e)  $\text{H}_2\text{O}$

(b)  $\text{H}_2\text{SO}_4$  (d)  $\text{CH}_4$  (f)  $\text{NH}_3$

**13-8.** What is the conjugate acid of each of the following?

(a)  $\text{CH}_3\text{NH}_2$  (c)  $\text{NO}_3^-$  (e)  $\text{HCN}$

(b)  $\text{HPO}_4^{2-}$  (d)  $\text{O}^{2-}$  (f)  $\text{H}_2\text{O}$



**13-42.** Write balanced acid–base neutralization reactions that would lead to formation of the following salts or acid salts.

- (a)  $\text{Na}_2\text{SO}_3$  (c)  $\text{Mg}_3(\text{PO}_4)_2$   
 (b)  $\text{AlI}_3$  (d)  $\text{NaHCO}_3$

**13-43.** Write two equations illustrating the stepwise neutralization of  $\text{H}_2\text{S}$  with  $\text{LiOH}$ .

**13-44.** Write the two net ionic equations illustrating the two reactions in problem 13-43.

**13-45.** Write three equations illustrating the stepwise neutralization of  $\text{H}_3\text{AsO}_4$  with  $\text{LiOH}$ . Write the total reaction.

**13-46.** Write the net ionic equations for the three reactions in problem 13-45.

**13-47.** Write the equation illustrating the reaction of 1 mol of  $\text{H}_2\text{S}$  with 1 mol of  $\text{NaOH}$ .

**\*13-48.** Write the equation illustrating the reaction between 1 mol of  $\text{Ca}(\text{OH})_2$  and 2 mol of  $\text{H}_3\text{PO}_4$ .

### Equilibrium of Water and $K_w$ (SECTION 13-5)

**13-49.** If some ions are present in pure water, why isn't pure water considered to be an electrolyte?

**13-50.** Why can't  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-2}$  M in water? What would happen if we tried to make such a solution by mixing  $10^{-2}$  mol/L of  $\text{KOH}$  with  $10^{-2}$  mol/L of  $\text{HCl}$ ?

**13-51.** (a) What is  $[\text{H}_3\text{O}^+]$  when  $[\text{OH}^-] = 10^{-12}$  M?

(b) What is  $[\text{H}_3\text{O}^+]$  when  $[\text{OH}^-] = 10$  M?

(c) What is  $[\text{OH}^-]$  when  $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-5}$  M?

**13-52.** (a) What is  $[\text{OH}^-]$  when  $[\text{H}_3\text{O}^+] = 1.50 \times 10^{-3}$  M?

(b) What is  $[\text{H}_3\text{O}^+]$  when  $[\text{OH}^-] = 2.58 \times 10^{-7}$  M?

(c) What is  $[\text{H}_3\text{O}^+]$  when  $[\text{OH}^-] = 56.9 \times 10^{-9}$  M?

**13-53.** When 0.250 mol of the strong acid  $\text{HClO}_4$  is dissolved in 10.0 L of water, what is  $[\text{H}_3\text{O}^+]$ ? What is  $[\text{OH}^-]$ ?

**13-54.** Lye is a very strong base. What is  $[\text{H}_3\text{O}^+]$  in a 2.55 M solution of  $\text{NaOH}$ ? In the weakly basic household ammonia,  $[\text{OH}^-] = 4.0 \times 10^{-3}$  M. What is  $[\text{H}_3\text{O}^+]$ ?

**13-55.** Identify the solutions in problem 13-51 as acidic, basic, or neutral.

**13-56.** Identify the solutions in problem 13-52 as acidic, basic, or neutral.

**13-57.** Identify each of the following as an acidic, basic, or neutral solution.

(a)  $[\text{H}_3\text{O}^+] = 6.5 \times 10^{-3}$  M (c)  $[\text{OH}^-] = 4.5 \times 10^{-8}$  M

(b)  $[\text{H}_3\text{O}^+] = 5.5 \times 10^{-10}$  M (d)  $[\text{OH}^-] = 50 \times 10^{-8}$  M

**13-58.** Identify each of the following as an acidic, basic, or neutral solution.

(a)  $[\text{OH}^-] = 8.1 \times 10^{-8}$  M (c)  $[\text{H}_3\text{O}^+] = 4.0 \times 10^{-3}$  M

(b)  $[\text{H}_3\text{O}^+] = 10.0 \times 10^{-8}$  M (d)  $[\text{OH}^-] = 55 \times 10^{-8}$  M

### pH and pOH (SECTION 13-6)

**13-59.** What is the pH of the following solutions?

(a)  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-6}$  M (d)  $[\text{OH}^-] = 2.5 \times 10^{-5}$  M

(b)  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-9}$  M (e)  $[\text{H}_3\text{O}^+] = 6.5 \times 10^{-11}$  M

(c)  $[\text{OH}^-] = 1.0 \times 10^{-2}$  M

**13-60.** What is the pH of the following solutions?

(a)  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-2}$  M (d)  $[\text{OH}^-] = 3.6 \times 10^{-9}$  M

(b)  $[\text{OH}^-] = 1.0 \times 10^{-4}$  M (e)  $[\text{OH}^-] = 7.8 \times 10^{-4}$  M

(c)  $[\text{H}_3\text{O}^+] = 1.0$  M (f)  $[\text{H}_3\text{O}^+] = 42.2 \times 10^{-5}$  M

**13-61.** What are the pH and pOH of the following?

(a)  $[\text{H}_3\text{O}^+] = 0.0001$  (c)  $[\text{H}_3\text{O}^+] = 0.020$

(b)  $[\text{OH}^-] = 0.00001$  (d)  $[\text{OH}^-] = 0.000320$

**13-62.** What are the pH and pOH of the following?

(a)  $[\text{H}_3\text{O}^+] = 0.0000001$  (c)  $[\text{OH}^-] = 0.0568$

(b)  $[\text{OH}^-] = 0.0001$  (d)  $[\text{H}_3\text{O}^+] = 0.00082$

**13-63.** What is  $[\text{H}_3\text{O}^+]$  of the following?

(a) pH = 3.00 (d) pOH = 6.38

(b) pH = 3.54 (e) pH = 12.70

(c) pOH = 8.00

**13-64.** What is  $[\text{H}_3\text{O}^+]$  of the following?

(a) pH = 9.0 (c) pH = 2.30

(b) pOH = 9.0 (d) pH = 8.90

**13-65.** Identify each of the solutions in problems 13-59 and 13-63 as acidic, basic, or neutral.

**13-66.** Identify each of the solutions in problems 13-60 and 13-64 as acidic, basic, or neutral.

**13-67.** A solution has pH = 3.0. What is the pH of a solution that is 100 times less acidic? What is the pH of a solution that is 10 times more acidic?

**13-68.** A solution has pOH = 4. What is the pOH of a solution that is 1000 times more acidic? What is the pOH of a solution that is 100 times more basic?

**13-69.** What is the pH of a 0.075 M solution of the strong acid  $\text{HNO}_3$ ?

**13-70.** What is the pH of a 0.0034 M solution of the strong base  $\text{KOH}$ ?

**13-71.** What is the pH of a 0.018 M solution of the strong base  $\text{Ca}(\text{OH})_2$ ?

**13-72.** A weak monoprotic acid is 10.0% ionized in solution. What is the pH of a 0.10 M solution of this acid?

**13-73.** A weak base is 5.0% ionized in solution. What is the pH of a 0.25 M solution of this base? (Assume one  $\text{OH}^-$  per formula unit.)

**13-74.** Identify each of the following solutions as strongly basic, weakly basic, neutral, weakly acidic, or strongly acidic.

(a) pH = 1.5 (d) pH = 13.0 (g) pOH = 7.5

(b) pOH = 13.0 (e) pOH = 7.0 (h) pH = -1.0

(c) pH = 5.8 (f) pH = 8.5

**13-75.** Arrange the following substances in order of increasing acidity.

(a) household ammonia, pH = 11.4

(b) vinegar,  $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-3}$  M

(c) grape juice,  $[\text{OH}^-] = 1.0 \times 10^{-10}$  M

(d) sulfuric acid, pOH = 13.6

(e) eggs, pH = 7.8

(f) rainwater,  $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-6}$  M

**13-76.** Arrange the following substances in order of increasing acidity.

(a) lime juice,  $[\text{H}_3\text{O}^+] = 6.0 \times 10^{-2}$  M

(b) antacid tablet in water,  $[\text{OH}^-] = 2.5 \times 10^{-6}$  M

(c) coffee, pOH = 8.50

(d) stomach acid, pH = 1.8

(e) saliva,  $[\text{H}_3\text{O}^+] = 2.2 \times 10^{-7}$  M

(f) a soap solution, pH = 8.3

(g) a solution of lye, pOH = 1.2

(h) a banana,  $[\text{OH}^-] = 4.0 \times 10^{-10}$  M



**\*13-77.** What is the pH of a 0.0010 M solution of  $\text{H}_2\text{SO}_4$ ? (Assume that the first ionization is complete but the second is only 25% complete.)

### Hydrolysis of Salts (SECTION 13-7)

**13-78.** Two of the following act as weak bases in water. Write the appropriate reactions illustrating the weak base behavior.

- (a)  $\text{ClO}_4^-$  (b)  $\text{C}_2\text{H}_3\text{O}_2^-$  (c)  $\text{NH}_3$  (d) HF

**13-79.** Two of the following act as weak acids in water. Write the appropriate reactions illustrating the weak acid behavior.

- (a)  $\text{H}_2\text{CrO}_4$  (b)  $\text{NH}_4^+$  (c)  $\text{NH}_2\text{CH}_3$  (d)  $\text{CrO}_4^{2-}$

**13-80.** Three of the following molecules or ions do not affect the pH of water. Which are they and why do they not affect the pH?

- (a)  $\text{K}^+$  (b)  $\text{NH}_3$  (c)  $\text{HCO}_3^-$  (d)  $\text{NO}_3^-$  (e)  $\text{O}_2$  (f)  $\text{N}_2\text{H}_5^+$

**13-81.** Complete the following hydrolysis equilibria.

- (a)  $\text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{_____} + \text{OH}^-$   
 (b)  $\text{N}_2\text{H}_5^+ + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_4 + \text{_____}$   
 (c)  $\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{_____}$   
 (d)  $(\text{CH}_3)_2\text{NH}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{_____} + \text{H}_3\text{O}^+$

**13-82.** Complete the following hydrolysis equilibria.

- (a)  $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{_____}$   
 (b)  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{_____} + \text{H}_3\text{O}^+$   
 (c)  $\text{B}(\text{OH})_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{BO}_3 + \text{_____}$   
 (d)  $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+} + \text{_____}$

**13-83.** Write the hydrolysis equilibria (if any) for the following ions.

- (a)  $\text{F}^-$  (b)  $\text{SO}_3^{2-}$  (c)  $(\text{CH}_3)_2\text{NH}_2^+[(\text{CH}_3)_2\text{NH}]$  (d)  $\text{HPO}_4^{2-}$  (e)  $\text{CN}^-$  (f)  $\text{Li}^+$

[is a weak base like ammonia.]

**13-84.** Write the hydrolysis equilibria (if any) for the following ions.

- (a)  $\text{Br}^-$  (b)  $\text{HS}^-$  (c)  $\text{ClO}_4^-$  (d)  $\text{H}^-$  (e)  $\text{Ca}^{2-}$

**13-85.** Calcium hypochlorite is used to purify water. When dissolved, it produces a slightly basic solution. Write the equation illustrating the solution of calcium hypochlorite in water and the equation illustrating its basic behavior.

**13-86.** Aqueous NaF solutions are slightly basic, whereas aqueous NaCl solutions are neutral. Write the appropriate equation that illustrates this. Why aren't NaCl solutions also basic?

**13-87.** Predict whether aqueous solutions of the following salts are acidic, neutral, or basic.

- (a)  $\text{Ba}(\text{ClO}_4)_2$  (b)  $\text{N}_2\text{H}_5^+\text{NO}_3^-$  ( $\text{N}_2\text{H}_4$  is a weak base.) (c)  $\text{LiC}_2\text{H}_3\text{O}_2$  (d) KBr (e)  $\text{NH}_4\text{Cl}$  (f)  $\text{BaF}_2$

**13-88.** Predict whether aqueous solutions of the following salts are acidic, neutral, or basic.

- (a)  $\text{Na}_2\text{CO}_3$  (b)  $\text{K}_3\text{PO}_4$  (c)  $\text{NH}_4\text{ClO}_4$  (d)  $\text{SrI}_2$

**\*13-89.** Both  $\text{C}_2^{2-}$  and its conjugate acid  $\text{HC}_2^-$  hydrolyze 100% in water. From this information, complete the following equation.

$\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{_____}(g) + \text{Ca}^{2+}(aq) + 2\text{_____}(aq)$   
 (The gas formed—acetylene—can be burned as it is produced. This reaction was once important for this purpose as a source of light in old miners' lamps.)

**\*13-90.** Aqueous solutions of  $\text{NH}_4\text{CN}$  are basic. Write the two hydrolysis reactions and indicate which takes place to the greater extent.

**13-91.** Aqueous solutions of  $\text{NaHSO}_3$  are acidic. Write the two equations (one hydrolysis and one ionization) and indicate which takes place to the greater extent.

### Buffers (SECTION 13-9)

**13-92.** Identify which of the following form buffer solutions when 0.50 mol of each compound is dissolved in 1 L of water.

- (a)  $\text{HNO}_2$  and  $\text{KNO}_2$  (b)  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  (c)  $\text{HNO}_3$  and  $\text{KNO}_2$  (d)  $\text{HNO}_3$  and  $\text{KNO}_3$  (e)  $\text{HClO}$  and  $\text{Ca}(\text{ClO})_2$  (f)  $\text{HCN}$  and  $\text{KClO}$  (g)  $\text{NH}_3$  and  $\text{BaBr}_2$  (h)  $\text{H}_2\text{S}$  and  $\text{LiHS}$  (i)  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$

**13-93.** A certain solution contains dissolved HCl and NaCl. Why can't this solution act as a buffer?

**13-94.** Write the equilibrium involved in the  $\text{N}_2\text{H}_4$ ,  $\text{N}_2\text{H}_5\text{Cl}$  buffer system. ( $\text{N}_2\text{H}_4$  is a weak base.) Write equations illustrating how this system reacts with added  $\text{H}_3\text{O}^+$  and added  $\text{OH}^-$ .

**13-95.** Write the equilibrium involved in the  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  buffer system. Write equations illustrating how this system reacts with added  $\text{H}_3\text{O}^+$  and added  $\text{OH}^-$ .

**13-96.** Write the equilibrium involved in the  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  buffer system. Write equations illustrating how this system reacts with added  $\text{H}_3\text{O}^+$  and added  $\text{OH}^-$ .

**13-97.** If 0.5 mol of KOH is added to a solution containing 1.0 mol of  $\text{HC}_2\text{H}_3\text{O}_2$ , the resulting solution is a buffer. Explain.

**13-98.** A solution contains 0.50 mol each of HClO and NaClO. If 0.60 mol of KOH is added, will the buffer prevent a significant change in pH? Explain.

### Oxides as Acids and Bases (SECTION 13-9)

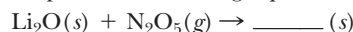
**13-99.** Write the formula of the acid or base formed when each of the following anhydrides is dissolved in water.

- (a) SrO (b)  $\text{SeO}_3$  (c)  $\text{P}_4\text{O}_{10}$  (d)  $\text{Cs}_2\text{O}$  (e)  $\text{N}_2\text{O}_3$  (f)  $\text{Cl}_2\text{O}_5$

**13-100.** Write the formula of the acid or base formed when each of the following anhydrides is dissolved in water.

- (a) BaO (b)  $\text{SeO}_2$  (c)  $\text{Cl}_2\text{O}$  (d)  $\text{Br}_2\text{O}$  (e)  $\text{K}_2\text{O}$

**13-101.** Carbon dioxide is removed from the space shuttle by bubbling the air through an LiOH solution. Show the reaction and complete the following equation.



### General Problems

**13-103.** Iron reacts with an acid, forming an aqueous solution of iron(II) iodide and a gas. Write the equation illustrating the reaction.

**13-104.** Aluminum reacts with perchloric acid. Write the equation illustrating this reaction.

**13-105.** Nitric acid reacts with sodium sulfite, forming sulfur dioxide gas and a salt. Write the equation illustrating the reaction.



**13-106.** Perbromic acid reacts with sodium sulfide to form a pungent gas, hydrogen sulfide. Write the equation illustrating the reaction.

**13-107.** There are acid–base systems based on solvents other than  $\text{H}_2\text{O}$ . One is ammonia ( $\text{NH}_3$ ), which is also amphiprotic. Write equations illustrating each of the following.

- (a) the reaction of  $\text{HCN}$  with  $\text{NH}_3$  acting as a base
- (b) the reaction of  $\text{H}^-$  with  $\text{NH}_3$  acting as an acid
- (c) the reaction of  $\text{HCO}_3^-$  with  $\text{NH}_3$  acting as a base
- (d) the reaction between  $\text{NH}_4\text{Cl}$  and  $\text{NaNH}_2$  in ammonia

**13-108.** The conjugate base of methyl alcohol ( $\text{CH}_3\text{OH}$ ) is  $\text{CH}_3\text{O}^-$ . Its conjugate acid is  $\text{CH}_3\text{OH}_2^+$ . Write equations illustrating each of the following.

- (a) the reaction of  $\text{HCl}$  with methyl alcohol acting as a base
- (b) the reaction of  $\text{NH}_2^-$  with methyl alcohol acting as an acid

**13-109.** Sulfite ion ( $\text{SO}_3^{2-}$ ) and sulfur trioxide ( $\text{SO}_3$ ) look similar at first glance, but one forms a strongly acidic solution whereas the other is weakly basic. Write equations illustrating this behavior.

**13-110.** Tell whether each of the following compounds forms an acidic, basic, or neutral solution when added to pure water. Write the equation illustrating the acidic or basic behavior where appropriate.

- (a)  $\text{H}_2\text{S}$
- (b)  $\text{KClO}$
- (c)  $\text{NaI}$
- (d)  $\text{NH}_3$
- (e)  $\text{N}_2\text{H}_5^+\text{Br}^-$
- (f)  $\text{Ba}(\text{OH})_2$
- (g)  $\text{Sr}(\text{NO}_3)_2$
- (h)  $\text{LiNO}_2$
- (i)  $\text{H}_2\text{SO}_3$
- (j)  $\text{Cl}_2\text{O}_3$

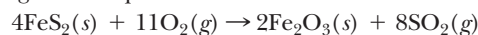
**13-111.** Tell whether each of the following compounds forms an acidic, basic, or neutral solution when added to pure water. Write the equation illustrating the acidic or basic behavior where appropriate.

- (a)  $\text{HBrO}$
- (b)  $\text{CaO}$
- (c)  $\text{NH}_4\text{ClO}_4$
- (d)  $\text{N}_2\text{H}_4$
- (e)  $\text{SO}_2$
- (f)  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$
- (g)  $\text{RbBr}$

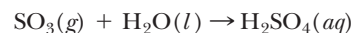
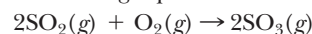
**13-112.** In a lab there are five different solutions with pH's of 1.0, 5.2, 7.0, 10.2, and 13.0. The solutions are  $\text{LiOH}$ ,  $\text{SrBr}_2$ ,  $\text{KClO}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{HI}$ , all at the same concentration. Which pH corresponds to which compound? What must be the concentration of all of these solutions?

**13-113.** When one mixes a solution of baking soda ( $\text{NaHCO}_3$ ) with vinegar ( $\text{HC}_2\text{H}_3\text{O}_2$ ), bubbles of gas appear. Write equations for two reactions that indicate the identity of the gas.

**\*13-114.** High-sulfur coal contains 5.0% iron pyrite ( $\text{FeS}_2$ ). When the coal is burned, the iron pyrite also burns according to the equation



What mass of sulfuric acid can eventually form from the combustion of 100 kg of coal? Sulfuric acid is formed according to the following equations.



**13-115.** A 2.50-g quantity of  $\text{HCl}$  is dissolved in 245 mL of water and then diluted to 890 mL. What is the pH of the concentrated and the dilute solution?

**13-116.** A 0.150-mole quantity of  $\text{NaOH}$  is dissolved in 2.50 L of water. In a separate container, 0.150 mole of  $\text{HCl}$  is present in 2.50 L of water. What is the pH of each solution? What is the pH of a solution made by mixing the two?

**\*13-117.** A solution is prepared by mixing 10.0 g of  $\text{HCl}$  with 10.0 g of  $\text{NaOH}$ . What is the pH of the solution if the volume is 1.00 L?

**\*13-118.** A solution is prepared by mixing 25.0 g of  $\text{H}_2\text{SO}_4$  with 50.0 g of  $\text{KOH}$ . What is the pH of the solution if the volume is 500 mL?

**\*13-119.** A solution is prepared by mixing 500 mL of 0.10 M  $\text{HNO}_3$  with 500 mL of 0.10 M  $\text{Ca}(\text{OH})_2$ . What is the pH of the solution after mixing?

## STUDENT WORKSHOP

### Plotting the Titration of a Strong Acid with a Strong Base

**Purpose:** To calculate pH, and create a graph which demonstrates how the pH of an acid solution changes as it is titrated with a base. (Work in groups of three or four. Estimated time: 25 min)

In this activity, you will make a graph showing how the pH of a solution changes as you titrate a strong acid with a strong base. The graph paper (sideways) should be scaled from 0 to 14 on the y-axis (this will be the pH) and from 0 mL to 50 mL on the x-axis (the volume of added  $\text{NaOH}$ ). The data for this experiment are for 25.0 mL of 0.10 M  $\text{HNO}_3$  being titrated with 0.10 M  $\text{NaOH}$ .

At 25.0 mL of added  $\text{NaOH}$ , you will be at the equivalence point in the titration, and the pH will be 7.00. Prior to that, we expect acidic pH's, and past that point, pH's should be in the base range, as we add more base than there is acid to neutralize. The accompanying table records the acid or base concentration for each amount of added  $\text{NaOH}$ , after the reaction is complete. You should determine the pH at each point, plot the graph of pH versus added  $\text{NaOH}$ , and answer the following questions.


| mL of $\text{NaOH}$ added | mol/L [Acid] | mol/L [Base] |
|---------------------------|--------------|--------------|
| 0.0                       | 0.10         |              |
| 5.0                       | 0.067        |              |
| 10.0                      | 0.043        |              |
| 15.0                      | 0.025        |              |
| 20.0                      | 0.011        |              |
| 24.0                      | 0.0020       |              |
| 25.0                      | 0            | 0            |
| 26.0                      |              | 0.0020       |
| 30.0                      |              | 0.0091       |
| 35.0                      |              | 0.017        |
| 40.0                      |              | 0.023        |
| 50.0                      |              | 0.033        |

- Over what range(s) of added base is the pH changing the least?
- Around what volume is the pH changing the most?
- If the indicator changes color from pH 8 to pH 10, how much base does it take to cause the color to change?
- The plot you have created is referred to as an S curve. Using the Internet, can you find other areas where S-curve behavior applies?



CHAPTER  
14

# Oxidation–Reduction Reactions



**E**lectricity generated by this large Tesla coil is dramatic and awesome. In fact, electricity has been essential to our lives for well over a century. In this chapter, we are concerned with how electricity is generated by chemical reactions.

**PART A**  
**REDOX REACTIONS—THE**  
**EXCHANGE OF ELECTRONS**

**14-1** The Nature of Oxidation and  
Reduction and Oxidation States



**MAKING IT REAL**

*Lightning Bugs (Fireflies)—Nature's Little  
Night-Lights*

**14-2** Balancing Redox Equations:  
Oxidation State Method

**14-3** Balancing Redox Equations: Ion-  
Electron Method

**PART B**  
**SPONTANEOUS AND**  
**NONSPONTANEOUS REDOX**  
**REACTIONS**

**14-4** Predicting Spontaneous Redox  
Reactions

**14-5** Voltaic Cells



**MAKING IT REAL**

*Fuel Cells—The Future Is (Almost) Here*

**14-6** Electrolytic Cells

**SETTING THE STAGE** A distant rumble signals the ominous gathering of thunderstorms. We may cast a cautious eye toward the sky and think of shelter. The roll of thunder warns us about one force of nature for which we have a great respect, so we try to get out of its way. That, of course, is lightning. Lightning has no doubt caused fear as well as amazement in the human race since people first looked to the sky and wondered about its nature. But this force was not harnessed until modern times. The use of electricity (the same force as lightning) is so common to us now that it is taken for granted. Huge generating plants dot the rural landscape with towering smokestacks discharging smoke and steam. Not many decades ago, however, electricity was mainly a laboratory curiosity, until the experiments of inventors such as James Watt, Alexander Graham Bell, and Thomas Edison tapped its limitless potential. Even now, when we turn on a cell phone or an iPod or start a car, a flow of electrons (electricity) from a battery is put to immediate use. The electricity used by these devices originates from chemical reactions that involve an exchange of electrons between reactants.

Electron exchanges have not previously been defined as a specific type of reaction, but many of the classifications discussed in Chapter 5 fit into this broad category. Most combination, all combustion, and all single-replacement reactions can also be categorized as electron exchange reactions.

In Part A, we will examine the nature of these reactions and how the equations representing these reactions are balanced. The practical applications of redox reactions, such as the generation of electricity in batteries or to release metals from their ores, are among the topics discussed in Part B.

**PART A**  
**REDOX REACTIONS—THE**  
**EXCHANGE OF ELECTRONS**

**SETTING A GOAL**

- You will learn of an important classification of chemical reactions that involve an exchange of electrons.

**OBJECTIVES**

- 14-1** Calculate oxidation states and determine the species oxidized, the species reduced, the oxidizing agent, and the reducing agent in an electron exchange reaction.
- 14-2** Balance redox reactions by the bridge method.
- 14-3** Balance redox reactions by the ion-electron method.

▶ **OBJECTIVE FOR**  
**SECTION 14-1**

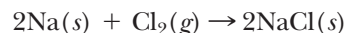
Calculate oxidation states and determine the species oxidized, the species reduced, the oxidizing agent, and the reducing agent in an electron exchange reaction.

## 14-1 THE NATURE OF OXIDATION AND REDUCTION AND OXIDATION STATES

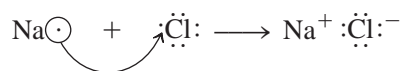


**LOOKING AHEAD!** The driving force of two general types of reactions involves an exchange of the two parts of a hydrogen atom, the proton and the electron. In Chapter 13, we described the actions of acids and bases in water as an exchange of a proton. In this chapter, we describe reactions involving the electron. In this section, we examine this exchange and the terms used to describe it. ■

Sodium metal and chlorine gas react in a spectacular demonstration of chemical power. A small chunk of sodium placed in a flask filled with chlorine gas immediately glows white hot as the elements combine to form ordinary table salt. (See Figure 14-1.) We will examine the reaction of sodium and chlorine to illustrate the process of an electron exchange reaction. The equation for this reaction is as follows.



In Section 9-2, we briefly explained what was happening in the reaction. A sodium atom loses one electron, which is gained by a chlorine atom, resulting in the formation of two ions. The gain and loss of an electron were predicted as a logical consequence of the octet rule.



**FIGURE 14-1** Formation of NaCl An active metal reacts with a poisonous gas to form ordinary table salt (NaCl).

### 14-1.1 Half-Reactions

In the acid–base reactions discussed in the previous chapter, the atoms in the reactants keep their quota of electrons in changing to products. Such is not the case in the reaction shown above, however. We will now take a closer look at what happens as reactants change into products. An electron exchange reaction can be viewed as the sum of two half-reactions. A **half-reaction** represents either the loss of electrons or the gain of electrons as a separate balanced equation. Thus the half-reaction involving only sodium is



In this half-reaction, notice that the neutral sodium atom has lost an electron to form a sodium ion. A substance that loses electrons in a chemical reaction is said to be **oxidized**.

Now consider what happens to the chlorine molecule in going from reactant to product.



In this half-reaction, the neutral chlorine molecule has gained two electrons to form two chloride ions. A substance that gains electrons in a chemical reaction is said to



be **reduced**. A simple mnemonic helps us remember these two terms: OIL RIG can be used to recall **Oxidation Is Loss** (of electrons)—**Reduction Is Gain**.

### 14-1.2 Redox Reactions

Obviously, the two processes (oxidation and reduction) complement each other. If there is an oxidation occurring, then there must also be a reduction, giving us the basis for this classification of chemical reaction. *Reactions involving an exchange of electrons are known as **oxidation–reduction**, or simply, **redox reactions**.*

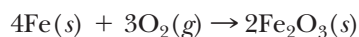
Now consider how the two half-reactions add together to make a complete, balanced equation. *An important principle of a redox reaction is that the electrons gained in the reduction process must equal the electrons lost in the oxidation process.* Note in our sample reaction that the reduction process involving  $\text{Cl}_2$  requires two electrons. Therefore, the oxidation process must involve two Na's to provide these two electrons. The electrons on both sides of the equation must be equal so that they can be eliminated by subtraction when the two half-reactions are added.



Instead of identifying a reactant by what happened to it (i.e., it was oxidized or reduced), in this type of reaction it is sometimes more useful to emphasize what it does. *The substance that causes the oxidation (i.e., by accepting electrons) is called the **oxidizing agent**, and the substance that causes the reduction (i.e., by providing the electrons) is called the **reducing agent**.* Thus, the substance reduced is the oxidizing agent and the substance oxidized is the reducing agent.

In the example above, Na is the *reducing agent* and is oxidized to  $\text{Na}^+$ .  $\text{Cl}_2$  is the *oxidizing agent* and is reduced to  $\text{Cl}^-$ .

Many other familiar chemical changes are redox reactions. For example, the corrosion of iron to form rust involves an exchange of electrons. The formation of rust [iron(III) oxide] is illustrated below.



Originally, the term *oxidation* referred specifically to such a reaction in which a substance like iron adds oxygen. In the reverse reaction, oxygen is removed from iron(III) oxide, which “reduces” its mass. Thus, the removal of oxygen was known as “reduction.” Now we define the process in terms of the exchange of electrons, so the terms are used regardless of whether oxygen is involved or not. In many redox reactions, however, the species undergoing electron exchange are not as obvious as the two examples that we have used in this section. So we need a tool to help us. This leads us to a concept known as oxidation states.



An iron nail soon forms a coating of rust when exposed to moisture and air.

### 14-1.3 Oxidation States

In Chapter 9 we presented Lewis structures for molecules and ions where electrons were shared between two atoms. With the concept of electronegativity (see Section 9-6), however, we found that electrons are not shared equally. The greater share of



the electron pair in the bond is closer to the more electronegative atom, which gives it a partial negative charge. As a convenient method of keeping track of electrons in redox reactions, we will now assign *all* of the electrons in a bond to the more electronegative atom. The **oxidation state** (or **oxidation number**) of an atom in a molecule or ion is the charge that atom would have if all electrons in its bonds were assigned to the more electronegative atom. The most electronegative element is fluorine, oxygen is second, and the electronegativity of the elements then decreases in the direction of the metal–nonmetal borderline in the periodic table. We actually don't need to know all the electronegativities of elements in order to assign oxidation states, however. A few general rules will suffice. These rules and some practice exercises follow.

1. The oxidation state of an element in its free (natural) state is zero [e.g., Cu(s), B(s)]. This includes polyatomic elements [e.g., Cl<sub>2</sub>(g), P<sub>4</sub>(s)].
2. The oxidation state of a monatomic ion is the same as the charge on that ion (e.g., Na<sup>+</sup> = +1 oxidation state, O<sup>2-</sup> = -2, Al<sup>3+</sup> = +3).
  - a. Alkali metal ions are always +1 (same as the group number).
  - b. Alkaline earth metal ions are always +2 (same as the group number).
3. The halogens are in a -1 oxidation state in binary (two-element) compounds, whether ionic or covalent, *when bound to a less electronegative element*.
4. Oxygen in a compound is usually -2. Certain compounds (which are rare) called peroxides or superoxides contain oxygen in a less negative oxidation state. Oxygen is positive only when bound to the more electronegative fluorine.
5. Hydrogen in a compound is usually +1. When combined with a less electronegative element (usually a metal), hydrogen has a -1 oxidation state (e.g., LiH).
6. The sum of the oxidation states of all the atoms in a neutral compound is zero. For a polyatomic ion, the sum of the oxidation states equals the charge on the ion.

**EXAMPLE 14-1****Calculating Oxidation States**

What is the oxidation state of the following?

- (a) Fe in FeO      (c) S in H<sub>2</sub>SO<sub>3</sub>  
 (b) N in N<sub>2</sub>O<sub>5</sub>    (d) As in AsO<sub>4</sub><sup>3-</sup>

**PROCEDURE**

An algebraic equation can be constructed from rule 6. For example, assume that we have a hypothetical compound M<sub>2</sub>A<sub>3</sub>. Then, from rule 6,

$$[2 \times (\text{oxidation state of M})] + [3 \times (\text{oxidation state of A})] = 0$$

or, to simplify,

$$2(\text{ox. state M}) + 3(\text{ox. state A}) = 0$$

If the formula represents a polyatomic ion, the quantity on the left is equal to the charge rather than zero.

**SOLUTION**

- (a) FeO: The oxidation states of the two elements add to zero (rule 6).

$$(\text{ox. state Fe}) + (\text{ox. state O}) = 0$$

Since the oxidation of state of oxygen is -2 (rule 4),

$$\begin{aligned} \text{ox. state Fe} + (-2) &= 0 \\ \text{ox. state Fe} &= \underline{+2} \end{aligned}$$

- (b) N<sub>2</sub>O<sub>5</sub>: The oxidation states add to zero (rule 6), as shown by the equation

$$2(\text{ox. state N}) + 5(\text{ox. state O}) = 0$$

Since ox. state O is  $-2$  (rule 4),

$$\begin{aligned}2(\text{ox. state N}) + 5(-2) &= 0 \\2(\text{ox. state N}) &= +10 \\ \text{ox. state N} &= \underline{+5}\end{aligned}$$

(c)  $\text{H}_2\text{SO}_3$ : The oxidation states add to zero (rule 6).

$$2(\text{ox. state H}) + (\text{ox. state S}) + 3(\text{ox. state O}) = 0$$

H is usually  $+1$  and O is usually  $-2$  (rules 4 and 5).

$$\begin{aligned}2(+1) + \text{ox. state S} + 3(+2) &= 0 \\ \text{ox. state S} &= \underline{+4}\end{aligned}$$

(d)  $\text{AsO}_4^{3-}$ : The sum of the oxidation states of the atoms equals the charge on the ion (rule 6).

$$(\text{ox. state As}) + 4(\text{ox. state O}) = -3$$

Since O is  $-2$  (rule 4),

$$\begin{aligned}\text{ox. state As} + 4(-2) &= -3 \\ \text{ox. state As} &= \underline{+5}\end{aligned}$$

### ANALYSIS

All charges on monatomic ions are oxidation states, though not all oxidation states are charges. The oxidation state of an atom in a molecule or ion would be the charge on the atom if all the other atoms were present as ions. For example, in the sulfate ion ( $\text{SO}_4^{2-}$ ), if all atoms were ions, we would have  $[\text{S}^{6+}4\text{O}^{2-}]^{2-}$ . This is certainly not the case, since electrons are shared between the sulfur and oxygen atoms, as we illustrated in Chapter 9. However, even though the sulfur is not present as a  $+6$  ion, the  $+6$  assigned to the sulfur represents its oxidation state. We will see why we need this important information next.

### SYNTHESIS

Sometimes, in assigning oxidation states, we have to choose between a rule that says “always” and one that says “usually.” For example, in the compound magnesium hydride ( $\text{MgH}_2$ ) all atoms cannot have positive oxidation states. However, magnesium is “always”  $+2$ , so the hydrogen, which is “usually”  $+1$ , must have a  $-1$  oxidation state in this case. In the compound  $\text{O}_2\text{F}_2$ , all atoms could not have negative oxidation states. In this case, fluorine is the more electronegative, so it has a  $-1$  oxidation state. This means that each oxygen must be in a  $+1$  oxidation state. There are even a few cases where we find oxidation states that are not even numbers. What would the oxidation state of the iron atoms be in  $\text{Fe}_3\text{O}_4$ ? If the oxygens are  $-2$  each, then their total is  $-8$ . The three iron atoms must have oxidation states that add to  $+8$ , so each one is  $+2.67$ . (In fact,  $\text{Fe}_3\text{O}_4$  is a one to one combination of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ .) Fortunately, all the odd exceptions are not enough to worry about, so our rules will hold in almost all cases that we will encounter.

## 14-1.4 Using Oxidation States in Redox Reactions

By noting the change of oxidation state of the same atom in going from a reactant to a product, we can trace the exchange of electrons in the reaction. We can now add to our definition of oxidation and reduction in terms of oxidation state. *Oxidation is a loss of electrons as indicated by an increase in the oxidation state. Reduction is a gain of electrons as indicated by a decrease (or reduction) in the oxidation state.* In the reaction of sodium with chlorine discussed in Section 14-1, notice that the oxidation state of the sodium increased from zero to  $+1$ , indicating oxidation, and that of chlorine decreased from zero to  $-1$ , indicating reduction.

In most compounds, usually only one of the elements undergoes a change in redox reactions. Thus, it is often necessary to calculate the oxidation states of all the elements in all compounds so that we can see which ones have undergone the change. With experience, however, the oxidized and reduced species are more easily recognized. In the following examples, we will find all the oxidation states so that we can identify the changes and label them appropriately.

**EXAMPLE 14-2****Identifying Oxidized and Reduced Species**

In the following unbalanced equations, indicate the reactant oxidized, the reactant reduced, the oxidizing agent, and the reducing agent. Indicate the products that contain the elements that were oxidized or reduced.

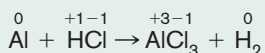
- (a)  $\text{Al} + \text{HCl} \rightarrow \text{AlCl}_3 + \text{H}_2$   
 (b)  $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$   
 (c)  $\text{MnO}_2 + \text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$   
 (d)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{SnCl}_2 + \text{HCl} \rightarrow \text{CrCl}_3 + \text{SnCl}_4 + \text{KCl} + \text{H}_2\text{O}$

**PROCEDURE**

In the equations, we wish to identify the species that contain atoms of an element undergoing a change in oxidation state. At first, it may be necessary to calculate the oxidation state of every atom in the equation until you can recognize the changes by inspection.

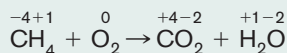
**SOLUTION**

- (a) Oxidation states of elements:



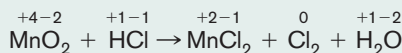
| Reactant | Change   | Agent     | Product         |
|----------|----------|-----------|-----------------|
| Al       | oxidized | reducing  | $\text{AlCl}_3$ |
| HCl      | reduced  | oxidizing | $\text{H}_2$    |

- (b) Oxidation states of elements:



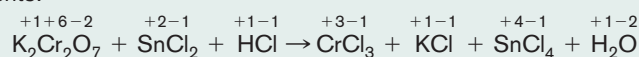
| Reactant      | Change   | Agent     | Product                           |
|---------------|----------|-----------|-----------------------------------|
| $\text{CH}_4$ | oxidized | reducing  | $\text{CO}_2$                     |
| $\text{O}_2$  | reduced  | oxidizing | $\text{CO}_2, \text{H}_2\text{O}$ |

- (c) Oxidation states of elements:



| Reactant       | Change   | Agent     | Product         |
|----------------|----------|-----------|-----------------|
| HCl            | oxidized | reducing  | $\text{Cl}_2$   |
| $\text{MnO}_2$ | reduced  | oxidizing | $\text{MnCl}_2$ |

- (d) Oxidation states of elements:



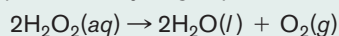
| Reactant                          | Change   | Agent     | Product         |
|-----------------------------------|----------|-----------|-----------------|
| $\text{SnCl}_2$                   | oxidized | reducing  | $\text{SnCl}_4$ |
| $\text{K}_2\text{Cr}_2\text{O}_7$ | reduced  | oxidizing | $\text{CrCl}_3$ |

**ANALYSIS**

You will notice that any substance present as a free element in a reaction is involved in either the oxidation or the reduction process. Also, hydrogen and oxygen are generally not oxidized or reduced if they remain part of compounds. They are involved only if present as free elements in either the reactants or products. Further note that none of the analysis done for this problem requires a balanced reaction. It is sufficient simply to know the identities of the reactants and their products.

**SYNTHESIS**

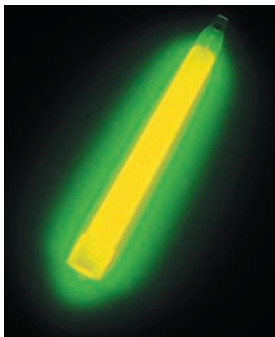
Consider the equation illustrating the decomposition of hydrogen peroxide:



What has been oxidized and what has been reduced? In this case  $\text{H}_2\text{O}_2$  plays both roles. In one molecule of  $\text{H}_2\text{O}_2$ , the oxidation state of the oxygen has decreased from  $-1$  to  $-2$  to form  $\text{H}_2\text{O}$ , so it has been reduced. In the other molecule of  $\text{H}_2\text{O}_2$ , the oxygen has increased from  $-1$  to  $0$ , so it has been oxidized. One molecule of hydrogen peroxide is the oxidizing agent and one is the reducing agent. In such a case, we say that the  $\text{H}_2\text{O}_2$  has been *disproportionated*.



## Lightning Bugs (Fireflies)—Nature's Little Night-Lights



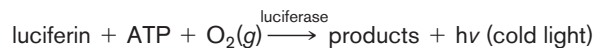
Glowsticks—an example of chemiluminescence.

Tiny little flashes of light on a summer night—those of us east of the Rockies know the sources as lightning bugs, also called fireflies. They have been a source of curiosity since ancient times, but only recently have we known how these tiny creatures can light up.

In photochemical reactions, such as photosynthesis, light energy *initiates* a chemical reaction. In the firefly, we have just the opposite situation.

That is, light energy is *produced* by a chemical reaction. The production of light energy by a chemical reaction is known as *chemiluminescence*. If it is produced by living organisms, such as the firefly, it is known as *bioluminescence*.

We now have some understanding of what goes on in the firefly. The chemical reaction is an oxidation–reduction reaction, with  $O_2$  from the air serving as the oxidizing agent. The other chemicals are complex molecules, so we will simply refer to them by name (luciferin) or initials (ATP). Also involved is an enzyme (luciferase), which acts as a catalyst. This reaction is represented as follows:



By studying the bioluminescent chemistry of the firefly, we also discovered that all fireflies have the same luciferin, but each species produces a different color of light. The color was found to be determined by the luciferase that is unique to each species of firefly. An amazing discovery about this reaction is that the production of light is incredibly efficient. Eighty out of 100 molecules that react produce light, thus giving it an 80% efficiency.

It wasn't until 1928 that a scientist, H. O. Albrecht, first described a nonbiological chemical reaction that could be conducted in a laboratory to generate chemiluminescence, but with only 0.1% efficiency. The reaction is similar to the one shown above except that nonbiological chemicals available to the scientist were used along with hydrogen peroxide ( $H_2O_2$ ) as the oxidizing agent. In the early 1960s, other chemiluminescent reactions were discovered and patented. Today a substance called Cyalume™, a trademark product of American Cyanamid, is used to produce light with about 5% efficiency.

When you see children with glowsticks or other decorative jewelry that glows in the dark, thank the firefly for its amazing contribution to our world of chemistry.

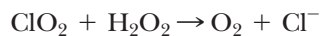
### ASSESSING THE OBJECTIVE FOR SECTION 14-1

**EXERCISE 14-1(a) KNOWLEDGE:** Fill in the blanks.

If all the atoms in a compound were ions, the charge on the ions would be the same as their \_\_\_\_\_. For oxygen in compounds, this is usually \_\_\_\_\_. Hydrogen is usually \_\_\_\_\_ in compounds. A substance oxidized undergoes a \_\_\_\_\_ of electrons and an \_\_\_\_\_ in oxidation state. This substance is also known as a \_\_\_\_\_ agent.

**EXERCISE 14-1(b) KNOWLEDGE:** What is the oxidation state of (a) B in  $H_3BO_3$  and (b) S in  $S_2O_3^{2-}$ ?

**EXERCISE 14-1(c) ANALYSIS:** In the following reaction, indicate the substance oxidized, the substance reduced, the oxidizing agent, and the reducing agent.



**EXERCISE 14-1(d) ANALYSIS:** Consider the following unbalanced equation



What has been oxidized and what has been reduced?

**EXERCISE 14-1(e) SYNTHESIS:** Is it possible to have a reduction without an oxidation or an oxidation without a reduction? Why or why not?

For additional practice, work chapter problems 14-1, 14-6, 14-10, and 14-12.

**OBJECTIVE FOR SECTION 14-2**

Balance redox reactions by the bridge method.

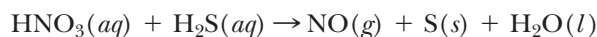
## 14-2 BALANCING REDOX EQUATIONS: OXIDATION STATE METHOD



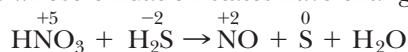
**LOOKING AHEAD!** An important principle of redox reactions is that “electrons lost equal electrons gained.” In the next two sections, we will put this concept to use as the key to balancing some rather complex reactions that would be quite difficult to balance by inspection, as we did in Chapter 5. There are two procedures for this endeavor. The oxidation state method, discussed in this section, is useful for balancing equations in molecular form. ■

In a typical redox reaction, only two atoms undergo a change in their oxidation states. By identifying these two atoms and calculating the change in the oxidation state, we can arrive at a balanced equation. *The oxidation state, or bridge method, focuses on the atoms of the elements undergoing a change in oxidation state.*

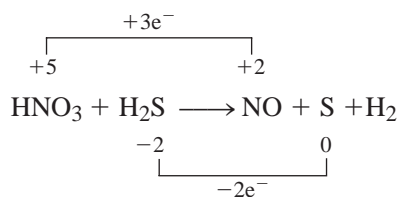
The following reaction will be used to illustrate the procedures for balancing equations by the oxidation state method.



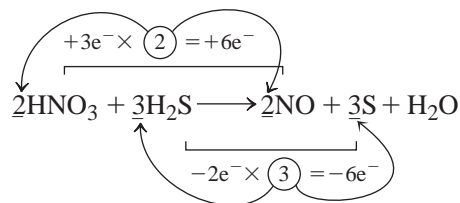
- Identify the atoms whose oxidation states have changed.



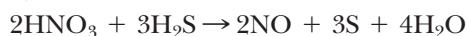
- Draw a bridge between the same atoms whose oxidation states have changed, indicating the electrons gained or lost. This is the change in oxidation state.



- Multiply the two numbers (+3 and -2) by whole numbers that produce a common multiple. For 3 and 2 the common multiple is 6. (For example,  $+3 \times 2 = +6$ ;  $-2 \times 3 = -6$ .) Use these multipliers as coefficients of the respective compounds or elements.  
Note that six electrons are lost (bottom) and six are gained (top).



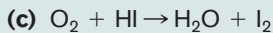
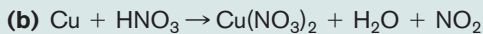
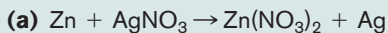
- Balance the rest of the equation by inspection. Note that there are eight H's on the left, so *four* H<sub>2</sub>O's are needed on the right. If the equation has been balanced correctly, the O's should balance. Note that they do.



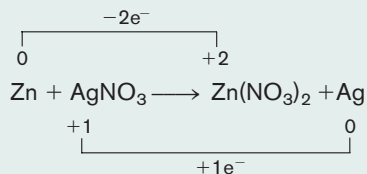


**EXAMPLE 14-3**
**Balancing Equations by the Oxidation State Method**

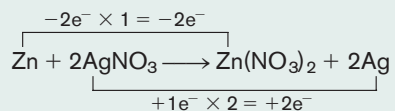
Balance the following equations by the oxidation state method.


**PROCEDURE (a)**

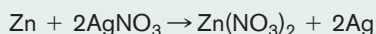
(1) Determine the elements that have been oxidized and reduced. (2) From the oxidation state change, determine the common multiple and use the two multipliers as coefficients in the equation.

**SOLUTION (a)**


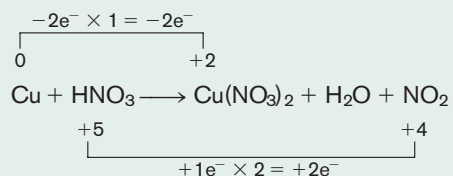
The oxidation (top) should be multiplied by 1, and the reduction process (bottom) should be multiplied by 2.



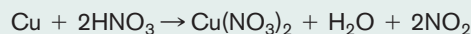
The final balanced equation is


**PROCEDURE (b)**

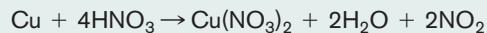
Write a bridge between Cu and N, which have undergone oxidation state changes.

**SOLUTION (b)**


The equation, so far, is



Note, however, that four N's are present on the right, but only two are on the left. The addition of two more  $\text{HNO}_3$ 's balances the N's, and the equation is completely balanced with two  $\text{H}_2\text{O}$ 's on the right.



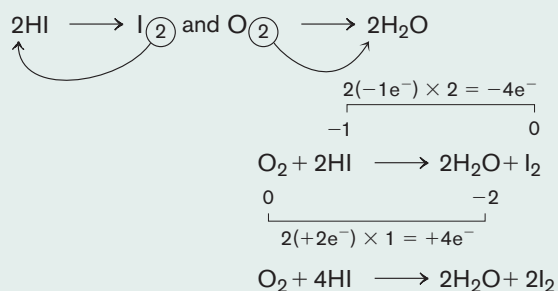
(In this aqueous reaction,  $\text{HNO}_3$  serves two functions. Two  $\text{HNO}_3$ 's are reduced to two  $\text{NO}_2$ 's, and the other two  $\text{HNO}_3$ 's provide anions for the  $\text{Cu}^{2+}$  ion. These latter  $\text{NO}_3^-$  ions are present in the solution as spectator ions. Spectator ions are not oxidized, reduced, or otherwise changed during the reaction.)

**PROCEDURE (c)**

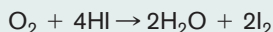
The elements undergoing a change in oxidation state are oxygen and iodine. If an atom that has changed is in a compound where it has a subscript other than 1, first balance these atoms by adding a temporary coefficient.



When a copper penny reacts with nitric acid, nitrogen dioxide gas (brown) is formed.

**SOLUTION (c)**

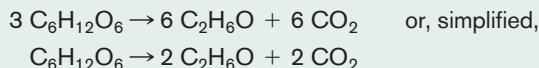
The final balanced equation is

**ANALYSIS**

In (c), a common mistake is failing to ensure that the element undergoing a change is balanced first. If one neglected to do this, the change would be from 0 in  $\text{O}_2$  to  $-2$  in  $\text{H}_2\text{O}$ , for a loss of two electrons. Notice that there is actually a loss of four electrons, since the  $\text{O}_2$  is reduced to two  $\text{H}_2\text{O}$  molecules. Likewise, there is a gain of two electrons when  $2\text{HI}$  is oxidized to  $\text{I}_2$ .

**SYNTHESIS**

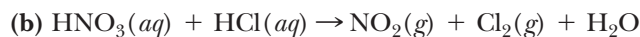
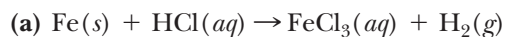
Consider the following reaction:  $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{C}_2\text{H}_6\text{O} + \text{CO}_2$ . This is the process of fermentation to form alcohol ( $\text{C}_2\text{H}_6\text{O}$ ) from sugar ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), and it is significantly more complex than shown here. Based on this reaction, the carbon in  $\text{C}_6\text{H}_{12}\text{O}_6$  would be assigned an oxidation state of zero. The carbons in the products would be  $-2$  and  $+4$ , respectively. If you follow the procedure, you would predict that this equation balances thusly:



The point here, though, is that while the average oxidation states of the carbons were 0,  $-2$ , and  $+4$ , respectively, the actual oxidation states of the six carbons in sugar and the two carbons in alcohol vary. They merely average to those respective values. To be specific, in alcohol the oxidation states of the two carbons are actually  $-3$  and  $-1$ , due to having different surrounding atoms. In the sugar, the oxidation states vary from  $-1$  to  $+2$ , depending on the type of sugar. Be careful, whenever there are multiple atoms of the same type in a molecule, not to necessarily assume that all have the same oxidation state.

**ASSESSING THE OBJECTIVE FOR SECTION 14-2**

**EXERCISE 14-2(a) ANALYSIS:** Balance the following equations by the bridge method.



**EXERCISE 14-2(b) SYNTHESIS:** In an alkaline dry cell (battery), manganese(IV) oxide reacts with water and zinc to produce manganese(III) oxide and zinc(II) hydroxide. Write the equation illustrating this reaction and balance the equation by the bridge method.

*For additional practice, work chapter problems 14-16 and 14-17.*

## 14-3 BALANCING REDOX EQUATIONS: ION-ELECTRON METHOD

### ▶ OBJECTIVE FOR SECTION 14-3

Balance redox reactions by the ion-electron method.



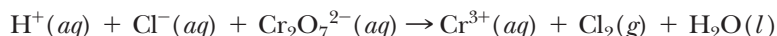
**LOOKING AHEAD!** One problem with the oxidation state method is that it may give the impression that some atoms exist as ions when they are actually *part* of a compound or ion (e.g.,  $\text{N}^{5+}$ ). The second method that we will discuss focuses on the entire ion or molecule containing the atom undergoing a change. This is a more realistic representation of the species involved. ■

While it is generally true that only two atoms actually undergo oxidation state changes, we can also consider the entire species that changes (e.g.,  $\text{NO}_3^-$  rather than  $\text{N}^{5+}$ ). In the **ion-electron method** (also known as the *half-reaction method*), the total reaction is separated into half-reactions, which are balanced individually and then added back together. The ion-electron method recognizes the complete change of an ion or molecule as it goes from reactant to products. As we will see later in this chapter, a balanced half-reaction is how we represent a specific change that occurs in a battery.

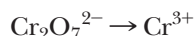
The rules for balancing equations are somewhat different in acidic solution [containing  $\text{H}^+(aq)$  ion] than in basic solution [containing  $\text{OH}^-(aq)$  ion]. The two solutions are considered separately, with acid solution reactions discussed first. To simplify the equations, only the net ionic equations are balanced.

### 14-3.1 Balancing Reactions in Acidic Solution

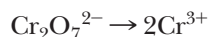
The balancing of an equation in aqueous acid solution is illustrated with the following unbalanced equation.



1. Separate out the molecule or ion that contains atoms of an element that has been oxidized or reduced and the product containing atoms of that element. If necessary, calculate the oxidation states of individual atoms until you are able to recognize the species that changes. In this method, it is actually not necessary to know the oxidation state. The reduction process is



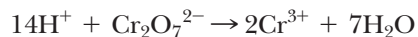
2. If a subscript of the atoms of the element undergoing a change in oxidation state is more than 1, balance those atoms with a temporary coefficient. In this case, it is the Cr.



3. Balance the oxygens by adding  $\text{H}_2\text{O}$  on the side needing the oxygens (one  $\text{H}_2\text{O}$  for each O needed).

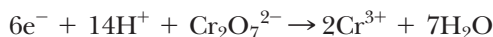


4. Balance the hydrogens by adding  $\text{H}^+$  on the other side of the equation from the  $\text{H}_2\text{O}$ 's ( $2\text{H}^+$  for each  $\text{H}_2\text{O}$  added). Note that the H and O have not undergone a change in oxidation state.

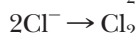
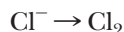


5. The atoms in the half-reaction are now balanced. Check to make sure. Now comes the important step of balancing the charge on both sides of the equation. The charge is determined separately on each side of the equation. This is accomplished by multiplying the coefficient of any ion present times the charge on that ion. Neutral molecules are excluded from charge determination. Notice that there are 14  $\text{H}^+$  ions. The charge due to  $\text{H}^+$  is 14 times the

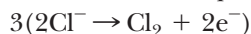
charge on the proton (+1), or +14. This is then added to the charge on the dichromate (−2), which makes a total charge on the left (i.e., the reactant side) of +12 [i.e.,  $(14 \times +1) + (-2) = +12$ ]. On the right (i.e., the product side), the charge on the Cr (+3) is multiplied by its coefficient (2), making a charge of +6 on the right. The  $\text{H}_2\text{O}$  is a neutral molecule, so it is not included. The total charge on the left is +12, and on the right it is +6. The charges on both sides of the reaction must now be balanced. To do this, add the appropriate number of *negative* electrons (−1 each) to the more *positive* side. Adding  $6e^-$  on the left (the more positive side) balances the charges on both sides, and the half-reaction is balanced (i.e.,  $+12 - 6 = +6$ ).



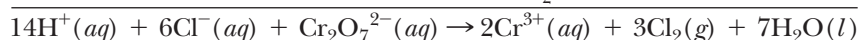
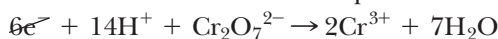
6. Repeat the same procedure for the other half-reaction.



7. Before the two half-reactions are added, we must make sure that electrons gained equal electrons lost. Sometimes the half-reactions must be multiplied by factors that give the same number of electrons. In this case, if the oxidation process is multiplied by 3 (and the reduction process by 1), there will be an exchange of  $6e^-$ . When these two half-reactions are added, the  $6e^-$  can be subtracted from both sides of the equation.



Addition produces the balanced net ionic equation.

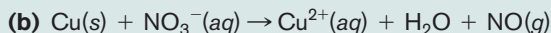
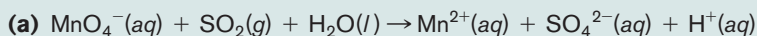


An excellent way to check our answer is to make sure the net charge on both sides of the equation is the same. The net charge on the right is  $(14 \times +1) + (6 \times -1) + (-2) = +6$ . On the left the charge is  $(2 \times +3) = +6$ .

### EXAMPLE 14-4

#### Balancing Redox Equations in Acidic Solution

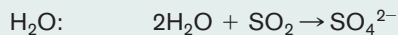
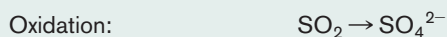
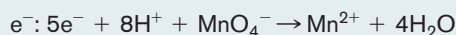
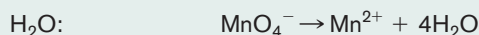
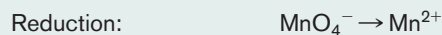
Balance the following equations for reactions occurring in acid solution by the ion-electron method.

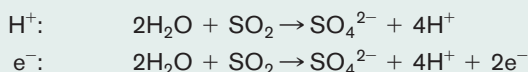


#### PROCEDURE

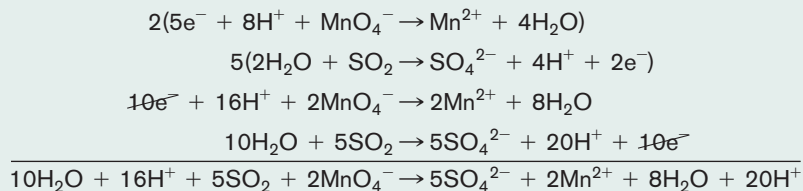
Balance each half-reaction in the following order: (1) the element that changes, (2) oxygens, (3) hydrogens, and (4) the charge. Add the two half-reactions together, and subtract out anything that appears on both sides.

#### SOLUTION (a)





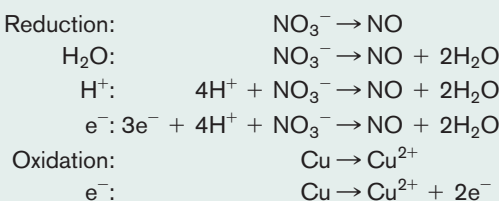
The reduction reaction is multiplied by 2 and the oxidation by 5 to produce 10 electrons for each process, as shown below.



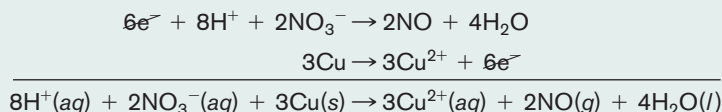
Note that  $\text{H}_2\text{O}$  and  $\text{H}^+$  are present on both sides of the equation. Therefore,  $8\text{H}_2\text{O}$  and  $16\text{H}^+$  can be subtracted from *both sides*, leaving the final balanced net ionic equation as



### SOLUTION (b)



Multiply the reduction half-reaction by 2 and the oxidation half-reaction by 3, and then add the two half-reactions.



### ANALYSIS

When checking to see that redox reactions are properly balanced, remember that both the number of atoms and the charge must be the same on both sides. In (a), there are 4 hydrogens, 20 oxygens, 5 sulfurs, and 2 manganese atoms on each side. In addition, the total charge on the left side is  $2 \times (-1)$ , or  $-2$ , and on the right side it is  $[2 \times (+2)] + [5 \times (-2)] + [4 \times (+1)]$ , or  $-2$ , as well. Both atoms and charges balance. What is the atom and electron inventory for the reaction in (b)? Does it balance?

### SYNTHESIS

In the chapter problems, you will notice that some acids are represented as molecules and others as ions. Thus, nitric acid,  $\text{HNO}_3$ , appears as  $\text{H}^+ + \text{NO}_3^-$  in ionic equations, but sulfurous acid,  $\text{H}_2\text{SO}_3$ , appears as  $\text{H}_2\text{SO}_3$ . Why is this so? Recall our previous discussion about the difference between strong acids and weak acids. Strong acids (e.g.,  $\text{HNO}_3$ ) do not exist as molecules in aqueous solution, since they are completely ionized. Weak acids (e.g.,  $\text{H}_2\text{SO}_3$ ), on the other hand, are present mostly as neutral molecules. A weak acid forms very limited amounts of  $\text{H}^+$  in solution, so we represent it in its more prevalent form as a molecule.

## 14-3.2 Balancing Reactions in Basic Solution

In a basic solution,  $\text{OH}^-$ , rather than  $\text{H}^+$ , is in excess. Perhaps the simplest way to adjust to this condition is to follow the same procedure as in acid solution but change either each half-reaction or the total reaction to basic solution after it is otherwise balanced. We do this by adding one  $\text{OH}^-$  to *both sides* of the equation for each  $\text{H}^+$  present in the equation. As we learned in the previous chapter, the  $\text{H}^+$  ion combines with an  $\text{OH}^-$  ion to form  $\text{H}_2\text{O}$  [i.e.,  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ ]. In effect, this procedure converts an  $\text{H}^+$  ion to an  $\text{H}_2\text{O}$  on one side, leaving one  $\text{OH}^-$  ion on the opposite side of the equation. For example, consider the half-reaction shown below, which is balanced in acid solution. We will adjust the equation to a basic solution as follows.

1. Reduction half-reaction balanced in acid solution:

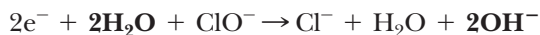




2. Add  $2\text{OH}^-$  to both sides for the two  $\text{H}^+$ 's shown on the left:



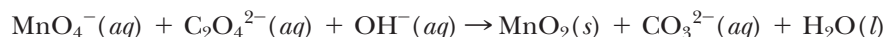
3. Convert  $2\text{H}^+ + 2\text{OH}^-$  to  $2\text{H}_2\text{O}$ :



4. Simplify by subtracting the fewer number of  $\text{H}_2\text{O}$ 's (1) from both sides of the equation:



Now consider a typical unbalanced equation representing a total redox reaction. The presence of  $\text{OH}^-$  ion in the equation tells us that this reaction occurs in basic solution.



Because tables of half-reactions are represented as either acidic (with  $\text{H}^+$  ions) or basic (with  $\text{OH}^-$  ions), we will change each half-reaction to basic solution. (Alternatively, we could balance the total equation as if in acid solution and then change the final balanced equation to basic solution.)

1. Balance the reduction half-reaction involving  $\text{MnO}_4^-$  and  $\text{MnO}_2$  in acid solution.



2. Change to basic solution by adding  $4\text{OH}^-$  to each side.



3. Combine  $4\text{H}^+$  and  $4\text{OH}^-$  to form  $4\text{H}_2\text{O}$  and then subtract  $2\text{H}_2\text{O}$  from both sides of the equation.



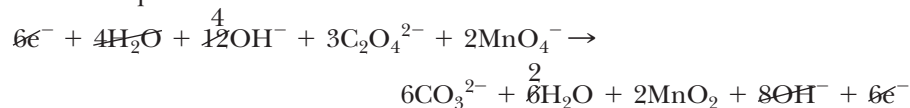
4. Balance the oxidation half-reaction involving  $\text{C}_2\text{O}_4^{2-}$  and  $\text{CO}_3^{2-}$  in acid solution.



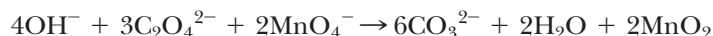
5. Change to basic solution as before by adding  $4\text{OH}^-$  to each side and simplify by subtracting out  $2\text{H}_2\text{O}$ .



6. Multiply the reduction reaction by 2 and the oxidation half-reaction by 3 and add equations.



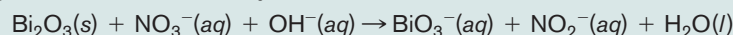
7. Simplify by subtracting out  $6\text{e}^-$ ,  $4\text{H}_2\text{O}$ , and  $8\text{OH}^-$ .



### EXAMPLE 14-5

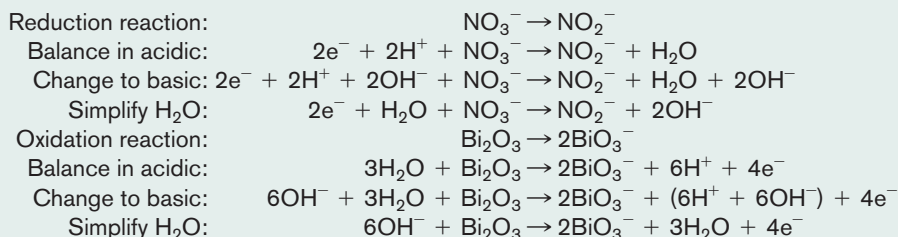
#### Balancing Redox Equations in Basic Solution

Balance the following equation in basic solution by the ion-electron method.

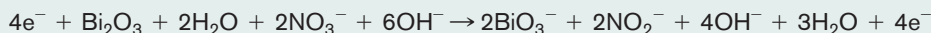


#### PROCEDURE

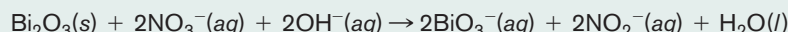
(1) Identify and separate the reduced and oxidized species and their products. (2) Balance in acidic solution. (3) Change from acidic to basic solution. (4) Simplify.

**SOLUTION**

Multiply the reduction reaction by 2 and add to the oxidation half-reaction.



Simplify by subtracting  $2\text{H}_2\text{O}$ ,  $4\text{OH}^-$ , and  $4e^-$  from both sides of the equation.

**ANALYSIS**

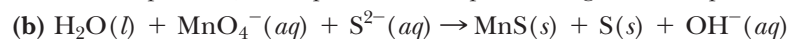
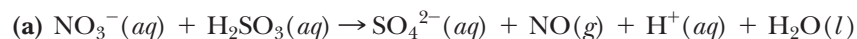
Balancing equations in basic solution requires a direct application of the material from the previous chapter. In an aqueous solution, you have at your disposal  $\text{H}_2\text{O}$  and excess  $\text{H}^+$  or  $\text{OH}^-$ , depending on whether the solution is acidic or basic. By adding an  $\text{OH}^-$  ion to an  $\text{H}^+$  ion, you are essentially changing the  $\text{H}^+$  to an  $\text{H}_2\text{O}$ . This is the net ionic equation of a neutralization reaction between a strong acid and a strong base. Remember to add an  $\text{OH}^-$  to both sides of the equation, however.

**SYNTHESIS**

We make distinctions between acidic and basic solutions because some compounds produce reactions that are different in each case. For example,  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  in acid solution but to  $\text{MnO}_2$  in basic solution. In another example,  $\text{Fe}^{3+}$  is present in acidic solution but forms insoluble  $\text{Fe}(\text{OH})_3$  in basic solution. Alternately, different forms of the compounds exist in different pH's.  $\text{HClO}$  is present in acidic solutions and can be reduced to  $\text{Cl}_2$ .  $\text{ClO}^-$  is present in basic solutions and can be reduced to  $\text{Cl}^-$ . Furthermore, as we'll see in the next section, each one of these reactions has a different potential for occurring, so the amount of energy we can get out of the reaction varies in each case.

**ASSESSING THE OBJECTIVE FOR SECTION 14-3**

**EXERCISE 14-3(a) ANALYSIS:** Balance the following equations by the ion-electron method.



(Notice some sulfide ions change and others do not.)

**EXERCISE 14-3(b) SYNTHESIS:** When elemental tin is placed in a nitric acid solution, a spontaneous redox reaction occurs, producing tin(IV) oxide and nitrogen dioxide. Write the equation illustrating this reaction and balance the equation by the ion-electron method. (Water is also a product.)

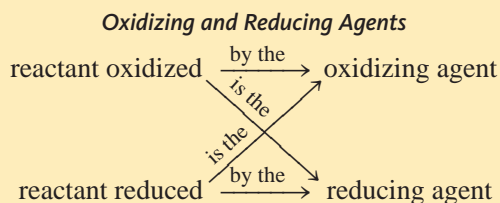
For additional practice, work chapter problems 14-18, 14-20, 14-22, and 14-24.

**PART A SUMMARY****KEY TERMS**

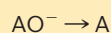
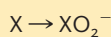
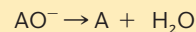
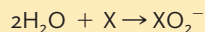
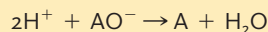
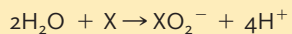
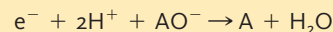
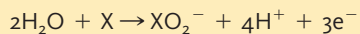
- 14-1.1** **Half-reactions** indicate either the **oxidation** or **reduction** process. pp. 438–439
- 14-1.2** An electron exchange reaction is known as an **oxidation-reduction**, or simply **redox**, reaction. p. 439
- 14-1.2** The species reduced is known as the **oxidizing agent**, the species oxidized is known as the **reducing agent**. p. 439
- 14-1.3** **Oxidation states** (or **oxidation numbers**) are used to identify the elements that change in redox reactions. p. 440

- 14-2** The **oxidation state** or **bridge method** balances equations by focusing on the oxidation state changes. p. 444
- 14-3** The **ion-electron method** is used to balance half-reactions separately before adding to the total reaction. p. 447

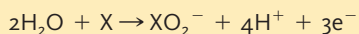
## SUMMARY CHARTS

*Balancing Redox Reactions in Aqueous Solution*Unbalanced core reaction:  $X + AO^- \rightarrow XO_2^- + A$ **Acidic solution**

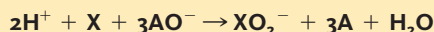
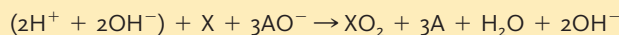
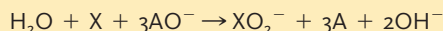
Separate into two half-reactions

Add  $H_2O$ Add  $H^+$ Add  $e^-$ 

Balance electron exchange



Add two reactions and simplify

**To change to a basic solution**Add  $OH^-$  (on both sides) for each  $H^+$ Combine  $H^+$  and  $OH^-$  to make  $H_2O$  and simplify

**PART B**  
SPONTANEOUS AND  
NONSPONTANEOUS REDOX  
REACTIONS

**SETTING A GOAL**

- You will understand the extensive practical applications of redox reactions.

**OBJECTIVES**

- 14-4** Using a table of relative strengths of oxidizing agents, determine whether a specific redox reaction is spontaneous.
- 14-5 (a)** Describe the parts of a voltaic cell and how it generates electricity. **(b)** List the types of batteries discussed and a particular use or advantage of each type.
- 14-6 (a)** Write the reaction that occurs when a salt is electrolyzed. **(b)** Describe the various applications for electrolytic cells.

## 14-4 PREDICTING SPONTANEOUS REDOX REACTIONS

### ▶ OBJECTIVE FOR SECTION 14-4

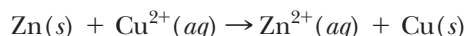
Using a table of relative strengths of oxidizing agents, determine whether a specific redox reaction is spontaneous.



**LOOKING AHEAD!** In the previous chapter, we found that favorable (spontaneous) reactions occur between a stronger acid and a stronger base, forming a weaker acid and a weaker base. Electron exchange reactions between a stronger oxidizing agent and a stronger reducing agent to produce a weaker oxidizing and reducing agent are also spontaneous. In addition, by observing the results of a few reactions, we can rank oxidizing and reducing agents and compile this information into a table. We can then use this table to predict the occurrence of a large number of reactions. ■

When zinc metal is immersed in an aqueous solution containing  $\text{Cu}^{2+}$  ions, an oxidation–reduction reaction occurs spontaneously, as indicated by the coating of copper that forms on the zinc metal. (In Chapter 5, we referred to this same reaction as a single-replacement reaction.) The zinc metal is oxidized to  $\text{Zn}^{2+}$  and the  $\text{Cu}^{2+}$  ion is reduced to copper metal with the transfer of two electrons from the zinc metal to the copper ion. (See Figure 5-5, Section 5-4.) On the other hand, copper metal placed in a solution of  $\text{Zn}^{2+}$  ions does not react. The reverse reaction does not occur spontaneously, since reactions are spontaneous (favorable) in one direction only. (See Figure 5-6, Section 5-4.1.)

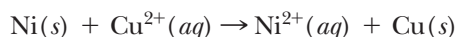
The net ionic equation for the spontaneous reaction is



A spontaneous reaction occurs between the stronger oxidizing agent and the stronger reducing agent to form weaker oxidizing and reducing agents. Since the spontaneous reaction is from left to right, we can make the following conclusions about the relative strengths of the two oxidizing and reducing agents.

1.  $\text{Cu}^{2+}$  is a better oxidizing agent than  $\text{Zn}^{2+}$ .
2. Zn metal is a better reducing agent than Cu metal.

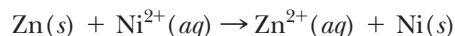
Now compare Cu to Ni instead of Zn. In similar experiments, we find that copper metal also forms a coating on a strip of Ni immersed in a  $\text{Cu}^{2+}$  solution. This spontaneous reaction is illustrated by the following equation.



This result provides similar conclusions as the Zn–Cu experiments.

3.  $\text{Cu}^{2+}$  is a better oxidizing agent than  $\text{Ni}^{2+}$ .
4. Ni metal is a better reducing agent than Cu metal.

Zinc and nickel are both better reducing agents than copper, but how do they compare to each other? Another experiment is necessary, which shows us that zinc metal forms a coating of nickel when immersed in an  $\text{Ni}^{2+}$  solution but not the opposite. This spontaneous reaction is represented below.



Our conclusions from this experiment are:

5.  $\text{Ni}^{2+}$  is a better oxidizing agent than  $\text{Zn}^{2+}$ .
6. Zn metal is a better reducing agent than Ni metal.

We can now rank all three ions as oxidizing agents in order of decreasing strength as follows.



Notice that the strength of the metals as reducing agents is inversely related to the strength of their ions as oxidizing agents. Because of the inverse relationship, the ranking of the three metals as reducing agents is in the reverse order.



| TABLE 14-1 Oxidizing Agents and Reducing Agents |   |                          |
|---|---|--------------------------|
| Strongest oxidizing agent                       | $F_2 + 2e^- \rightleftharpoons 2F^-$          | Weakest reducing agent   |
|   | $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$        |                          |
|   | $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$  |                          |
|   | $Br_2 + 2e^- \rightleftharpoons 2Br^-$        |                          |
|   | $Ag^+ + e^- \rightleftharpoons Ag$            |                          |
|   | $Cu^{2+} + 2e^- \rightleftharpoons Cu$        |                          |
|   | $2H^+ + 2e^- \rightleftharpoons H_2$          |                          |
|   | $Pb^{2+} + 2e^- \rightleftharpoons Pb$        |                          |
|   | $Sn^{2+} + 2e^- \rightleftharpoons Sn$        |                          |
|   | $Ni^{2+} + 2e^- \rightleftharpoons Ni$        |                          |
|   | $Fe^{2+} + 2e^- \rightleftharpoons Fe$        |                          |
|   | $Cr^{3+} + 3e^- \rightleftharpoons Cr$        |                          |
|   | $Zn^{2+} + 2e^- \rightleftharpoons Zn$        |                          |
|   | $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ |                          |
|   | $Al^{3+} + 3e^- \rightleftharpoons Al$        |                          |
|   | $Mg^{2+} + 2e^- \rightleftharpoons Mg$        |                          |
| Weakest oxidizing agent                         | $Na^+ + e^- \rightleftharpoons Na$            | Strongest reducing agent |

These three metals were included in the *activity series* that was discussed in Chapter 5. In this chapter, we now explain the activity series by comparing the strengths of the metals as reducing agents and of their ions as oxidizing agents.

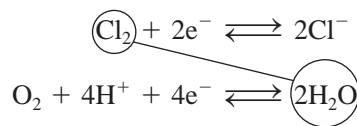
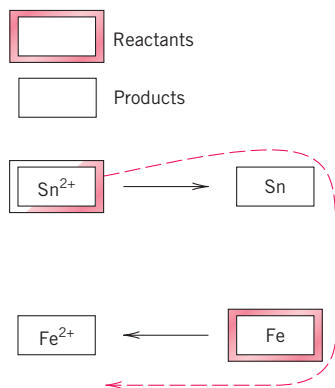
More experiments can provide additional ions and molecular species for our ranking. Eventually, we can construct a table of oxidizing agents ordered according to strength. Such a ranking is given in Table 14-1 and is an extension of the activity series of metals introduced in Chapter 5. In some cases, instruments are required to give quantitative values, known as *reduction potentials*, which indicate the comparative strength of a given oxidizing agent in relation to a defined standard. The strengths of the oxidizing agents are compared in these measurements at the same

concentration for all ions involved (1.00 M) and at the same partial pressure of all gases involved (1.00 atm).

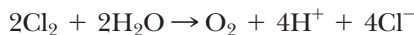
A redox reaction takes place between an oxidizing agent on the left and a reducing agent on the right. A favorable or spontaneous reaction occurs between an element, ion, or compound on the left (an oxidizing agent) with a species on the right (a reducing agent) that lies below it in the table. The strongest oxidizing agent ( $F_2$ ) is at the top of Table 14-1, on the left. It will oxidize any reducing agent listed on the right. On the other hand, the reducing agents, shown on the right, become stronger down the table. Na is the strongest reducing agent listed and so will reduce any oxidizing agent listed on the left. The spontaneous reaction can be visualized as taking place in a clockwise direction, with the oxidizing agent reacting to the right and the reducing agent below it reacting in the opposite direction to the left. (See Figure 14-2.)

Table 14-1 is particularly useful in predicting the reactions of certain elements with water. (All the reactions shown in the table are assumed to occur in aqueous solution.) The boxed reaction near the top of the table represents the oxidation of water when read from right to left. Note that the gaseous elements  $F_2$  and  $Cl_2$  spontaneously oxidize water to produce oxygen gas and an acid. (The reaction of  $Cl_2$  with water is quite slow, however.)

The spontaneous reaction is  
 $Sn^{2+} + Fe \rightarrow Sn + Fe^{2+}$



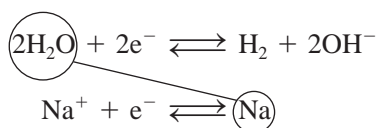
The spontaneous reaction is



**FIGURE 14-2**  
**Spontaneous Reaction** The stronger oxidizing agent reacts with the stronger reducing agent.

The boxed reaction near the bottom of the table represents the reduction of water when read from left to right. Note that the metals Al, Mg, and Na spontaneously reduce water to produce hydrogen gas and a base. (We can say that Na reduces water, or, conversely, we can say that water oxidizes Na.)



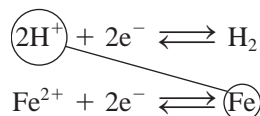


The spontaneous reaction is

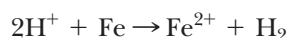


These metals are known as *active* metals because of their chemical reactivity with water.

The third boxed reaction, near the middle of the table, represents the reduction of aqueous acid solutions (1.00 M  $\text{H}^+$ ) to form hydrogen gas. Note that metals such as Ni and Fe are not oxidized by water but are oxidized by strong acid solutions.



The spontaneous reaction is



Acid rain is so named because it contains a considerably higher  $\text{H}^+$  concentration than ordinary rain. From this discussion, we can understand why metals such as iron and nickel are more likely to be corroded by acid rain.

Two of the metals shown in the table—Cu and Ag—are not oxidized by either water or acid solutions.\* Thus, these metals are relatively unreactive and find use in jewelry and coins.



Iron is oxidized by a strong acid solution to form iron(II) ions and hydrogen gas.

### EXAMPLE 14-6

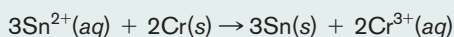
#### Determining the Direction of a Spontaneous Reaction

A strip of tin is placed in an aqueous solution of  $\text{Cr}(\text{NO}_3)_3$  in one experiment. In another, a strip of chromium is placed in an aqueous solution of  $\text{Sn}(\text{NO}_3)_2$ . Write the equation illustrating the spontaneous reaction that occurs.

#### PROCEDURE

In Table 14-1, note that  $\text{Sn}^{2+}$  is a stronger oxidizing agent than  $\text{Cr}^{3+}$  and Cr is a stronger reducing agent than Sn. The reactants are, therefore,  $\text{Sn}^{2+}$  and Cr. A balanced equation is obtained by multiplying the  $\text{Sn}^{2+}$  half-reaction by 3 and the Cr half-reaction by 2 for an exchange of six electrons.

#### SOLUTION



#### ANALYSIS

Notice that the spontaneous reaction takes place in a clockwise direction in the table.  $\text{Sn}^{2+}$  is in the higher position in the table as an oxidizing agent and reacts to the right, forming its product, Sn. Cr is below Sn so is the stronger reducing agent. It reacts to the left, forming its product,  $\text{Cr}^{3+}$ . Six electrons are exchanged to balance the equation. In using the table, remember that one species reacts to the right and one to the left.

#### SYNTHESIS

Nonmetal elements tend to be at the upper left of the reduction table and metal elements at the bottom right. These represent the reactive extremes of the table. As you move up the left side and down the right side, the elements become more reactive. It is not surprising that this order is also roughly close to the historical order in which these elements were discovered, isolated, and identified. The more reactive an element is, the harder it becomes to produce it in its elemental state. Metals at the upper right, like copper and silver, have been known since the beginning of civilization. So have iron, lead, mercury, and tin, which require only modest efforts to liberate from their ores. Metal ions of medium reduction potential, such as nickel, cobalt, and manganese, were isolated in the mid-1700s. The most reactive metals were finally isolated after electricity became a viable technique for promoting difficult chemical reactions in the nineteenth century. These include sodium, potassium, lithium, magnesium, and aluminum.

\*Copper is dissolved by nitric acid solutions, but the copper is oxidized by the nitrate ion, not the hydronium ion. See Example 14-3(b).

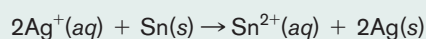
Another factor, of course, is the relative abundance of the element, with rarer elements being more difficult to find. A very low reduction potential of the metal ions, though, was the primary roadblock to these elements' discovery.

**EXAMPLE 14-7****Writing a Spontaneous Single-Replacement Reaction**

A strip of tin metal is placed in an  $\text{AgNO}_3$  solution. If a reaction takes place, write the equation illustrating the spontaneous reaction.

**PROCEDURE**

In Table 14-1, note that the oxidizing agent  $\text{Ag}^+$  is above the reducing agent Sn. Therefore, a spontaneous reaction does occur. Write the balanced equation, noticing that two electrons are exchanged.

**SOLUTION****ANALYSIS**

Again, notice that the spontaneous reaction is in a clockwise direction. The  $\text{Ag}^+$  reacts to the right and the Sn reacts to the left.

**SYNTHESIS**

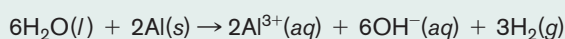
A practical application of this reaction is to “silver coat” tin or some other metal, such as iron or nickel, that lies lower than  $\text{Ag}^+$  in the table.  $\text{Au}^{3+}$  also ranks high in the table as an oxidizing agent like  $\text{Ag}^+$ . This means that a cheaper metal can be “gold plated” to give it the outer appearance of gold.

**EXAMPLE 14-8****Writing a Spontaneous Reaction of a Metal with Water**

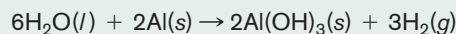
A length of aluminum wire is placed in water. Does the aluminum react with water? What is the spontaneous reaction involving aluminum and water?

**PROCEDURE**

In Table 14-1, note that aluminum is an active metal and would react with water (as an oxidizing agent). The aluminum is oxidized and the water is reduced.

**SOLUTION**

Since  $\text{Al}(\text{OH})_3$  is insoluble in water, however, the equation should be written as

**ANALYSIS**

How many electrons are being exchanged in this reaction? The oxidation of aluminum to  $\text{Al}^{3+}$  is a 3-electron half-reaction. In water, hydrogen is reduced from +1 to 0 in  $\text{H}_2$ , but two hydrogen atoms require 2 electrons. The least common multiple of 3 and 2 is 6, so there are 6 electrons exchanging in this reaction.

**SYNTHESIS**

Theoretically, aluminum should dissolve (i.e., react) in water. However, metallic aluminum reacts with oxygen in the air to form a coating of  $\text{Al}_2\text{O}_3$ , which protects the metal from coming into contact with water. In other words, it “self-paints.” Thus, it is a useful metal even for the hulls of boats, despite its high chemical reactivity.

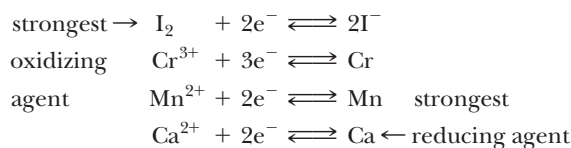
**ASSESSING THE OBJECTIVE FOR SECTION 14-4****EXERCISE 14-4(a) KNOWLEDGE:** Fill in the blanks.

Spontaneous redox reactions occur between the \_\_\_\_\_ oxidizing and reducing agents to produce \_\_\_\_\_ oxidizing and reducing agents. In a table, the stronger oxidizing agent is located \_\_\_\_\_ in the table than the reducing agent.

**EXERCISE 14-4(b) ANALYSIS:** In which of the following would a spontaneous reaction occur? Write the balanced equation for that reaction.

- (a) A strip of Pb is placed in a  $\text{Cr}^{3+}$  solution.  
 (b) A strip of Cr is placed in a  $\text{Pb}^{2+}$  solution.

**EXERCISE 14-4(c) SYNTHESIS:** Given the following table of oxidizing and reducing agents, answer the questions below.



- (a) Is the following reaction spontaneous or nonspontaneous?  

$$\text{Mn} + \text{Ca}^{2+} \rightarrow \text{Ca} + \text{Mn}^{2+}$$
- (b) Write a balanced equation representing a spontaneous reaction involving the Cr,  $\text{Cr}^{3+}$  and the Mn,  $\text{Mn}^{2+}$  half-reactions.
- (c) If an aqueous solution of  $\text{I}_2$  (an antiseptic) is spilled on a chromium-coated automobile bumper, will a reaction occur? If so, write the balanced equation for the reaction.
- (d) Which substance in the table will react with  $\text{Mn}^{2+}$ ?
- (e) Which substances in the table will not react with any other in the table?

**EXERCISE 14-4(d) SYNTHESIS:** Write a balanced equation illustrating how a metal such as iron could be “gold plated” from an  $\text{Au}^{3+}$  solution.

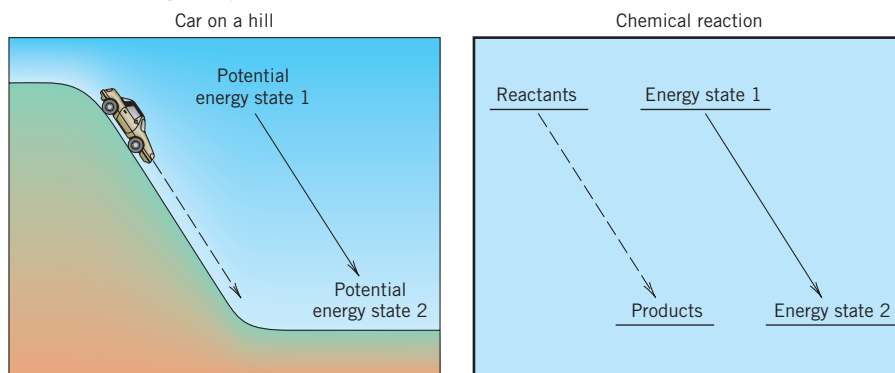
For additional practice, work chapter problems 14-20, 14-27, 14-31, and 14-32.

## 14-5 VOLTAIC CELLS



**LOOKING AHEAD!** The electrons exchanged in a spontaneous redox reaction can be detoured through a wire and put to work. This is the principle used in all the different types of batteries that we depend on to run our calculators, remotes, cell phones, and even iPods and MP3 players. How this is accomplished is the topic of this section. ■

Releasing the brake on an automobile parked on the side of a hill brings no surprise. The automobile spontaneously rolls down the hill because the bottom of the hill represents a lower potential energy than the top. Chemical reactions occur spontaneously for the same reason. The products represent a position of lower potential energy than the reactants. In the case of the car, the difference in potential energy is due to position and the attraction of gravity; in the case of a chemical reaction, the difference in potential energy is due to the composition of the reactants and products. (See Figure 14-3.) When the car rolls down the hill, the difference in energy is transformed into the kinetic energy of the moving car and heat from friction. When a chemical reaction proceeds spontaneously from reactants to products, the difference is given off as heat, light, or electrical energy. In this



**FIGURE 14-3 Energy States** A chemical reaction proceeds in a certain direction for the same reason that a car rolls down a hill.

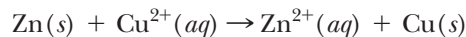
### OBJECTIVES FOR SECTION 14-5

- (a) Describe the parts of a voltaic cell and how it generates electricity.  
 (b) List the types of batteries discussed and a particular use or advantage of each type.

section, we are concerned with the electrical energy provided by spontaneous redox reactions.

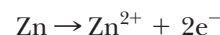
### 14-5.1 The Daniell Cell

A **voltaic cell** (also called a *galvanic cell*) uses a favorable or spontaneous redox reaction to generate electrical energy through an external circuit. One of the earliest voltaic cells put to use the spontaneous reaction discussed in the previous section, which is



This voltaic cell is known as the *Daniell cell* and was used to generate electrical current for the new telegraph and doorbells in homes.

In an earlier experiment discussed in the previous section, we found that a strip of zinc placed in a  $\text{Cu}^{2+}$  solution forms a coating of metallic copper on the zinc strip. To generate electricity, however, the oxidation reaction must be separated from the reduction reaction so that the electrons exchanged can flow in an external wire where they can be put to use. The Daniell cell is illustrated in Figure 14-4. A zinc strip is immersed in a  $\text{Zn}^{2+}$  solution, and, in a separate compartment, a copper strip is immersed in a  $\text{Cu}^{2+}$  solution. A wire connects the two metal strips. The two metal strips are called electrodes. *The electrodes are the surfaces in a cell at which the reactions take place. The electrode at which oxidation takes place is called the anode. Reduction takes place at the cathode.* In the compartment on the left, the strip of Zn serves as the anode, since the following reaction occurs when the circuit is connected.



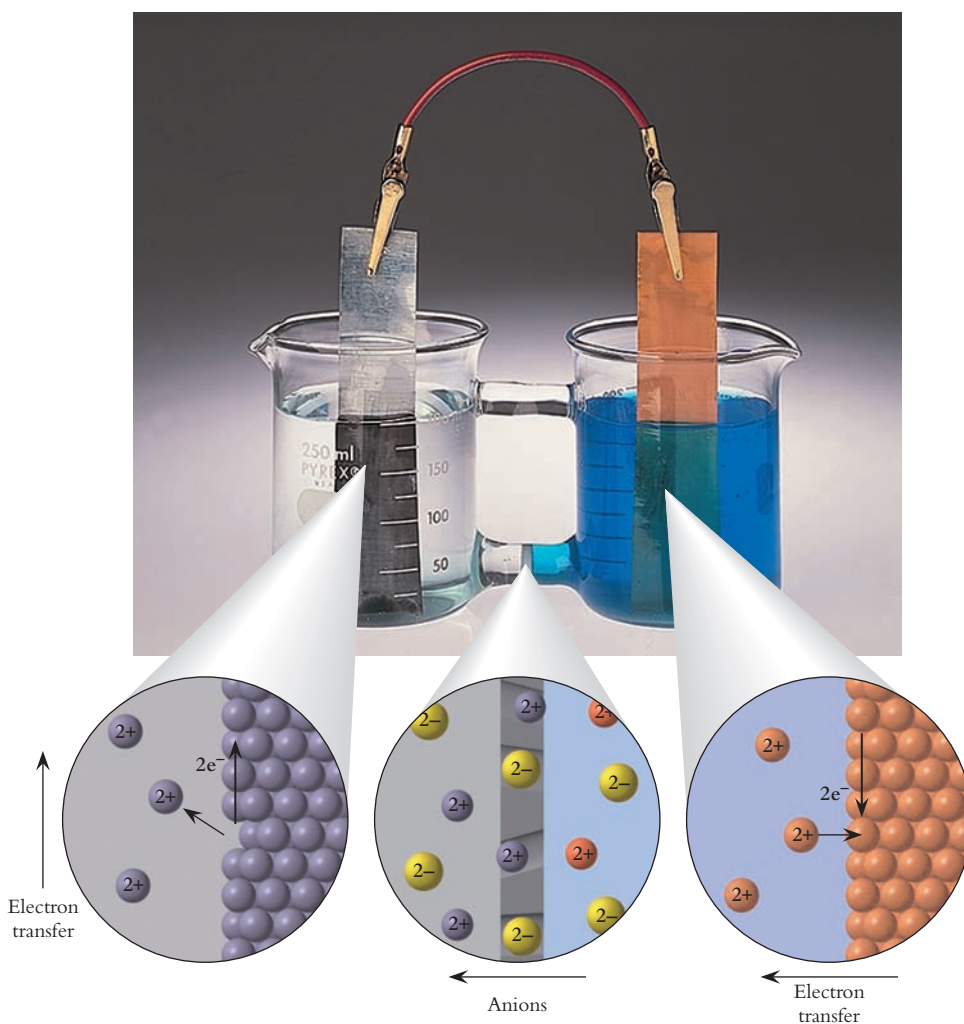
When the circuit is complete, the two electrons travel in the external wire to the Cu electrode, which serves as the cathode. The reduction reaction occurs at the cathode.



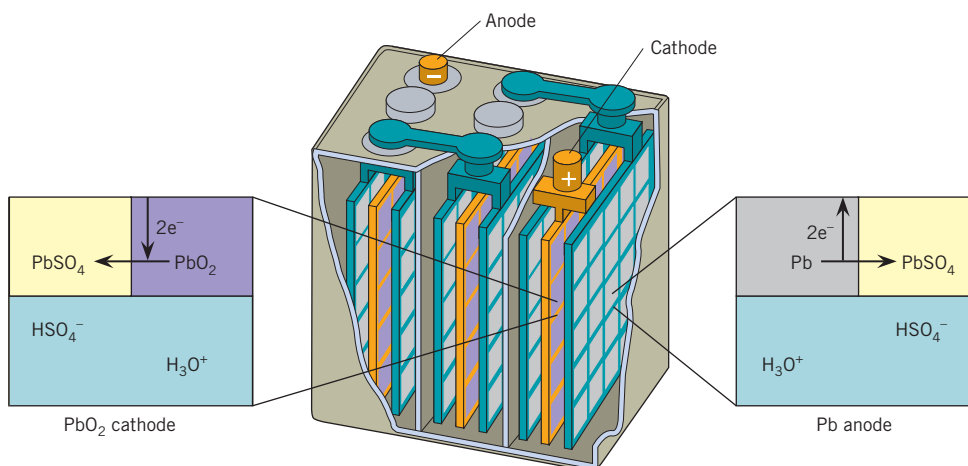
To maintain neutrality in the solution, some means must be provided for the movement of a  $\text{SO}_4^{2-}$  ion (or some other negative ion) from the right compartment, where a  $\text{Cu}^{2+}$  has been removed, to the left compartment, where a  $\text{Zn}^{2+}$  has been produced. The salt bridge is an aqueous gel that allows ions to migrate between compartments but does not allow the mixing of solutions.

A porous plate separating the two solutions, as shown in Figure 14-4, also serves this function. (If  $\text{Cu}^{2+}$  ions mixed into the left compartment, they would form a coating of Cu on the Zn electrode, thus short-circuiting the cell.)

The electrodes in this cell are called active electrodes because they are involved in the reaction. As the cell discharges (generates electrical energy), the Zn electrode



**FIGURE 14-4** The Daniell Cell This chemical reaction produced electricity for the first telegraphs.



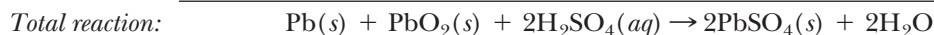
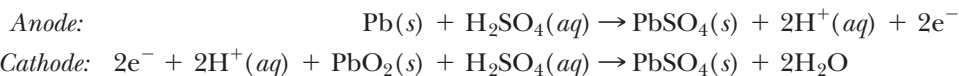
**FIGURE 14-5 Lead Storage Battery** The lead storage battery is rechargeable.

becomes smaller but the Cu electrode becomes larger. The reaction can be stopped by interrupting the external circuit with a switch. If the circuit is open, the electrons can no longer flow, so no further reaction occurs until the switch is again closed. The energy of the cell can thus be stored between uses.

### 14-5.2 Common Batteries

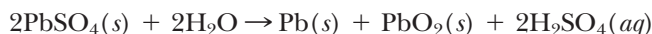
Two of the most common voltaic cells in use today are the dry cell (flashlight battery) and the lead–acid cell (car battery). (A **battery** is a collection of one or more separate cells joined together in one unit.)

A three-cell, lead–acid storage battery is illustrated in Figure 14-5. Each cell is composed of two grids separated by an inert spacer. One grid of a fully charged battery contains metallic lead. The other contains  $\text{PbO}_2$ , which is insoluble in  $\text{H}_2\text{O}$ . Both grids are immersed in a sulfuric acid solution (battery acid). When the battery is discharged by connecting the electrodes, the following half-reactions take place spontaneously.



The electrons released at the Pb anode travel through the external circuit to run a car's lights, starter, radio, or whatever is needed. The electrons return to the  $\text{PbO}_2$  cathode to complete the circuit. As the reaction proceeds, both electrodes are converted to  $\text{PbSO}_4$ , and the  $\text{H}_2\text{SO}_4$  is depleted. Since  $\text{PbSO}_4$  is also insoluble, it remains attached to the grids as it forms. The degree of discharge of a battery can be determined by the density of the battery acid. Since the density of a fully discharged battery is 1.15 g/mL, the difference in density between this value and the density of a fully charged battery (1.35 g/mL) gives the amount of charge remaining in the battery. As the electrodes convert to  $\text{PbSO}_4$ , the battery loses power and eventually becomes “dead.” Most lead batteries sold today are sealed, however, so density cannot be used to determine its condition.

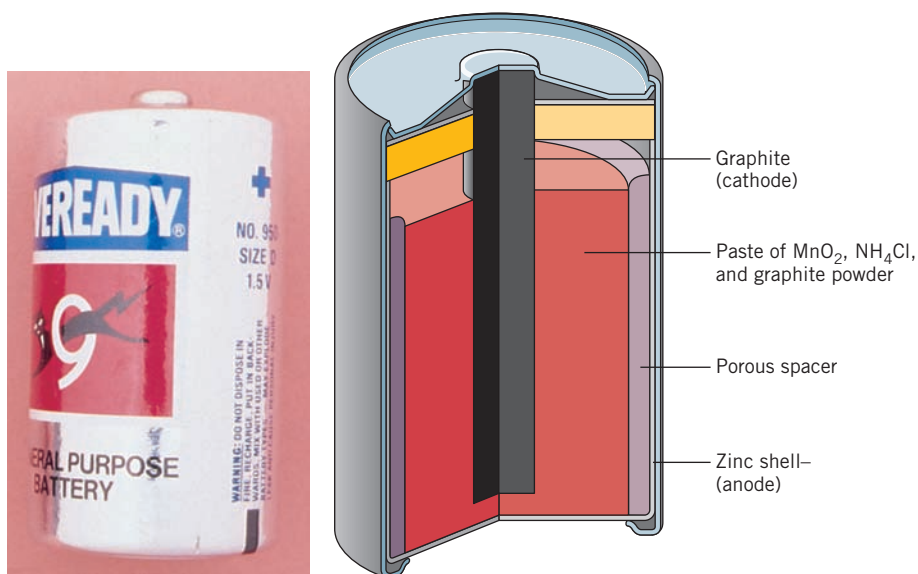
The convenience of a car battery is that it can be recharged. After the engine starts, an alternator or generator is engaged to push electrons back into the cell in the opposite direction from which they came during discharge. This forces the reverse, nonspontaneous reaction to proceed.



When the battery is fully recharged, the alternator shuts off, the circuit is open, and the battery is ready for the next start.

The dry cell (invented by Leclanché in 1866) is not rechargeable to any extent but is comparatively inexpensive and easily portable. (In contrast, the lead–acid battery is

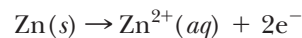




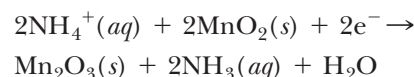
**FIGURE 14-6 Dry Cell**  
The dry cell (left) is comparatively inexpensive, light, and portable. Its contents are depicted on the right.

heavy and expensive and must be kept upright.) The dry cell illustrated in Figure 14-6 consists of a zinc anode, which is the outer rim, and an inert graphite electrode. (An *inert* or *passive* electrode provides a reaction surface but does not itself react.) In between is an aqueous paste containing  $\text{NH}_4\text{Cl}$ ,  $\text{MnO}_2$ , and carbon. The reactions are as follows.

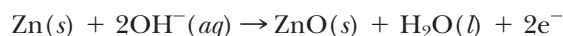
*Anode:*



*Cathode:*



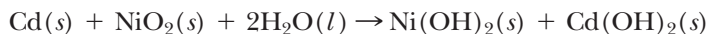
A disadvantage of the dry cell is that the  $\text{NH}_4^{+}$  ion creates an acidic solution. (In the previous chapter, we discussed how this cation undergoes hydrolysis to form a weakly acidic solution.) The zinc electrode slowly reacts with the weakly acidic solution, so the shelf-life of these batteries is a matter of only a few months. In an *alkaline battery*,  $\text{NaOH}$  or  $\text{KOH}$  is substituted for the  $\text{NH}_4\text{Cl}$ , so the solution is basic and zinc reacts much more slowly. Alkaline batteries are more expensive, but they have much longer shelf-lives. The anode reaction in the alkaline battery is



Other types of batteries that have been developed in modern times are more useful for calculators and wristwatches. These batteries are very small and deliver a small amount of current for a long time. Some batteries can produce current for three to five years. One is the *silver battery*, which uses a zinc anode and a silver(I) oxide cathode. Another, known as the *mercury battery*, also uses a zinc anode but a mercury(II) oxide cathode. (See Figure 14-7.) The two reactions in these batteries are

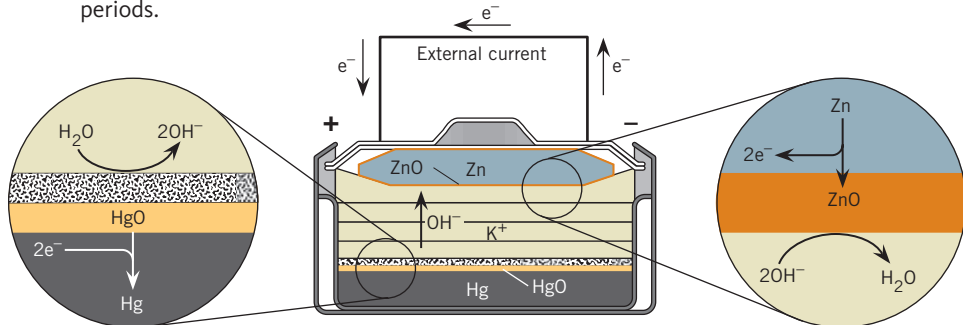


A battery that substitutes for dry cells is known as a *nickel–cadmium battery*. The advantage of this battery is that it is rechargeable. However, it is considerably more expensive initially. The reversible reaction that takes place in this cell is



There are many other batteries that have special uses, such as the *lithium battery*, which takes advantage of the light weight and strong reducing ability of lithium. Most

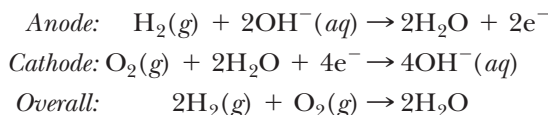
**FIGURE 14-7 Mercury Battery** These small batteries deliver electrical current for long periods.



laptop computers use what is known as a *lithium ion battery*. It provides a good source of power and is both rechargeable and comparatively light. It actually does not involve a redox reaction, however. Electrical energy is supplied by the movement of lithium ions from one electrode to another that is associated with the movement of electrons through an external circuit. Lithium ion batteries are now under development for use in an electrical automobile to be produced by General Motors.

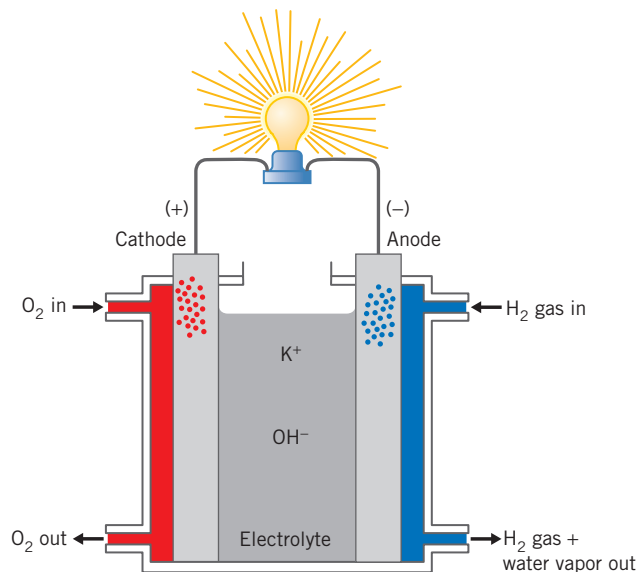
### 14-5.3 Fuel Cells

Space travel requires a tremendous source of electrical energy. The requirements are that the source be continuous (no recharging necessary), lightweight, and dependable. Solar energy directly converts rays from the sun into electricity and is used in the international space station (as well as in an increasing number of homes). It is not practical for shorter runs such as the space shuttle. Although expensive, a source of power that fills the bill nicely is the fuel cell. A **fuel cell** uses the direct reaction of hydrogen or a hydrogen compound and oxygen to produce electrical energy. Figure 14-8 is an illustration of a fuel cell. Hydrogen and oxygen gases are fed into the cell, where they form water. As long as the gases enter the cell, power is generated. The water that is formed can be removed and used for other purposes in the spacecraft. Since reactants are supplied from external sources, the electrodes are not consumed, and the cell does not have to be shut down to be regenerated, as a car battery does. The best inert electrode surfaces at which the gases react are made of the extremely expensive metal platinum. The reactions that take place in a basic solution in the fuel cell are



Fuel cells have had some large-scale application in power generation for commercial purposes. Currently, a great deal of research money and effort is being expended in fuel cell research. See Making it Real, “Fuel Cells—The Future Is (Almost) Here.”

More efficient and durable batteries are the focus of much research at the current time. For example, an efficient and relatively inexpensive electric automobile is the object of intensive efforts. A small electric car using lead–acid batteries requires at least 18 batteries. These have to be replaced every year or so, depending on use. Also, much of the power of these heavy batteries must be used just to move the heavy batteries around, not including the car and passengers. There have been some encouraging possibilities for lighter, more durable batteries, and several types of electric automobiles are in the testing phase.



**FIGURE 14-8 Fuel Cell**  
The fuel cell can generate power without interruption for recharging.

#### ASSESSING THE OBJECTIVES FOR SECTION 14-5

#### EXERCISE 14-5(a) KNOWLEDGE: Fill in the blanks.

A spontaneous chemical reaction is used in a \_\_\_\_\_ cell. An example is the Daniell cell, where \_\_\_\_\_ is oxidized at the \_\_\_\_\_ and \_\_\_\_\_ is reduced at the \_\_\_\_\_. An electrolytic balance is maintained by means of a \_\_\_\_\_ bridge. In the lead–acid battery, \_\_\_\_\_ is \_\_\_\_\_ at the anode and \_\_\_\_\_ is reduced at the \_\_\_\_\_.

**EXERCISE 14-5(b) ANALYSIS:** A cell is constructed of a  $\text{Br}_2, \text{Br}^-$  half-cell connected to an  $\text{Fe}^{2+}, \text{Fe}$  half-cell. Write a balanced equation representing the spontaneous reaction that occurs.

**EXERCISE 14-5(c) SYNTHESIS:** If you were asked to design a battery to replace the lead–acid battery for an automobile, what balanced equation would you propose from the oxidizing and reducing agents listed in Table 14-1? Three things should be considered (in addition to cost, which we will ignore). (1) The mass of the reactants is important. (2) The farther apart the oxidizing and reducing agents are in the table, the more powerful the battery (i.e., the higher voltage). (3) The overall chemical reactivity of the reactants is important. For example, if a reactant explodes in air or water, we would not want to use it.

For additional practice, work chapter problems 14-36, 14-38, and 14-40.



## Fuel Cells—The Future Is (Almost) Here



Special vehicles are currently testing fuel cells as a power source.

The simplest combustion reaction, hydrogen plus oxygen to form water, may be the key to the future. On a mass-of-fuel basis, it is by far the most energetic reaction. The combustion of two moles (4 g) of hydrogen produces 570 kJ of energy, much more than any other fuel. Since the

combustion of hydrogen is a redox reaction, the energy can be released as electrical energy. This is the principle of the fuel cell, first demonstrated in the nineteenth century. It has long been used in the space program by NASA to continuously generate electricity without releasing toxic products. The two reactions that occur in the fuel cell and a diagram were illustrated in Section 14-5.3 and Figure 14-8.

The use of the fuel cell has been limited by the expense of inert electrodes that have traditionally contained rare platinum and/or palladium, which are more expensive than gold. Also, although hydrogen was previously discussed as the perfect fuel, it is hazardous to handle, it is not cheap in the pure state, and it is not easy to store in large quantities. Another problem involves the high operating temperatures necessary in a fuel cell.

All these problems, however, are being addressed with billions of dollars of investment and research. Much of the hope of making fuel cells practical in the short run rests in using fuels such as methane (natural gas), butane, methanol, ethanol, or even gasoline rather than pure hydrogen. These compounds are readily available and easy to transport. The problem with these fuels is that they tend to gunk up the electrodes and they produce carbon dioxide, which is a greenhouse gas. Still, it would be much easier to dispense natural gas or even butane at a service station rather than pure hydrogen. Hydrogen is ideal for the fuel cell, but its large-scale application may have to wait.

If you have not yet heard much about fuel cells, you will. Experimental cars and buses using fuel cells are already on the road. Reports come in almost daily about advancements in the research on fuel cells. The operating temperatures keep coming down; new and cheaper materials for the electrodes, along with more efficient use of fuels other than hydrogen, are being developed. Eventually, we will even have fuel cells generating electrical power scattered around a city, eliminating the need for extensive overhead transmission lines. Research is in progress to miniaturize the fuel cell so it can be used in cell phones and calculators. It would be smaller, cheaper (eventually), and easily refueled. (Some may even run on the alcohol in wine or beer.) Fuel cells are the power source of the future.

### ▶ OBJECTIVES FOR SECTION 14-6

(a) Write the reaction that occurs when a salt is electrolyzed. (b) Describe the various applications for electrolytic cells.

## 14-6 ELECTROLYTIC CELLS



**LOOKING AHEAD!** Spontaneous reactions are like cars rolling down a hill. They go to lower energy states. Can a car or a chemical reaction go up a hill? Of course—but in order for this to happen, energy in the form of a push for a car or energy for a chemical reaction must be supplied. Nonspontaneous redox reactions can occur if sufficient electrical energy is supplied from an outside source. This is the final topic of this chapter. ■

Back in the good old days before inexpensive but strong plastics, automobiles were equipped with beautiful chrome bumpers and other chromium accessories. Chromium not only looks great but is also resistant to rust, so it protects the underlying iron (which does rust) from exposure to air and water. How is iron metal coated with a layer of chromium? According to Table 14-1, we would *not* predict that a coating of chromium would spontaneously form on iron immersed in a  $\text{Cr}^{3+}$  solution. But that doesn't mean we can't *make* it happen. Nonspontaneous redox reactions occur if enough electrical energy is supplied from an outside source. *Cells that convert electrical energy into chemical energy are called electrolytic cells.* They involve nonspontaneous redox reactions.

An example of an electrolytic cell is shown in Figure 14-9. When sufficient electrical energy is supplied to the electrodes from an outside source, the following nonspontaneous reaction occurs.



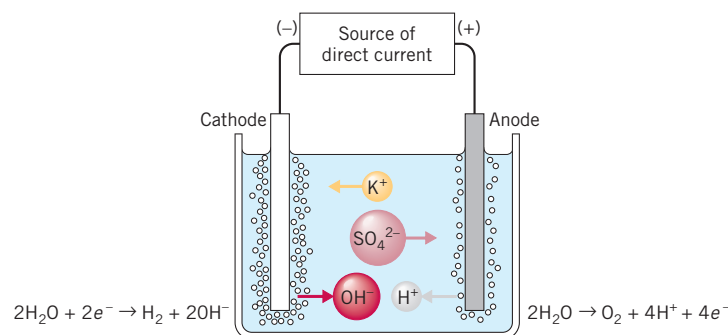
The electrolysis of water to produce hydrogen using solar energy seems to be a logical solution to the energy crisis. The hydrogen produced could be used in a fuel cell. Unfortunately, the process using solar energy is currently very inefficient and expensive. Currently, the cheapest source of hydrogen is from a hydrocarbon such as methane (natural gas). However, much research is underway to improve the process.

For electrolysis of water to occur, an electrolyte such as  $\text{K}_2\text{SO}_4$  must be present in solution. Pure water alone does not have a sufficient concentration of ions to allow conduction of electricity.

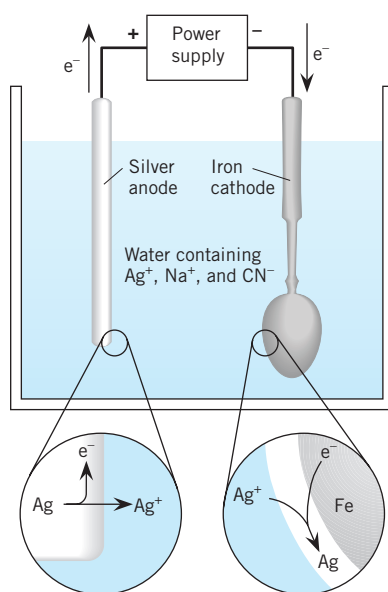
Another example of an electrolytic cell is the recharge cycle of the lead–acid battery described in Section 14-5.2. When energy from the engine activates the alternator, electrical energy is supplied to the battery, and the nonspontaneous reaction occurs as an electrolysis reaction. This reaction re-forms the original reactants.

Electrolysis has many useful applications. For example, in addition to chromium, silver and gold can be electroplated onto cheaper metals. In Figure 14-10 the metal spoon is the cathode and the silver bar serves as the anode. When electricity is supplied, the Ag anode produces  $\text{Ag}^+$  ions, and the spoon cathode reduces  $\text{Ag}^+$  ions to form a layer of Ag. The silver-plated spoon can be polished and made to look as good as sterling silver, which is more expensive.

Electrolytic cells are used to free elements from their compounds. Such cells are especially useful where metals are held in their compounds by strong chemical bonds. Examples are the metals aluminum, sodium, and magnesium. All aluminum is produced by the electrolysis of molten aluminum salts. Commercial quantities of sodium and chlorine are also produced by electrolysis of molten sodium chloride. An apparatus used for the electrolysis of molten sodium chloride is illustrated in Figure 14-11. At the high temperature required to keep the  $\text{NaCl}$  in the liquid state, sodium forms as a liquid and is drained from the top of the cell.



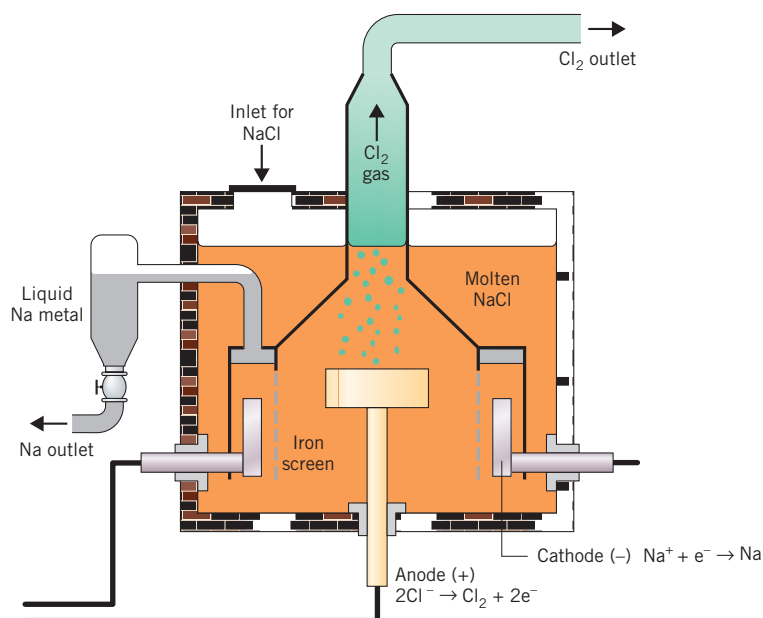
**FIGURE 14-9** An Electrolytic Cell Electrolysis of a solution of potassium sulfate gives hydrogen gas and oxygen gas as products.



**FIGURE 14-10** Electroplating With an input of energy, a spoon can be coated with silver. The service has been electroplated with silver.



**FIGURE 14-11 Electrolysis of NaCl** Cross section of the Downs cell used for the electrolysis of molten sodium chloride. The cathode is a circular ring that surrounds the anode. The electrodes are separated from each other by an iron screen. During the operation of the cell, molten sodium collects at the top of the cathode compartment, from which it is periodically drained. The chlorine gas bubbles out of the anode compartment and is collected.



### ASSESSING THE OBJECTIVES FOR SECTION 14-6

**EXERCISE 14-6(a) KNOWLEDGE:** List four uses for reversing a spontaneous redox reaction.

**EXERCISE 14-6(b) ANALYSIS:** Write the reaction that occurs when molten  $\text{MgCl}_2$  is electrolyzed.

**EXERCISE 14-6(c) SYNTHESIS:** If you want to coat a piece of iron with Cr, it must be electroplated. Is it necessary to electroplate Sn on a piece of iron? If not, why?

**EXERCISE 14-6(d) SYNTHESIS:** Aluminum cannot be electroplated from an aqueous solution containing  $\text{Al}^{3+}$  ions. Why not? Refer to Table 14-1.

*For additional practice, work chapter problem 14-43.*

### PART B SUMMARY

#### KEY TERMS

- 14-5.1** A **voltaic cell** harnesses a spontaneous redox reaction to generate electricity. p. 458
- 14-5.1** A voltaic cell consists of two **electrodes**, an **anode** for oxidation and a **cathode** for reduction. p. 458
- 14-5.2** A **battery** consists of one or more voltaic cells arranged in a series. p. 459
- 14-5.3** A **fuel cell** generates electricity from the reaction of gases at inert electrodes. p. 461
- 14-6** Electrical energy is supplied to an **electrolytic cell** to cause a nonspontaneous redox reaction. p. 463

#### SUMMARY CHART

| Reactions of Elements with Water                       |               |  |
|--|---------------|--|
| Elements   | Reaction      | Products   |
| Active nonmetals<br>( $\text{F}_2$ and $\text{Cl}_2$ ) | Oxidize water | $\text{O}_2$ and nonmetal acid<br>(HF, HCl)                                |
| Other nonmetals  | No reaction   |  |
| Active metals<br>(e.g., K, Ca, Al)                     | Reduce water  | $\text{H}_2$ and metal hydroxide<br>[e.g., KOH, $\text{Ca}(\text{OH})_2$ ] |
| Other metals<br>(e.g., Fe, Cu, Au)                     | No reaction   |  |



## CHAPTER SUMMARY

A common characteristic of a large number of chemical reactions is an exchange of electrons between reactants. These reactions are known as **oxidation–reduction reactions**, or simply **redox reactions**. In such reactions, the reactant that gives up or loses the electrons is **oxidized**, and the reactant that gains the electrons is **reduced**. The reactant oxidized is also known as a **reducing agent**, and the reactant reduced is known as an **oxidizing agent**.

To keep track of the electron exchange, we can follow the change in **oxidation states** (or **oxidation numbers**) of the elements in the compounds. The oxidation state increases in the substance oxidized and decreases in the substance reduced. We can use this understanding to balance equations by the **oxidation state (bridge) method**. In another method, a redox reaction can be divided into two **half-reactions**: an oxidation and a reduction. These two processes take place so that all electrons lost in the oxidation process are gained in the reduction process. This fact is useful in balancing oxidation–reduction reactions by the **ion-electron method**. Most of these reactions would, at best, be very difficult to balance by inspection methods, as described in Chapter 5.

Each substance has its own inherent strength as either an oxidizing agent or a reducing agent. A table can be constructed in which oxidizing and reducing agents are ranked by strength as determined by observation or

measurements with electrical instruments. From this table, a great many other spontaneous reactions can be predicted. In Table 14-1, stronger oxidizing agents are ranked higher on the left and stronger reducing agents are ranked lower on the right. Reactions can thus be predicted as shown in Figure 14-2. Also, the reactions (or lack of reactions) of certain elements with water can be predicted.

Spontaneous chemical reactions occur because reactants are higher in chemical (potential) energy than products. We are familiar with many exothermic reactions, where the difference in energy is released as heat. The energy can also be released as electrical energy in a **voltaic cell**. In a voltaic cell, the two half-reactions are physically separated so that electrons travel in an external circuit or wire between **electrodes**. The **anode** is the electrode at which oxidation takes place, and the **cathode** is the electrode at which reduction takes place. The Daniell cell, the car **battery**, the dry cell, and the **fuel cell** all involve spontaneous chemical reactions in which the chemical energy is converted directly into electrical energy.

Many reactions that are predicted to be unfavorable or nonspontaneous can be made to occur if electrical energy is supplied from an outside source. These are referred to as **electrolytic cells** and are useful in the commercial production of metals and in electroplating.

## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES         | EXERCISES          | CHAPTER PROBLEMS          |
|---------|---|------------------|--------------------|---------------------------|
| 14-1    | Calculate oxidation states and determine the species oxidized, the species reduced, the oxidizing agent, and the reducing agent in an electron exchange reaction. | 14-1, 14-2       | 1a, 1b, 1c, 1d, 1e | 1, 2, 6, 8, 9, 11, 12, 14 |
| 14-2    | Balance redox reactions by the bridge method.   | 14-3             | 2a, 2b             | 16, 17                    |
| 14-3    | Balance redox reactions by the ion-electron method.   | 14-4, 14-5       | 3a, 3b             | 19, 21, 23, 25            |
| 14-4    | Using a table or relative strengths of oxidizing agents, determine whether a specific redox reaction is spontaneous.  | 14-6, 14-7, 14-8 | 4a, 4b, 4c, 4d, 5b | 27, 28, 30, 32            |
| 14-5    | Describe the parts of a voltaic cell and how it generates electricity.  |                  | 5a, 5c             | 35, 39, 42                |
|         | List the types of batteries discussed and a particular use or advantage of each type.   |                  | 5c                 | 36, 37, 38                |
| 14-6    | Write the reaction that occurs when a salt is electrolyzed.   |                  | 6b                 | 43, 46                    |
|         | Describe the various applications for electrolytic cells.   |                  | 6a, 6c, 6d         | 47                        |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**14-1(a)** If all the atoms in a compound were ions, the charge on the ions would be the same as their oxidation

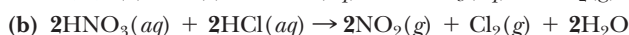
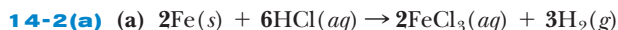
states. For oxygen in compounds, this is usually  $-2$ . Hydrogen is usually  $+1$  in compounds. A substance oxidized undergoes a loss of electrons and an increase in oxidation state. This substance is also known as a reducing agent.

**14-1(b)** (a)  $+3$  (b)  $+2$

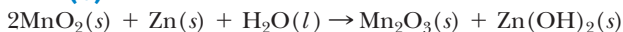
**14-1(c)**  $\text{ClO}_2 \rightarrow \text{Cl}^-$   $\text{ClO}_2$  is reduced and is the oxidizing agent.  $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$   $\text{H}_2\text{O}_2$  is oxidized and is the reducing agent.

**14-1(d)** Both ions in  $\text{CrI}_3$  are oxidized. The Cr is oxidized from +3 in  $\text{Cr}^{3+}$  to +6 in  $\text{CrO}_4^{2-}$ ; the I is oxidized from  $-1$  in  $\text{I}^-$  to 0 in  $\text{I}_2$ . The Cl is reduced from 0 in  $\text{Cl}_2$  to  $-1$  in  $\text{Cl}^-$ .

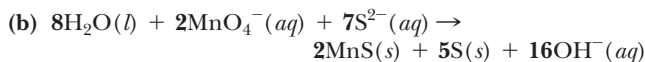
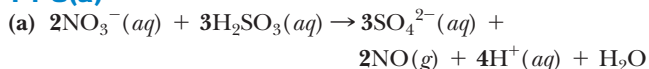
**14-1(e)** No, it is not. Reduction is the gain of electrons. They must come from somewhere. Oxidation is the loss of electrons. They must end up somewhere. The two processes always occur together. Certain reactions are referred to as being an oxidation or a reduction, but in these cases, it is because we focus on a molecule of interest. Other, less important molecules in these reactions are always undergoing the complementary process.



**14-2(b)**



**14-3(a)**



**14-3(b)**

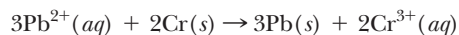


**PART B**

**EXERCISES**

**14-4(a)** Spontaneous redox reactions occur between the stronger oxidizing and reducing agents to produce weaker oxidizing and reducing agents. In a table, the stronger oxidizing agent is located higher in the table than the reducing agent.

**14-4(b)** A spontaneous reaction would occur in (b).



**14-4(c)** (a) nonspontaneous (b)  $2\text{Cr}^{3+} + 3\text{Mn} \rightarrow 2\text{Cr} + 3\text{Mn}^{2+}$  (c) Yes.  $3\text{I}_2 + 2\text{Cr} \rightarrow 2\text{Cr}^{3+} + 6\text{I}^-$  (d) only Ca (e)  $\text{Ca}^{2+}$  and  $\text{I}^-$

**CHAPTER PROBLEMS**

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

**Oxidation States (SECTION 14-1)**

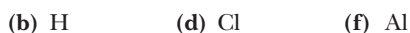
**14-1.** Give the oxidation states of the elements in the following compounds.



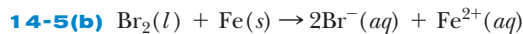
**14-2.** Give the oxidation states of the elements in the following compounds.



**14-3.** Which of the following elements form *only* the +1 oxidation state in compounds?

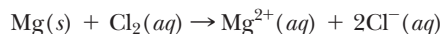


**14-5(a)** A spontaneous chemical reaction is used in a voltaic cell. An example is the Daniell cell, where zinc metal is oxidized at the anode and copper ion is reduced at the cathode. An electrolytic balance is maintained by means of a salt bridge. In the lead–acid battery, lead metal is oxidized at the anode and  $\text{PbO}_2$  is reduced at the cathode.



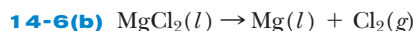
**14-5(c)** There actually isn't one correct answer, since the factors involved sometimes conflict, such as mass of the reactants versus the voltage of the cell. The reaction shown above for Exercise 14-5(b) is one possibility because neither reactant reacts directly with water. However, bromine is very corrosive and causes severe burns.

Although sodium metal is light and is the most powerful reducing agent, it is very difficult to use because it reacts violently with water. Likewise, fluorine is almost impossible to use because of its high reactivity. It reacts with almost any container. This leaves magnesium, which is very light and stable, since it reacts with water only at high temperatures, and chlorine gas, which reacts very slowly with water. The reaction is

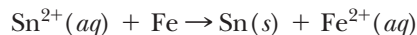


In fact, a workable battery has been made using Zn and  $\text{Cl}_2$ .

**14-6(a)** (1) electroplating metals like silver onto a surface (2) recharging batteries (3) producing fuels like hydrogen (4) producing reactive metals like aluminum and sodium

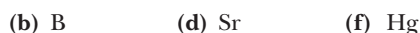


**14-6(c)** The formation of Sn from an  $\text{Sn}^{2+}$  solution onto a piece of iron is a spontaneous reaction, so energy does not need to be supplied. The spontaneous reaction is



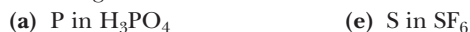
**14-6(d)** Aluminum or any other active metal that reacts with water, such as magnesium or sodium, cannot be electroplated from aqueous solution. All three of these metals are produced from electrolysis of their molten salts. Only metals above water (as a reducing agent) can be electroplated from solutions of their aqueous ions.

**14-4.** Which of the following elements form *only* the +2 oxidation state in compounds?



**14-5.** What is the only oxidation state of Al in its compounds?

**14-6.** What is the oxidation state of each of the following?



**14-7.** What is the oxidation state of the specified atom?

- (a) S in  $\text{SO}_3$  (d) N in  $\text{HNO}_3$   
 (b) Co in  $\text{Co}_2\text{O}_3$  (e) Cr in  $\text{K}_2\text{CrO}_4$   
 (c) U in  $\text{UF}_6$  (f) Mn in  $\text{CaMnO}_4$

**14-8.** What is the oxidation state of each of the following?

- (a) Se in  $\text{SeO}_3^{2-}$  (d) Cl in  $\text{HClO}_2$   
 (b) I in  $\text{H}_5\text{IO}_6$  (e) N in  $(\text{NH}_4)_2\text{S}$   
 (c) S in  $\text{Al}_2(\text{SO}_3)_3$

### Oxidation-Reduction (SECTION 14-1)

**14-9.** Which of the following reactions are oxidation-reduction reactions?

- (a)  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$   
 (b)  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$   
 (c)  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$   
 (d)  $2\text{HNO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$   
 (e)  $\text{AgNO}_3 + \text{KCl} \rightarrow \text{AgCl} + \text{KNO}_3$   
 (f)  $\text{Zn} + \text{CuCl}_2 \rightarrow \text{ZnCl}_2 + \text{Cu}$

**14-10.** Identify each of the following half-reactions as either oxidation or reduction.

- (a)  $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$   
 (b)  $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$   
 (c)  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$   
 (d)  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$   
 (e)  $\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$

**14-11.** Identify each of the following changes as either oxidation or reduction.

- (a)  $\text{P}_4 \rightarrow \text{H}_3\text{PO}_4$  (d)  $\text{Al} \rightarrow \text{Al}(\text{OH})_4^-$   
 (b)  $\text{NO}_3^- \rightarrow \text{NH}_4^+$  (e)  $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$   
 (c)  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}^{2+}$

**14-12.** For each of the following unbalanced equations, complete the table below.

- (a)  $\text{MnO}_2 + \text{H}^+ + \text{Br}^- \rightarrow \text{Mn}^{2+} + \text{Br}_2 + \text{H}_2\text{O}$   
 (b)  $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$   
 (c)  $\text{Fe}^{2+} + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+} + \text{H}_2\text{O}$

| Reaction | Reactant Oxidized* | Product of Oxidation | Reactant Reduced | Product of Reduction | Oxidizing Agent | Reducing Agent |
|----------|--------------------|----------------------|------------------|----------------------|-----------------|----------------|
| (a)      |                    |                      |                  |                      |                 |                |
| (b)      |                    |                      |                  |                      |                 |                |
| (c)      |                    |                      |                  |                      |                 |                |

\*Element, molecule, or ion.

**14-13.** For the following two unbalanced equations, construct a table like that in Problem 14-12.

- (a)  $\text{Al} + \text{H}_2\text{O} \rightarrow \text{AlO}_2^- + \text{H}_2 + \text{H}^+$   
 (b)  $\text{Mn}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \rightarrow \text{MnO}_4^- + \text{Cr}^{3+} + \text{H}_2\text{O}$

**14-14.** For the following equations, identify the reactant oxidized, the reactant reduced, the oxidizing agent, and the reducing agent.

- (a)  $\text{Sn} + \text{HNO}_3 \rightarrow \text{SnO}_2 + \text{NO}_2 + \text{H}_2\text{O}$   
 (b)  $\text{IO}_3^- + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{I}_2 + \text{SO}_4^{2-} + \text{H}^+$   
 (c)  $\text{CrI}_3 + \text{OH}^- + \text{Cl}_2 \rightarrow \text{CrO}_4^{2-} + \text{IO}_4^- + \text{Cl}^- + \text{H}_2\text{O}$   
 (d)  $\text{I}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + \text{H}_2\text{O} + \text{OH}^-$

**14-15.** Identify the product or products containing the elements oxidized and reduced in problem 14-14.

### Balancing Equations by the Bridge Method (SECTION 14-2)

**14-16.** Balance each of the following equations by the oxidation state method.

- (a)  $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$   
 (b)  $\text{Sn} + \text{HNO}_3 \rightarrow \text{SnO}_2 + \text{NO}_2 + \text{H}_2\text{O}$   
 (c)  $\text{Cr}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{KNO}_3 \rightarrow \text{CO}_2 + \text{Na}_2\text{CrO}_4 + \text{KNO}_2$   
 (d)  $\text{Se} + \text{BrO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SeO}_3 + \text{Br}^-$

**14-17.** Balance the following equations by the oxidation state method.

- (a)  $\text{I}_2\text{O}_5 + \text{CO} \rightarrow \text{I}_2 + \text{CO}_2$   
 (b)  $\text{Al} + \text{H}_2\text{O} \rightarrow \text{AlO}_2^- + \text{H}_2 + \text{H}^+$   
 (c)  $\text{HNO}_3 + \text{HCl} \rightarrow \text{NO} + \text{Cl}_2 + \text{H}_2\text{O}$   
 (d)  $\text{I}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HIO}_3 + \text{HCl}$

### Balancing Equations by the Ion-Electron Method (SECTION 14-3)

**14-18.** Balance the following half-reactions in acidic solution.

- (a)  $\text{Sn}^{2+} \rightarrow \text{SnO}_2$  (d)  $\text{I}_2 \rightarrow \text{IO}_3^-$   
 (b)  $\text{CH}_4 \rightarrow \text{CO}_2$  (e)  $\text{NO}_3^- \rightarrow \text{NO}_2$   
 (c)  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$

**14-19.** Balance the following half-reactions in acidic solution.

- (a)  $\text{P}_4 \rightarrow \text{H}_3\text{PO}_4$  (d)  $\text{NO}_3^- \rightarrow \text{NH}_4^+$   
 (b)  $\text{ClO}_3^- \rightarrow \text{Cl}^-$  (e)  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$   
 (c)  $\text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-}$

**14-20.** Balance each of the following by the ion-electron method. All are in acidic solution.

- (a)  $\text{S}^{2-} + \text{NO}_3^- + \text{H}^+ \rightarrow \text{S} + \text{NO} + \text{H}_2\text{O}$   
 (b)  $\text{I}_2 + \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$   
 (c)  $\text{SO}_3^{2-} + \text{ClO}_3^- \rightarrow \text{Cl}^- + \text{SO}_4^{2-}$   
 (d)  $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$   
 (e)  $\text{AsO}_4^{3-} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{AsO}_3^{3-} + \text{H}_2\text{O}$   
 (f)  $\text{Zn} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{NH}_4^+ + \text{H}_2\text{O}$

**14-21.** Balance each of the following by the ion-electron method. All are in acidic solution.

- (a)  $\text{Mn}^{2+} + \text{BiO}_3^- + \text{H}^+ \rightarrow \text{MnO}_4^- + \text{Bi}^{3+} + \text{H}_2\text{O}$   
 (b)  $\text{IO}_3^- + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{I}_2 + \text{SO}_4^{2-} + \text{H}^+$   
 (c)  $\text{Se} + \text{BrO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SeO}_3 + \text{Br}^-$   
 (d)  $\text{P}_4 + \text{HClO} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + \text{Cl}^- + \text{H}^+$   
 (e)  $\text{Al} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \rightarrow \text{Al}^{3+} + \text{Cr}^{3+} + \text{H}_2\text{O}$   
 (f)  $\text{ClO}_3^- + \text{I}^- + \text{H}^+ \rightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}$   
 (g)  $\text{As}_2\text{O}_3 + \text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{AsO}_4^{3-} + \text{NO} + \text{H}^+$

**14-22.** Balance the following half-reactions in basic solution.

- (a)  $\text{SnO}_2^{2-} \rightarrow \text{SnO}_3^{2-}$  (c)  $\text{Si} \rightarrow \text{SiO}_3^{2-}$   
 (b)  $\text{ClO}_2^- \rightarrow \text{Cl}_2$  (d)  $\text{NO}_3^- \rightarrow \text{NH}_3$

**14-23.** Balance the following half-reactions in basic solution.

- (a)  $\text{Al} \rightarrow \text{Al}(\text{OH})_4^-$  (c)  $\text{N}_2\text{H}_4 \rightarrow \text{NO}_3^-$   
 (b)  $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$

**14-24.** Balance each of the following by the ion-electron method. All are in basic solution.

- (a)  $\text{S}^{2-} + \text{OH}^- + \text{I}_2 \rightarrow \text{SO}_4^{2-} + \text{I}^- + \text{H}_2\text{O}$   
 (b)  $\text{MnO}_4^- + \text{OH}^- + \text{I}^- \rightarrow \text{MnO}_4^{2-} + \text{IO}_4^- + \text{H}_2\text{O}$   
 (c)  $\text{BiO}_3^- + \text{SnO}_2^{2-} + \text{H}_2\text{O} \rightarrow \text{SnO}_3^{2-} + \text{OH}^- + \text{Bi}(\text{OH})_3$   
 (d)  $\text{CrI}_3 + \text{OH}^- + \text{Cl}_2 \rightarrow \text{CrO}_4^{2-} + \text{IO}_4^- + \text{Cl}^- + \text{H}_2\text{O}$   
 [Hint: In (d), two ions are oxidized; include both in one half-reaction.]

**14-25.** Balance each of the following by the ion-electron method. All are in basic solution.

- (a)  $\text{ClO}_2 + \text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$   
 (b)  $\text{OH}^- + \text{Cr}_2\text{O}_3 + \text{NO}_3^- \rightarrow \text{CrO}_4^{2-} + \text{NO}_2^- + \text{H}_2\text{O}$   
 (c)  $\text{Cr}(\text{OH})_4^- + \text{BrO}^- + \text{OH}^- \rightarrow \text{Br}^- + \text{CrO}_4^{2-} + \text{H}_2\text{O}$   
 (d)  $\text{Mn}^{2+} + \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{MnO}_2$   
 (e)  $\text{Ag}_2\text{O} + \text{Zn} + \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + \text{Ag}$

**14-26.** Balance the following two equations by the ion-electron method, first in acidic solution and then in basic solution.



### Predicting Redox Reactions (SECTION 14-4)

**14-27.** Using Table 14-1, predict whether the following reactions occur in aqueous solution. If not, write N.R. (no reaction).

- (a)  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{NaOH}$   
 (b)  $\text{Pb} + \text{Zn}^{2+} \rightarrow \text{Pb}^{2+} + \text{Zn}$   
 (c)  $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$   
 (d)  $\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2$   
 (e)  $\text{Cu} + 2\text{Ag}^+ \rightarrow 2\text{Ag} + \text{Cu}^{2+}$   
 (f)  $2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Cl}^- + \text{O}_2 + 4\text{H}^+$   
 (g)  $3\text{Zn}^{2+} + 2\text{Cr} \rightarrow 2\text{Cr}^{3+} + 3\text{Zn}$

**14-28.** Using Table 14-1, predict whether the following reactions occur in aqueous solution. If not, write N.R.

- (a)  $\text{Sn}^{2+} + \text{Pb} \rightarrow \text{Pb}^{2+} + \text{Sn}$   
 (b)  $\text{Ni}^{2+} + \text{H}_2 \rightarrow 2\text{H}^+ + \text{Ni}$   
 (c)  $\text{Cu} + \text{F}_2 \rightarrow \text{CuF}_2$   
 (d)  $\text{Ni}^{2+} + 2\text{Br}^- \rightarrow \text{Ni} + \text{Br}_2$   
 (e)  $3\text{Ni}^{2+} + 2\text{Cr} \rightarrow 2\text{Cr}^{3+} + 3\text{Ni}$   
 (f)  $2\text{Br}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Br}^- + \text{O}_2 + 4\text{H}^+$

**14-29.** If a reaction occurs, write the balanced molecular equation.

- (a) Nickel metal is placed in water.  
 (b) Bromine is dissolved in water that is in contact with tin metal.  
 (c) Silver metal is placed in an  $\text{HClO}_4$  solution.  
 (d) Oxygen gas is bubbled into an  $\text{HBr}$  solution.  
 (e) Liquid bromine is placed on a sheet of aluminum.

**14-30.** If a reaction occurs, write the balanced molecular equation.

- (a) Bromine is added to an  $\text{HCl}$  solution.  
 (b) Sodium metal is heated with solid aluminum chloride.  
 (c) Iron is placed in a  $\text{Pb}(\text{ClO}_4)_2$  solution.  
 (d) Oxygen gas is bubbled into an  $\text{HCl}$  solution.  
 (e) Fluorine gas is added to water.

**14-31.** Which of the following elements react with water:

- (a) Pb, (b) Ag, (c)  $\text{F}_2$ , (d)  $\text{Br}_2$ , (e) Mg? Write the balanced equation for any reaction that occurs.

**14-32.** Which of the following species will be reduced by hydrogen gas in aqueous solution: (a)  $\text{Br}_2$ , (b) Cr, (c)  $\text{Ag}^+$ , (d)  $\text{Ni}^{2+}$ ? Write the balanced equation for any reaction that occurs.

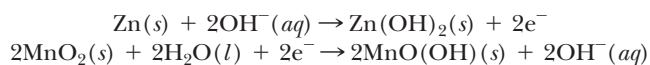
**14-33.** In Chapter 13, we mentioned the corrosiveness of acid rain. Why does rain containing a higher  $\text{H}^+$  (*aq*) concentration cause more damage to iron exposed in bridges and buildings than pure  $\text{H}_2\text{O}$ ? Write the reaction between Fe and  $\text{H}^+$  (*aq*).

**14-34.**  $\text{Br}_2$  can be prepared from the reaction of  $\text{Cl}_2$  with  $\text{NaBr}$  dissolved in seawater. Explain. Write the reaction. Can  $\text{Cl}_2$  be used to prepare  $\text{F}_2$  from  $\text{NaF}$  solutions?

### Voltaic Cells (SECTION 14-5)

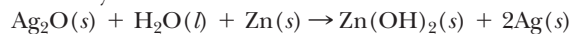
**14-35.** What is the function of the salt bridge in the voltaic cell?

**14-36.** In an alkaline battery, the following two half-reactions occur.



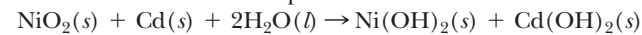
Which reaction takes place at the anode and which at the cathode? What is the total reaction?

**14-37.** The following overall reaction takes place in a silver oxide battery.



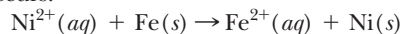
The reaction takes place in basic solution. Write the half-reaction that takes place at the anode and the half-reaction that takes place at the cathode.

**14-38.** The nickel–cadmium (nicad) battery is used as a replacement for a dry cell because it is rechargeable. The overall reaction that takes place is



Write the half-reactions that take place at the anode and the cathode.

**14-39** Sketch a galvanic cell in which the following overall reaction occurs.



(a) What reactions take place at the anode and the cathode?

(b) In what direction do the electrons flow in the wire?

(c) In what direction do the anions flow in the salt bridge?

**14-40.** Describe how a voltaic cell could be constructed from a strip of iron, a strip of lead, an  $\text{Fe}(\text{NO}_3)_2$  solution, and a  $\text{Pb}(\text{NO}_3)_2$  solution. Write the anode reaction, the cathode reaction, and the total reaction.

**14-41.** Judging from the relative difference in the strengths of the oxidizing agents ( $\text{Fe}^{2+}$  vs.  $\text{Pb}^{2+}$ ) and ( $\text{Zn}^{2+}$  vs.  $\text{Cu}^{2+}$ ), which do you think would be the more powerful cell, the one in problem 14-40 or the Daniell cell? Why?

**\*14-42.** The power of a cell depends on the strength of both the oxidizing and the reducing agents. Write the equation illustrating the most powerful redox reaction possible between an oxidizing agent and a reducing agent *in aqueous solution*. Consider only the species shown in Table 14-1.

### Electrolytic Cells (SECTION 14-6)

**14-43.** Chrome plating is an electrolytic process. Write the reaction that occurs when an iron bumper is electroplated using a  $\text{CrCl}_3$  solution. Are there any metals shown in Table 14-1 on which a chromium layer would spontaneously form?

**14-44.** Why can't elemental sodium be formed in the electrolysis of an aqueous  $\text{NaCl}$  solution? Write the reaction that does occur at the cathode. How is elemental sodium produced by electrolysis?

**14-45.** Why can't elemental fluorine be formed by electrolysis of an aqueous  $\text{NaF}$  solution? Write the reaction that does occur at the anode. How is elemental fluorine produced?

**14-46.** A "tin can" is made by forming a layer of tin on a sheet of iron. Is electrolysis necessary for such a process or does it occur spontaneously? Write the equation for this reaction. Is electrolysis necessary to form a layer of tin on a sheet of lead? Write the relevant equation.

**14-47.** Certain metals can be purified by electrolysis. For example, a mixture of Ag, Zn, and Fe can be dissolved so that their metal ions are present in aqueous solution. If a solution containing these ions is electrolyzed, which metal ion would be reduced to the metal first?



## General Problems

**14-48.** Nitrogen exists in nine oxidation states. Arrange the following compounds in order of increasing oxidation state of N:  $K_3N$ ,  $N_2O_4$ ,  $N_2$ ,  $NH_2OH$ ,  $N_2O$ ,  $Ca(NO_3)_2$ ,  $N_2H_4$ ,  $N_2O_3$ ,  $NO$ .

**14-49.** Given the following information concerning metal strips immersed in certain solutions, write the net ionic equations representing the reactions that occur.

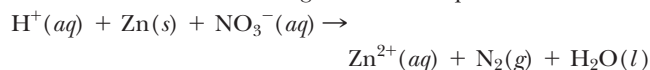
| Metal Strip | Solution | Reaction          |
|-------------|----------|-------------------|
| Cd          | $NiCl_2$ | Ni coating formed |
| Cd          | $FeCl_2$ | no reaction       |
| Zn          | $CdCl_2$ | Cd coating formed |
| Fe          | $CdCl_2$ | no reaction       |

Where does  $Cd^{2+}$  rank as an oxidizing agent in Table 14-1?

**14-50.** A hypothetical metal (M) forms a coating of Sn when placed in an  $SnCl_2$  solution. However, when a strip of Ni is placed in an  $MCl_2$  solution, a coating of the metal M forms on the nickel. Write the net ionic equations representing the reactions that occur. Where does  $M^{2+}$  rank as an oxidizing agent in Table 14-1?

**14-51.** A solution of gold ions ( $Au^{3+}$ ) reacts spontaneously with water to form metallic gold. Metallic gold does not react with chlorine but does react with fluorine. Write the equations representing the two spontaneous reactions, and locate  $Au^{3+}$  in Table 14-1 as an oxidizing agent.

**14-52.** Given the following unbalanced equation



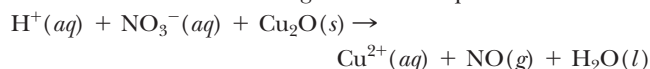
what mass of Zn is required to produce 0.658 g of  $N_2$ ?

**14-53.** Given the following unbalanced equation



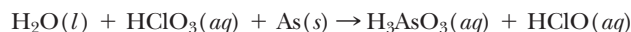
what mass of  $MnO_2$  reacts with 228 mL of 0.560 M HBr?

**14-54.** Given the following unbalanced equation



what volume of NO gas measured at STP is produced by the complete reaction of 10.0 g of  $Cu_2O$ ?

**\*14-55.** Given the following unbalanced equation in acid solution



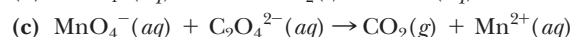
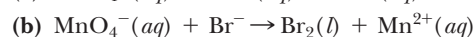
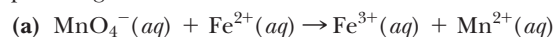
If 200 g of As reacts with 200 g of  $HClO_3$ , what mass of  $H_3AsO_3$  is produced? (*Hint:* Calculate the limiting reactant.)

**\*14-56.** Given the following unbalanced equation in basic solution



what volume of  $NH_3$  is produced by 6.54 g of Zn? The  $NH_3$  is measured at 27.0°C and 1.25 atm pressure.

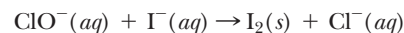
**14-57.** Solutions of potassium permanganate are a deep-purple color. Permanganate is a strong oxidizing agent that forms the  $Mn^{2+}$  ion in acid solution when it is reduced. When these purple solutions are added to a reducing agent, the purple color disappears until all of the reducing agent reacts. So we have a very convenient way to know when the reducing agent is used up—the solution suddenly turns purple. Balance the following net ionic reactions involving permanganate in acidic solution.



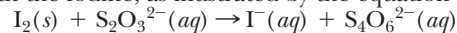
**14-58.** Using the balanced equation from problem 14-57, determine the volume (in mL) of 0.220 M  $KMnO_4$  needed to completely react with 25.0 g of  $FeCl_2$  dissolved in water.

**14-59.** Using the balanced equation from problem 14-57, determine the volume (in mL) of 0.450 M KBr needed to completely react with 125 mL of 0.220 M  $KMnO_4$ .

**14-60.** The active ingredient in household bleach is sodium hypochlorite, which is a strong oxidizing agent. We can tell how much of the active ingredient is present in a two-step analysis. First the hypochlorite oxidizes excess iodide to elemental iodine according to the unbalanced equation that occurs in basic solution.



Next, a solution of sodium thiosulfate ( $Na_2S_2O_3$ ) is added to react with the iodine, as illustrated by the equation



Balance the two equations.

**\*14-61.** Household bleach is 5.00% by weight sodium hypochlorite. Using the balanced equations from problem 14-60, determine the volume (in mL) of 0.358 M  $Na_2S_2O_3$  solution needed to react with all the sodium hypochlorite in 100 mL of household bleach. Consider the density of bleach to be the same as water.

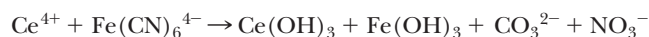
## STUDENT WORKSHOP

### Balancing Redox Reactions

**Purpose:** To practice balancing a complex redox reaction by the ion-electric method. (Work in groups of three or four. Estimated time: 10 min.)


This is a challenging problem about balancing redox reactions; it is best done as a group effort to make sure that no

atoms or charges are missed. Balance the following reaction in a basic solution, using the ion-electron method:



Once completed, do an atom and charge inventory to confirm that it is balanced. Then identify the oxidizing and reducing agents for the reaction.





CHAPTER  
15

# Reaction Rates and Equilibrium



**B**ecause water enters this small pond at the same rate that it leaves, the level of the pond stays the same. This is similar to the equilibrium that occurs in certain chemical reactions.

**PART A**  
**COLLISIONS OF MOLECULES  
AND REACTIONS  
AT EQUILIBRIUM**

**15-1** How Reactions Take Place

**15-2** Rates of Chemical Reactions

**15-3** Equilibrium and Le Châtelier's  
Principle



**MAKING IT REAL**

*The Lake That Exploded*

**PART B**  
**THE QUANTITATIVE ASPECTS  
OF REACTIONS AT  
EQUILIBRIUM**

**15-4** The Equilibrium Constant

**15-5** Equilibria of Weak Acids and  
Weak Bases in Water



**MAKING IT REAL**

*Buffers and Swimming Pool Chemistry*

**15-6** Solubility Equilibria

**SETTING THE STAGE** Many of us have probably neglected to put some food back into the refrigerator because it was hidden behind something or other. Unfortunately, in a matter of a day or two, mold or some bad-smelling, green life-form starts to grow on the food. This should lead to its quick disposal. In fact, the decay and formation of mold that we are witnessing on natural food products are chemical reactions that occur rapidly at room temperature. Had we remembered to put the food item in the refrigerator, however, these nasty chemical reactions could have been stopped or at least delayed for weeks. Decay, growth of mold or other unwanted life-forms, and, in fact, all chemical reactions slow down as the temperature is lowered. An understanding of how chemical reactions occur, as we will discuss in this chapter, can help us understand why temperature affects the rate of a reaction.

Some of the chemical reactions that are discussed in this chapter reach a point of “balance” between reactants and products. This is like the balance that many of us strive for between school or job and the need to relax and have fun. Or perhaps we seek the balance of having money come in at least as fast as it goes out. In a chemical sense, balance means an equilibrium between two competing reactions, one forming products and the other, in the reverse direction, re-forming the original reactants.

In Part A in this chapter, we will examine the path of chemical reactions from reactants to products and then discuss reversible reactions that reach a point of equilibrium. In Part B, we will emphasize the quantitative calculations associated with the distribution between reactants and products in reactions that reach a point of equilibrium.

**PART A**  
**COLLISIONS OF MOLECULES**  
**AND REACTIONS**  
**AT EQUILIBRIUM**

**SETTING A GOAL**

- You will learn how chemical reactions occur as well as the factors that affect how fast reactions occur and how much product they produce.

**OBJECTIVES**

- 15-1 (a)** Describe on a molecular level how a chemical reaction takes place. **(b)** Create an energy diagram for an exothermic or endothermic reaction.
- 15-2** List the factors that affect the rate of a chemical reaction.
- 15-3 (a)** Describe systems that reach a point of equilibrium. **(b)** Using Le Châtelier's principle, list the conditions that can affect the point of equilibrium.

▶ **OBJECTIVES FOR SECTION 15-1**

- (a)** Describe on a molecular level how a chemical reaction takes place. **(b)** Create an energy diagram for an exothermic or endothermic reaction.

## 15-1 HOW REACTIONS TAKE PLACE

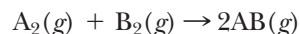


**LOOKING AHEAD!** Chemical reactions don't just happen. Somehow, reactant molecules or ions must find a way to come together so that the atoms can be reshuffled into product molecules or ions. The concept of how this happens is surprisingly straightforward and is the topic of this section. ■

### 15-1.1 Collision Theory

Taking a trip from Los Angeles to Chicago always raises a question. How are you going to get there? One could drive, fly, or take a train. In any case, we can't get from point A to point B without some means of transportation. Likewise, chemical reactions must have some way for reactant molecules to be transformed into product molecules. The chemist's view of how chemical reactions occur is actually quite simple. Since molecules have kinetic energy, they are all in constant motion in one way or another. In the gaseous and liquid states, this motion leads to frequent collisions between molecules. These collisions may lead to chemical changes. *The assumption that chemical reactions are due to the collisions of molecules is known as collision theory.* In some collisions chemical bonds are broken in the colliding molecules. If the molecular or atomic fragments created from the collision re-form in a different arrangement, a chemical reaction results. We will illustrate collision theory by means of a hypothetical chemical reaction that can be custom-designed to clearly illustrate the basic principles involved. Real-life reactions are generally more complicated, and explanations are required for each complication or exception, so we will keep it simple.

Our reaction involves the combination of two hypothetical diatomic gaseous elements,  $A_2$  and  $B_2$ , to form two molecules of a gaseous product,  $AB$ . The reaction is illustrated by the equation



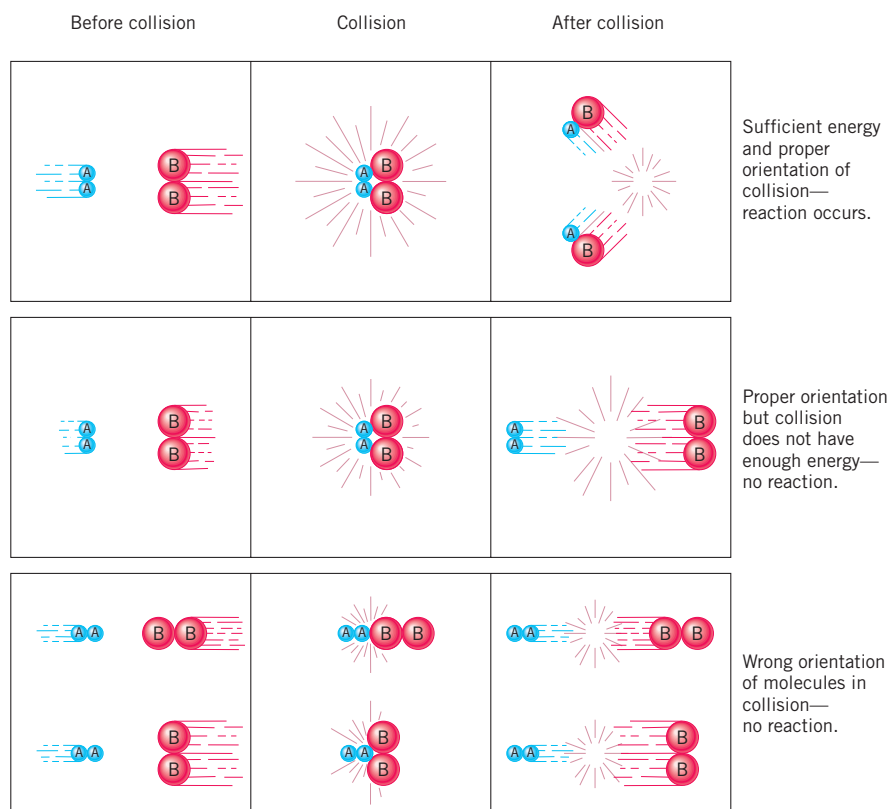
A reasonable assumption here is that the products form from the collision of an  $A_2$  molecule with a  $B_2$  molecule. If all collisions led to products, however, this and all other reactions would be essentially instantaneous because of the large number of collisions per second. However, two conditions are necessary for a collision to lead to the formation of products. First, *the collision between two reactant molecules must take place in the right geometric orientation.* As illustrated in Figure 15-1, for new bonds to form, the two reactant molecules must meet in a side-to-side manner rather than end to end or side to end. This condition, by itself, severely limits the number of collisions that can lead to a reaction. A second condition is that *the collision must occur with enough energy*

to break the bonds in the reactants so that new bonds can form in the products. The second condition even more severely limits the number of collisions that lead to product formation. If the two conditions are not met, the colliding molecules simply recoil from each other unchanged. (See Figure 15-1.)

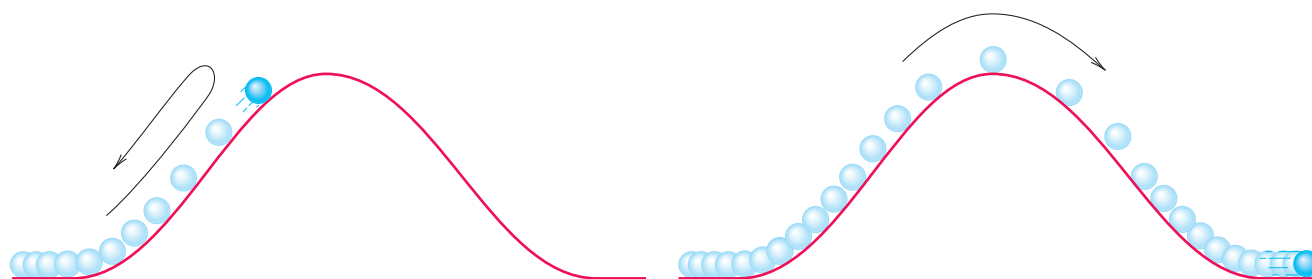
### 15-1.2 Activation Energy

Imagine that you are trying to roll a bowling ball over a small incline. When you swing the ball behind you and then release it, you are imparting motion (kinetic energy) to the ball. As it starts up the hill, however, it begins to slow. It slows because the kinetic energy is being converted into potential energy as a result of the increased elevation of the ball. If you swing the ball hard enough, it may have enough kinetic energy to overcome the potential energy barrier of the hill. In that case, it will make it to the top of the hill and go down the other side. If not, the ball will stop before reaching the top when all the kinetic energy has been converted into potential energy; the ball will then roll back at you as the potential energy converts back to the kinetic energy. (See Figure 15-2.)

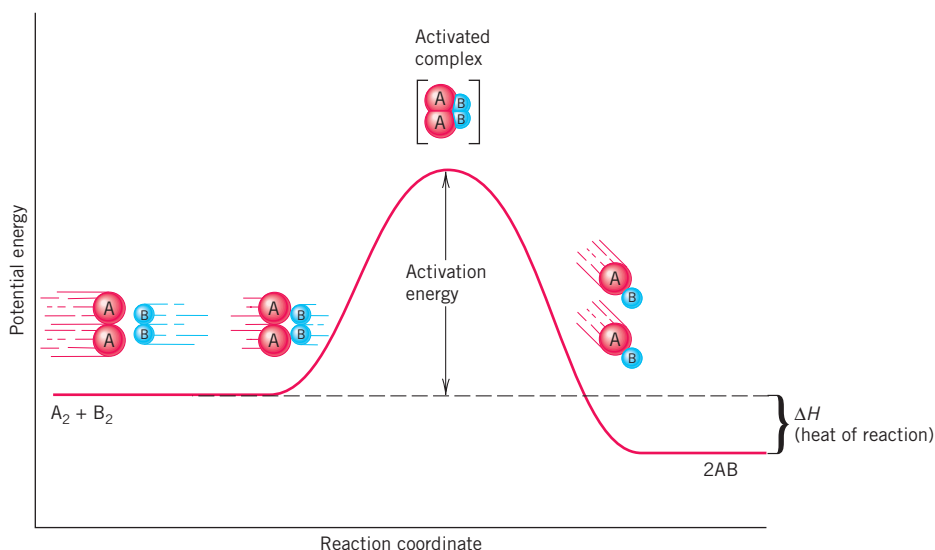
Chemical reactions also have an energy barrier. *The minimum kinetic energy needed for the reaction to occur is known as the activation energy.* If properly colliding molecules have kinetic energy equal to or greater than the activation energy (which represents the potential energy barrier), a reaction occurs; if not, they recoil unchanged. To illustrate, we will follow the fate of the two hypothetical diatomic elements  $A_2$  and  $B_2$  as they move from being far apart, to colliding with each other in a proper orientation that has enough energy for the reaction, and finally to forming products. Recall that energy is conserved, meaning that the sum of the kinetic energy and potential energy of the molecules remains the same as they collide. In Figure 15-3, we attempt to illustrate the progress of the reaction as the molecules collide. The curve represents the potential energy (on the vertical axis) of the species involved in the reaction. Notice that the separate molecules have a certain amount of potential energy before they collide. This energy is present in their chemical bonds. By moving to the right along the horizontal axis, we can follow the change in the potential energy of the reactant



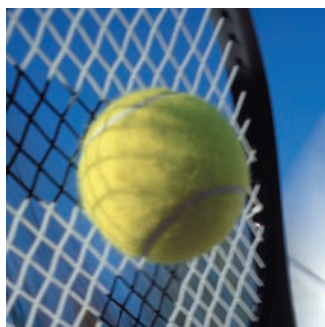
**FIGURE 15-1** Reaction of  $A_2$  and  $B_2$  Reactions occur only when colliding molecules have the minimum amount of energy and the right orientation.



**FIGURE 15-2** The Potential Energy Barrier On the left, the ball does not have enough kinetic energy to overcome the barrier. On the right, the ball has enough kinetic energy to make it over.



**FIGURE 15-3 Activation Energy** The activation energy is the potential energy difference between the activated complex and the reactants.



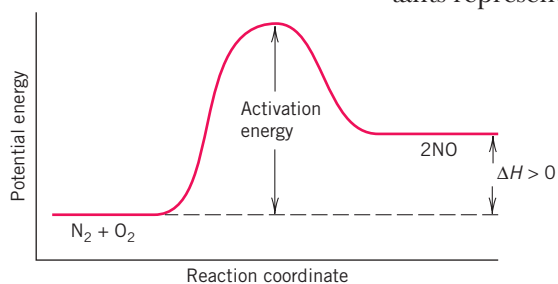
At the instant the tennis ball is not moving, all the energy is in the form of potential energy.

the motion stops for an instant and the potential energy is at a maximum. This is analogous to hitting a tennis ball with a racquet. As the ball makes contact with the racquet, it slows down and compresses. For just an instant, the ball has no motion but has maximum potential energy from compression. As the ball recoils, the potential energy of the ball reconverts to kinetic energy of motion and the ball speeds away. Likewise, *at maximum impact, both molecules are compressed together, forming what is known as an activated complex.* Since we are assuming a reaction takes place, the activated complex represents the state that is intermediate between reactants and products. That is, old bonds are partially broken and new ones are partially formed. The activation energy for the forward reaction is represented by the difference in potential energy of the activated complex (at the peak of the curve) and the reactants. As product molecules recoil, potential energy decreases as it is converted into the kinetic energy of the recoiling molecules. Notice in Figure 15-3 that the product molecules (AB) in this example end up with lower potential energy than the original reactants. This would be the result of some of the potential energy in the original chemical bonds (i.e., in  $A_2$  and  $B_2$ ) being released as kinetic energy to the product molecules. Since the product molecules have more kinetic energy than the original reactants, the product molecules move faster and are “hotter.”

molecules as they approach each other, collide, and eventually form products. This horizontal axis is referred to as the *reaction coordinate* (also called the *path of the reaction*) and can be viewed as a time axis. The potential energy of the molecules does not change until they make contact and begin to compress together. As they collide, the molecules lose velocity, which means they lose kinetic energy. This kinetic energy changes to potential energy as the molecules compress, so the potential energy of the compressing molecules rises as shown by the ascending curve. At maximum impact,

### 15-1.3 The Heat of the Reaction

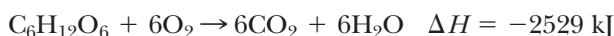
The difference between the potential energy of the products and that of the reactants represents the *heat of the reaction*, or *enthalpy*, and is given the symbol  $\Delta H$ . *In an exothermic process, the potential energy of the products is lower than the potential energy of the reactants, the difference being the heat that is released.* An analogy to an exothermic reaction is also found in the game of tennis. The ball should recoil at a faster rate from the racquet than when it first made contact. The player tries to give the ball some “heat.”



**FIGURE 15-4 An Endothermic Reaction** In an endothermic reaction, the potential energy of the reactants is less than that of the products.

When the potential energy of the products is higher than that of the reactants, the reaction is endothermic and the product molecules are “cooler.” Heat is required for the reaction to occur and is extracted from the environment. An actual endothermic reaction between  $N_2$  and  $O_2$  to form  $NO$  is represented in Figure 15-4.

Most spontaneous reactions are exothermic. For example, blood sugar or glucose ( $C_6H_{12}O_6$ ) undergoes combustion in the body as shown by the following equation.





The sum of all of the bond energies in the glucose and molecular oxygen reactants is less than the sum of the bond energies in the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  products. In other words, the bonds in the products are stronger (in total) than in the reactants. The difference in the total bond energies of reactants and products is the source of the enthalpy ( $\Delta H$ ) of the reaction. In the process of photosynthesis, chlorophyll from plants converts this same amount of light energy from the sun,  $\text{CO}_2$  from the air, and  $\text{H}_2\text{O}$  from the rain back into glucose or other carbohydrates. The reaction also recycles oxygen back into the air.

**ASSESSING THE OBJECTIVES FOR SECTION 15-1**

**EXERCISE 15-1(a) KNOWLEDGE:** Fill in the blanks.

Chemical reactions occur because of \_\_\_\_\_ between reactant molecules. In order for a reaction to take place, molecules must \_\_\_\_\_ in the proper orientation and with a \_\_\_\_\_ amount of energy, known as the \_\_\_\_\_ energy. An \_\_\_\_\_ forms at the point of maximum potential energy.

**EXERCISE 15-1(b) ANALYSIS:** In the reaction between  $\text{SO}_3$  and  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$ , the product molecule has less potential energy than the reactant molecules. Draw the energy diagram for this reaction.

**EXERCISE 15-1(c) SYNTHESIS:**  $\text{SO}_3$  molecules collide with  $\text{H}_2\text{O}$  molecules to produce an activated complex that eventually leads to sulfuric acid. Show what the activated complex would most likely look like. What rearrangements must the activated complex undergo to form the final product molecule?

*For additional practice, work chapter problems 15-1 and 15-2.*

## 15-2 RATES OF CHEMICAL REACTIONS

**OBJECTIVE FOR SECTION 15-2**

List the factors that affect the rate of a chemical reaction.



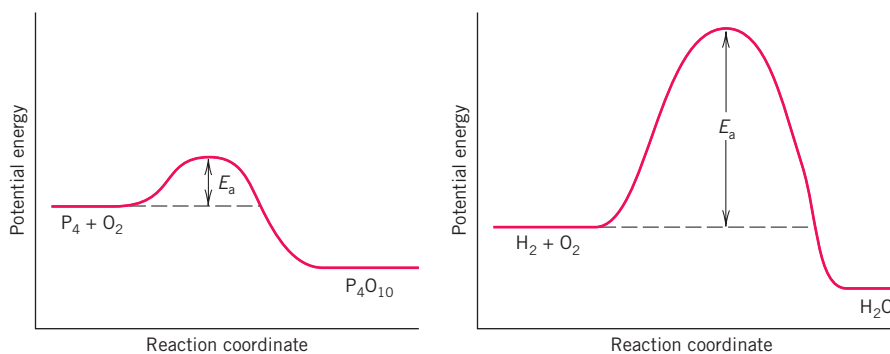
**LOOKING AHEAD!** Some reactions are essentially instantaneous, such as in an explosion, whereas others may take months, such as the rusting of a nail. Why the big range? We are now ready to examine the factors that affect the rate of a reaction. ■

One important question to be answered in deciding how one gets from Los Angeles to Chicago involves how fast you want to get there. If you fly, you may average 500 mi/hr, but if you drive you may average only 50 mi/hr. We measure the rate of travel by distance per unit of time, which in this case is hours. Chemical reactions also take place at specific rates. As any chemical reaction occurs, reactants disappear and products appear. *The rate of a reaction measures the increase in concentration of a product or the decrease in concentration of a reactant per unit of time.* There are several factors that affect the rate of a reaction. These include the magnitude of the activation energy, the temperature at which the reaction takes place, the concentration of reactants, the size of the particles of solid reactants, and the presence of a catalyst. We will discuss these factors individually.

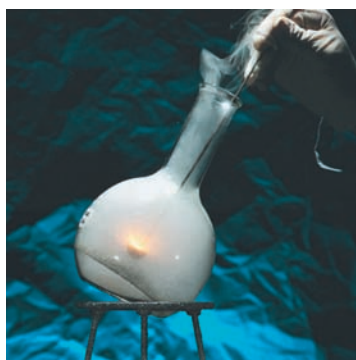
### 15-2.1 The Magnitude of the Activation Energy

Perhaps one of the most significant characteristics of any chemical reaction is its activation energy, which is determined by the nature of the reactants. Consider, for example, the reactions of two nonmetals with oxygen. An allotrope of phosphorus known as white phosphorus reacts almost instantly with the oxygen in the air, even at room

**FIGURE 15-5**  
**Combustion of  $P_4$  and  $H_2$**   $P_4$  undergoes combustion at room temperature because of its lower activation energy.



temperature, producing an extremely hot flame. As a result, this form of phosphorus must be stored under water to prevent exposure to the air. Hydrogen also reacts with oxygen to form water. This is also a highly exothermic reaction, one that is used in space rockets. A mixture of hydrogen and oxygen, however, does not react at room temperature. In fact, no appreciable reaction occurs unless the temperature is raised to at least  $400^\circ\text{C}$  or the mixture is ignited with a spark. The difference in the rates of combustion of these two elements at room temperature lies in the activation energies of the two reactions. Figure 15-5 illustrates the activation energies (labeled  $E_a$ ) for the combustion reactions of hydrogen and phosphorus. Note that the phosphorus reaction has a much lower activation energy than the hydrogen reaction. This explains why collisions between phosphorus molecules and oxygen have enough energy for reaction at room temperature, whereas collisions of the same energy between hydrogen and oxygen do not have the required energy to overcome the activation energy barrier.



White phosphorus ignites instantly in air because the reaction has a low activation energy.

## 15-2.2 The Temperature

We have to be very careful about the chicken salad on a hot summer day. Food spoilage occurs amazingly fast at a warm temperature. In fact, all chemical reactions occur faster on hot summer days. Previously, we established that the rate of a reaction depends on the kinetic energy of the reactant molecules.

$$r(\text{rate}) \propto \text{energy of colliding molecules}$$

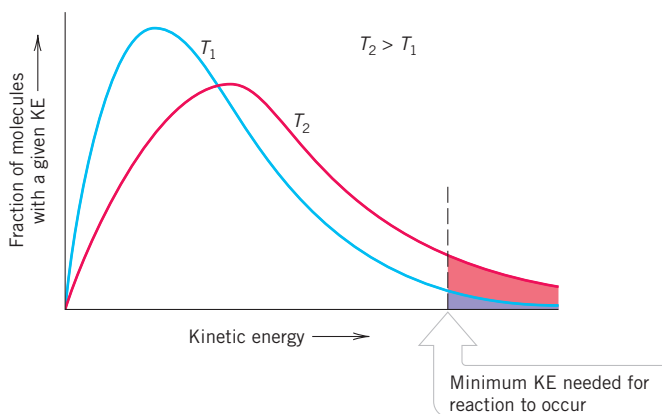
In Chapter 10 we discussed the distribution of kinetic energies of molecules at a given temperature. This is again illustrated in Figure 15-6. Notice that, since temperature is related to average kinetic energy, the higher the temperature, the higher the average kinetic energy of the molecules. In the figure, the dashed line represents the activation energy ( $E_a$ ). As mentioned, this is the minimum amount of kinetic energy that colliding molecules must have for products to form. Note that at the higher temperature ( $T_2$ ) the curve intersects the dashed line at a higher point than does  $T_1$ , meaning that a greater fraction of molecules can overcome the activation energy in a collision. As a result, the rates of chemical reactions increase as the temperature increases.

There is another reason why an increase in temperature increases the rate of a reaction. In addition to the energy of the collisions, the rate of a reaction depends on the frequency of collisions (the number of collisions per second).

$$r(\text{rate}) \propto \text{frequency of collisions}$$

Recall that the kinetic energy (K.E.) of a moving object is given by the relationship

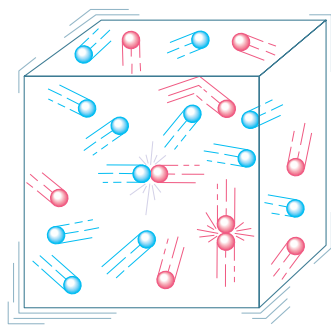
$$\text{K.E.} = \frac{1}{2}mv^2 \quad (m = \text{mass}, v = \text{velocity})$$



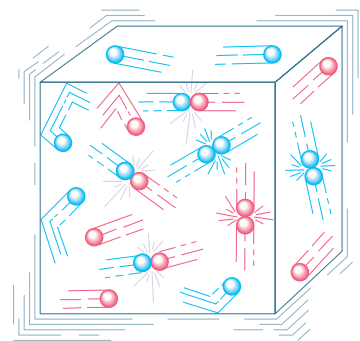
**FIGURE 15-6** Kinetic Energy Distributions for a Reaction Mixture at Two Different Temperatures The sizes of the shaded areas under the curves are proportional to the total fractions of the molecules that possess the minimum activation energy.

This indicates that the more kinetic energy a moving object has, the faster it is moving.

As the temperature increases, the average velocity of the molecules increases. This means that the frequency of collisions also increases. As an analogy, imagine a box containing red and blue Ping-Pong balls, as shown in Figure 15-7. If we jiggle the box, the balls move around and collide. If we jiggle the balls faster (analogous to a higher temperature), the balls move around faster and there are more frequent collisions. The increased noise we hear tells us that, indeed, collisions are not only more energetic but also more frequent. Most of the increase in the rate of a chemical reaction is due to the increased energy of the collisions, with a lesser contribution from the increased rate of collisions. A good rule of thumb for many typical chemical reactions is that the rate of reaction approximately doubles for each  $10^{\circ}\text{C}$  rise in temperature.



Slow jiggling (low  $T$ )



Fast jiggling (high  $T$ )

**FIGURE 15-7 Effect of Velocity on Collisions** Collisions occur more frequently and with more force as the velocity of the balls increases.

### 15-2.3 The Concentrations of Reactants

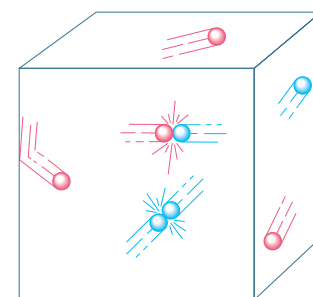
Increasing the rate at which we shake a box of Ping-Pong balls obviously increases the rate of collisions between the balls. Another way of increasing the rate of collisions is to increase the number of balls in the box. In Figure 15-8, we have two situations. In the box on top, there are four red and four blue balls. In the box at the bottom, there are four red balls, but the number of blue balls has been increased to eight. The concentration (number of balls per unit volume) has been increased. Increasing the number of balls of either color increases the number of blue—red collisions, which is signaled by the more intense noise even though the box is jiggled at the same rate (analogous to the same temperature). In the reaction of  $\text{A}_2$  and  $\text{B}_2$ , the same phenomenon applies. The greater the concentration of either or both of the reactants, the more frequent the collisions and the greater the rate of the reaction.

### 15-2.4 The Effect of Particle Size

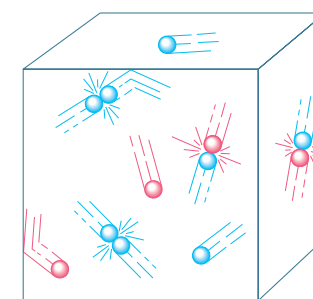
If we wish to burn an old dead tree, there is a slow way and there is a quick way. Trying to burn it as one big log could take days. If we cut the tree up into smaller logs, we could burn it in hours. In fact, if we changed the tree into a pile of sawdust and spread it around, we might burn it in a matter of minutes. Related to this is the inherent danger in the storage of grain in large silos. Normally, a pile of grain burns slowly. However, small particles of grain dust can become suspended in air, forming a dangerous mixture that can actually detonate. Such explosions have occurred. In the reaction between a solid and a gas, a solid and a liquid, or a liquid and a gas, the surface area of the solid or liquid obviously affects the rate of the reaction. The more area that is exposed, the faster the rate of the reaction.

### 15-2.5 The Presence of Catalysts

One of the principles of road building in the mountains is that if it's too difficult to go over the mountain, go through it. The mountain is like the activation energy of a reaction, and the tunnel represents a pathway or mechanism with a lower activation energy. A **catalyst** is a substance that provides an alternate mechanism with a lower activation energy. (See Figure 15-9.) As a result, a catalyst increases the rate of a reaction, but since the products are identical to the original reaction, the catalyst is not consumed in the reaction.

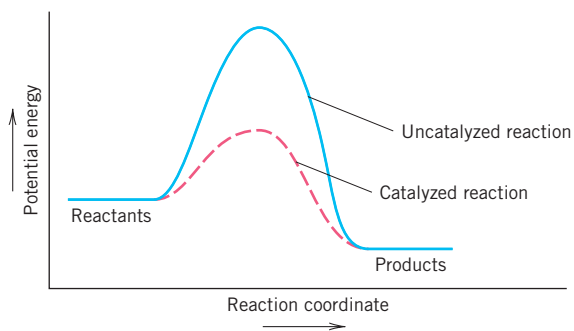


Four red and four blue balls (low concentration)



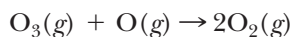
Four red and eight blue balls (high concentration)

**FIGURE 15-8 Effect of Concentration on Collisions** Collisions occur more frequently when there are more balls in the box.

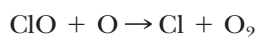
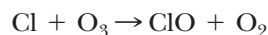


**FIGURE 15-9** Activation Energy and Catalysis A catalyst speeds a reaction by lowering the activation energy.

An environmentally important example of how catalysts work is provided by the catalytic destruction of ozone ( $\text{O}_3$ ) in the stratosphere. The following reaction is very slow in the absence of catalysts.



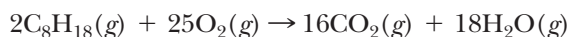
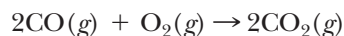
The atoms of oxygen (O) originate from the dissociation of normal oxygen molecules ( $\text{O}_2$ ) by solar radiation. Chlorofluorocarbons (e.g.,  $\text{CF}_2\text{Cl}_2$ ), used primarily as refrigerants, diffuse into the stratosphere and are also dissociated by solar radiation into Cl atoms (not  $\text{Cl}_2$  molecules). When an atom of chlorine is present, two reactions take place that lead to the rapid conversion of ozone to normal oxygen ( $\text{O}_2$ ).



There are two significant facts about these two reactions. First, the presence of chlorine atoms drastically increases the rate of conversion of ozone to oxygen. Of more importance is the fact that a chlorine atom is a reactant in the first reaction but is regenerated as a product in the second. This is how it acts as a catalyst. Because it is not consumed in the reaction, one chlorine atom can destroy thousands of ozone molecules. In fact, the series of reactions leading to the destruction of ozone in the stratosphere appears to be more complex than that shown above. Intense studies are currently under way to help us understand exactly how chlorine atoms interact with ozone. In the meantime, the use of chlorofluorocarbons has been phased out by international agreement and the situation seems to be improving.

In the reactions just described, the catalyst is intimately mixed with reactants and is actually involved in the reaction. Catalysts of this nature are referred to as *homogeneous catalysts*. In other cases, a catalyst may simply provide a surface on which reactions take place (*heterogeneous catalyst*).

Perhaps the most familiar application of heterogeneous catalysts is in the catalytic converter of an automobile. (See Figure 15-10.) The exhaust from the engine contains poisonous carbon monoxide, unburned fuel (mainly  $\text{C}_8\text{H}_{18}$ ), and nitric oxide (NO). All contribute to air pollution, which is still a serious environmental concern in many localities. The catalytic converter, which is attached to the exhaust pipe, contains finely divided platinum and/or palladium. These metals provide a surface for the following reactions, which normally occur only at a very high temperature in the absence of a catalyst.



All three reactions are exothermic, which explains why the catalytic converter becomes quite hot when the engine is running.



**FIGURE 15-10** The Catalytic Converter This device on the automobile helps to reduce air pollution.

## ASSESSING THE OBJECTIVE FOR SECTION 15-2

**EXERCISE 15-2(a) KNOWLEDGE:** Fill in the blanks.

The rate of appearance of a product as a function of \_\_\_\_\_ is a measure of the \_\_\_\_\_ of the reaction. At \_\_\_\_\_ temperatures, more molecules can overcome this energy barrier, so the rate of the reaction \_\_\_\_\_. Increasing the concentration of colliding molecules \_\_\_\_\_ the rate of the reaction. The presence of a \_\_\_\_\_ does not change the distribution of products, but it \_\_\_\_\_ the rate of the reaction.

**EXERCISE 15-2(b) SYNTHESIS:** Explain the following.

- In certain types of surgery the body is cooled, which allows more time for the procedure.
- In acetylene torches pure oxygen rather than compressed air is used to provide a hotter flame.
- Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) decomposes to water and oxygen very slowly. When solid manganese dioxide is added, however, oxygen evolves rapidly.
- People who are lactose intolerant cannot break down milk sugar (lactose). They lack the enzyme lactase.

For additional practice, work chapter problem 15-3.

## 15-3 EQUILIBRIUM AND LE CHÂTELIER'S PRINCIPLE



**LOOKING AHEAD!** Some chemical reactions or processes do not appear to go to completion. This is because these processes are reversible and reach what is called a point of equilibrium. A system at equilibrium has a remarkable ability to adapt to external changes. Equilibrium and how it is affected by conditions is the topic of this section. ■

### OBJECTIVES FOR SECTION 15-3

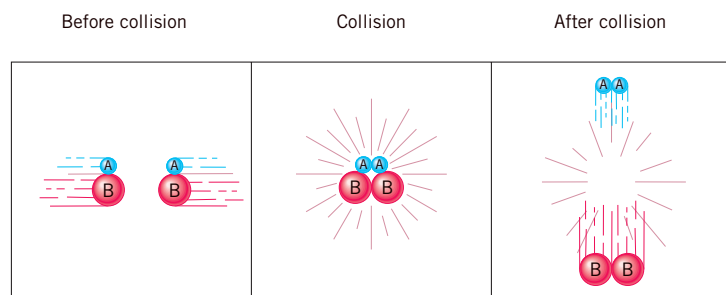
(a) Describe systems that reach a point of equilibrium. (b) Using Le Châtelier's principle, list the conditions that can affect the point of equilibrium.

### 15-3.1 Reversible Reactions

If we were sitting in a leaky boat on a large lake, we would certainly hope to maintain a point of equilibrium. That is, we would need to bail the water out of the boat as fast as it leaks in. If not, we might get very wet. Chemical reactions may also reach a point of equilibrium where product molecules are formed at the same rate as they re-form reactants. To illustrate chemical equilibrium, let's return to the hypothetical reaction discussed in Section 15-1 and illustrated in Figure 15-1. We will assume that this reaction is reversible. A **reversible reaction** is one where both a forward reaction (forming products) and a reverse reaction (re-forming reactants) can occur. Reversible reactions where both reactions occur simultaneously reach a point of equilibrium. The **point of equilibrium** in a reversible process is when both the forward and reverse processes proceed at the same rate, so the concentrations of reactants and products remain constant.

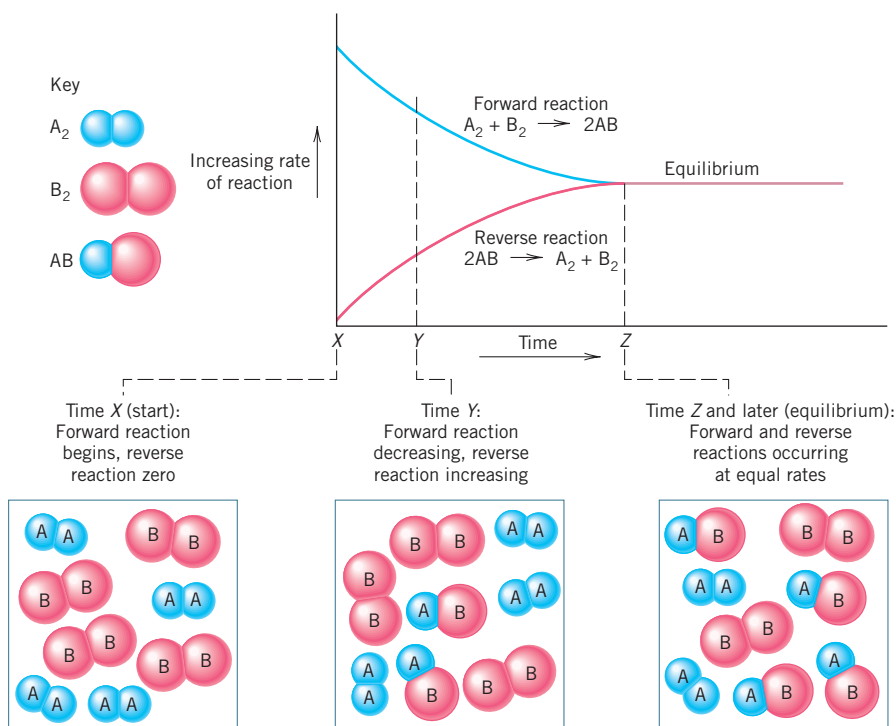
In our hypothetical reaction, the reaction mixture initially contains only  $\text{A}_2$  and  $\text{B}_2$ . As the reaction proceeds, the concentrations of these two molecules begin to decrease as the concentration of the product,  $\text{AB}$ , increases. The rate of buildup of  $\text{AB}$  begins to decrease until, eventually, the concentration of  $\text{AB}$  no longer changes despite the presence of excess reactant molecules. To understand this, we turn our attention to the product molecule  $\text{AB}$ . If we had started with pure  $\text{AB}$ , we would find that  $\text{AB}$  slowly decomposes to form  $\text{A}_2$  and  $\text{B}_2$ , just the reverse of the original reaction. This reaction occurs when two  $\text{AB}$  molecules collide with the proper orientation and sufficient energy to form  $\text{A}_2$  and  $\text{B}_2$ . (See Figure 15-11.)

Now we put these two reactions together. If we again start with pure  $\text{A}_2$  and  $\text{B}_2$ , at first only the forward reaction occurs, leading to the formation of  $\text{AB}$ . As the concentration of  $\text{AB}$  increases, however, the reverse reaction begins to occur. Eventually, the rate of formation of products (the forward reaction) is exactly offset by the rate of formation of reactants (the reverse reaction). That is, for every  $\text{A}_2$  and  $\text{B}_2$  that react to form two  $\text{AB}$ 's,



**FIGURE 15-11** Reaction of  $2\text{AB}$  Collisions between  $\text{AB}$  molecules having the minimum energy and correct orientation lead to the formation of reactants.

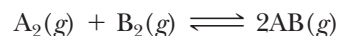




**FIGURE 15-12**  $A_2$ ,  $B_2$ ,  $AB$  Equilibrium Equilibrium is achieved when the rates of the forward and reverse reactions are equal.

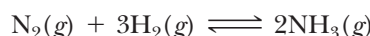
two  $AB$  molecules react to re-form one  $A_2$  and one  $B_2$ . At this point the concentrations of all species ( $A_2$ ,  $B_2$ , and  $AB$ ) remain constant. However, if we could follow the fate of one atom of  $A$ , we would find that part of the time it existed in a molecule of  $A_2$  and at other times it existed as part of the molecule  $AB$ . This phenomenon is referred to as a **dynamic equilibrium**, which emphasizes the changing identities of reactants and products despite the fact that the total amounts of each do not change. In Figure 15-12, the reaction and the point of equilibrium are graphically illustrated.

A reversible reaction that reaches a point of equilibrium is indicated by the use of double arrows instead of a single arrow, which implies a complete reaction. Thus our hypothetical reaction is represented as

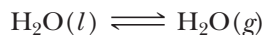


### 15-3.2 Systems at Equilibrium

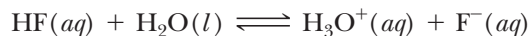
In earlier parts of this text, we have mentioned chemical and physical systems that reach a point of equilibrium. Our first mention of this phenomenon was in Chapter 5, where we discussed the formation of ammonia from its elements. This is a classic example of a system at equilibrium. Under the reaction conditions leading to the formation of ammonia, ammonia also decomposes back to its elements. This is just the reverse of the forward reaction.



We encountered a system in Chapter 11 involving equilibrium between two physical states of water. When water is placed in a closed container at a certain temperature, it establishes an equilibrium vapor pressure. At the point of equilibrium, the vapor pressure is constant, which means that the rate of condensation equals the rate of evaporation. The equation for this equilibrium is



The equilibrium reactions discussed most recently were in Chapter 13 and involved the weak acids and bases. Although the ionization of a weak acid in water is unfavorable, it does occur to a small but measurable extent. At equilibrium, most molecules are present in water in the molecular rather than the ionized state, as represented by the following equilibrium equation.



The quantitative aspects of the reactions of weak acids and bases in water are discussed later in this chapter.

### 15-3.3 Le Châtelier's Principle

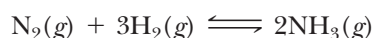
Life, at times, seems to be a continual attempt to maintain equilibrium despite all the stresses that come our way. If we spend too much money on clothes, we

have to counteract that loss by cutting back on expenses somewhere else. If we stay up too late one night (studying, naturally), we must compensate the next night by getting to bed early or, better yet, sleeping in the next morning. Chemical reactions are analogous. There are several external changes of conditions (stresses) that may affect the point of equilibrium and cause the system to compensate.

How a system at equilibrium reacts to a change in conditions is summarized by **Le Châtelier's principle**, which states: *When stress is applied to a system at equilibrium, the system reacts in such a way to counteract the stress.* The changes in a chemical system that affect the point of equilibrium include the following:

1. A change in concentration of a reactant or product
2. A change in the pressure on a gaseous system
3. A change in the temperature

We will discuss these three changes individually. To illustrate how these conditions affect the point of equilibrium, we will use the following reaction.



The synthetic conversion of elemental nitrogen to ammonia was arguably the most important discovery of the twentieth century. As mentioned previously, plants and people need nitrogen compounds, particularly as part of proteins, to sustain life. Nitrogen is plentiful in the atmosphere, but breaking the  $\text{N}_2$  bond to get nitrogen into compounds is not easy, and nature provides a very limited supply. The above reaction has a high activation energy, so it must be run at a very high temperature, (over  $1000^\circ\text{C}$ ) in order for it to occur at a reasonable rate. Unfortunately, little ammonia is produced at this high temperature, so it is not a feasible way to “fix” nitrogen without adjustments.

In 1914, a German scientist found a way to make this reaction economical. Unfortunately, the ammonia produced was first used to make explosives, which were used by Germany in World War I. Now, however, the reaction (known as the *Haber process*, after its discoverer, Fritz Haber) is used mainly to produce ammonia for fertilizer or other nitrogen compounds used for the same purpose. Without this process at work today, it is estimated that only about 40% of the world's population could be fed.

### 15-3.4 Changing Concentrations

If the system is at equilibrium and then an additional portion of a reactant is introduced, the system shifts to produce more products. We can rationalize this by consideration of collision theory. The increase in concentration of reactants causes more collisions between reactant molecules, which leads to the formation of more products. As the concentration of products increases, the rate of the reverse reaction increases. Eventually, equilibrium is reestablished, but with a higher concentration of products.

We can also rationalize this observation with Le Châtelier's principle. The additional  $\text{N}_2$  can be considered as a stress on a system initially at equilibrium. The stress can be relieved by removal of some of the additional  $\text{N}_2$  to form more product ammonia. We can generalize this observation. *An increase in the concentration of a reactant or product ultimately leads to an increase in the concentration of the species on the other side of the equation.* Conversely, a decrease in the concentration of a reactant or product ultimately leads to formation of more of that reactant or product.

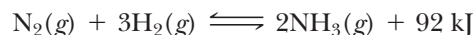
In reactions where a precipitate forms or a gas is evolved, that product is, in effect, entirely removed from the system. The system shifts to replace this loss, but if the loss is complete, the reaction continues to completion. This is known as an *irreversible reaction*, since products cannot re-form reactants.

### 15-3.5 Changing Pressure

In a gaseous system, a change in the volume of the reaction container or the pressure may also affect the point of equilibrium. Boyle's law tells us that *a decrease in volume of a quantity of gas is caused by an increase in pressure*. Increasing the pressure on a gaseous mixture of reactants and products at equilibrium (or decreasing the volume of the container) is another example of stress on a system. The system can counteract the stress of increased pressure by shifting to a lower volume if possible. In our sample system, there are four moles of gaseous reactants ( $\text{N}_2 + 3\text{H}_2$ ) but only two moles of the gaseous product ( $2\text{NH}_3$ ). Therefore, an increase in pressure on this system shifts the point of equilibrium to the right, increasing the concentration of  $\text{NH}_3$  until equilibrium is eventually reestablished. *In general, an increase in pressure on a gaseous system shifts the point of equilibrium in the direction of the smaller number of moles of gas*. Alternately, if there is the same number of moles of gas on each side of the equation, a change in pressure does not shift the point of equilibrium. When gases are not involved in a reaction at equilibrium, such as one in aqueous solution, pressure changes have negligible effect, since solids and liquids are essentially incompressible.

### 15-3.6 Changing Temperature

The reaction of  $\text{N}_2$  with  $\text{H}_2$  is an exothermic reaction, which means that heat energy is produced along with  $\text{NH}_3$ . The equation showing heat as a product can be written as follows.



Since heat can be considered a component of the reaction, it can be treated in the same way as any other component, as discussed above, according to Le Châtelier's principle. That is, if we add heat (increase the temperature), the reaction shifts in a direction to remove that heat. If we remove heat by cooling the reaction mixture, the equilibrium shifts in a direction to replace that heat loss. *For an exothermic reaction, cooling the reaction mixture increases the concentration of products when equilibrium is reestablished. For an endothermic reaction, where heat can be considered as a reactant, heating the reaction mixture increases the concentration of products at equilibrium*. In our system, an increased concentration of  $\text{NH}_3$  at equilibrium is favored at low temperatures. The system attempts to compensate for the loss of heat by formation of more  $\text{NH}_3$  and, with it, more heat.

### 15-3.7 Adding a Catalyst

In our example system, we have a problem as we lower the temperature to increase the equilibrium concentration of  $\text{NH}_3$ . Recall that the rate of the reaction decreases as the temperature decreases. Unfortunately, if we lower the temperature enough to get a reasonable amount of  $\text{NH}_3$  at equilibrium, the reaction essentially stops. Fritz Haber discovered a heterogeneous catalyst (certain transition metal oxides) that increased the rate of the reaction. In the presence of the catalyst, the reaction can be run at around  $400^\circ\text{C}$  instead of over  $1000^\circ\text{C}$  without a catalyst. At the lower temperature, the reaction proceeds smoothly with a significant yield of  $\text{NH}_3$ . The discovery of a catalyst was the key that made the process economically feasible and eventually changed the world.

Catalysts play a very significant role in many chemical reactions with industrial significance. *A catalyst in a system that reaches a point of equilibrium increases the rate of both the forward and reverse reactions proportionally but does not change the point of equilibrium*. The function of a catalyst is simply to reach the point of equilibrium in less time. However, with a catalyst, exothermic reactions can be run at considerably lower temperatures, thus increasing the yield of products.

MAKING

REAL

IT

### The Lake That Exploded



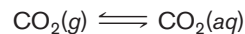
The explosion of carbon dioxide from this lake caused a disaster.

In 1986, Lake Nyos in Cameroon, a country in Africa, literally blew its top. What happened in this huge lake is the same thing that happens when one opens a well-shaken can of soda. As we all know, gas (carbon dioxide) comes out of solution and suddenly propels the liquid at whatever or whoever the opening of

the can is pointed. In the case of Lake Nyos, tons of carbon dioxide gas suddenly erupted from deep in the lake, forming a thick cloud. Since carbon dioxide is denser than air, the cloud hugged the ground, flowed over the rim of the crater, and began to creep down into the surrounding valleys. As the cloud moved, it pushed the air, with its life-sustaining oxygen, out of the way. Normal air is 0.03% CO<sub>2</sub>. If the concentration rises to 10%, it can be fatal. Eventually, 1700 people and many thousands of cattle were asphyxiated. Two years earlier, the same thing had happened at nearby Lake Monoun, causing 37 casualties.

What happened to cause such a calamity and how does this relate to equilibrium? The lake is what is known as a volcanic crater lake. From the hot magma, 50 miles down in the earth, carbon dioxide rises through vents underneath the lake and enters the cold water near the bottom. Recall that gases are more soluble at lower temperatures. Also, in the equilibrium between the gaseous state and dissolved state, the high pressure near the bottom of the lake favors keeping the gas in solution. In this equilibrium, higher

pressure favors the side of the equation with the lower volume, which is to the right with the CO<sub>2</sub> in the dissolved state (i.e., Le Châtelier's principle).



As long as it is not disturbed, the carbon dioxide stays in solution in the cold, lower layers of the lake. A small earthquake, an underwater landslide, or even a violent storm may have upset the layers. Once the layer of water containing the carbon dioxide came closer to the surface, the reduced pressure allowed the equilibrium to shift to the gaseous state, suddenly forming huge volumes of gas. Once it started, it continued violently, like when opening a shaken bottle of soda. The cloud of gas expanded for over 20 miles from the lake until it dissipated.

Crater Lake in Oregon is much like Lake Nyos, but it is deeper and has much more CO<sub>2</sub> injected into its lower depths. Can it explode? Probably not. In winter, the cold surface water sinks to the bottom because it is denser than warm water. The lake thus "turns over." As the bottom water moves toward the surface, the dissolved CO<sub>2</sub> is gradually released each year. In equatorial Africa, it is hot all year long, so the colder bottom water is trapped and gas can accumulate over the centuries until it is suddenly released.

Efforts are underway by scientists and engineers to prevent this from happening again in Lake Nyos and two other lakes like it. In one attempt, pumps extend to the deep parts of the lakes, bringing some of the lower layer to the surface in pipes. In this way, the carbon dioxide can be released gradually before it again builds to dangerous levels. Still, much needs to be done or this tragedy could happen again.

#### ASSESSING THE OBJECTIVES FOR SECTION 15-3

**EXERCISE 15-3(a) KNOWLEDGE:** Fill in the blanks.

Reactions that are reversible may reach a \_\_\_\_\_ where the concentrations of reactants and products remain \_\_\_\_\_. The point of equilibrium may be affected by a change of \_\_\_\_\_ of reactants, a change of \_\_\_\_\_, and a change of \_\_\_\_\_ (in a gaseous system).

**EXERCISE 15-3(b) KNOWLEDGE:** Which of the following is not the role of a catalyst?

- (a) increase the rate of the reaction
- (b) increase the amount of products formed
- (c) lower the activation energy for the forward reaction

- (d) lower the activation energy of the reverse reaction  
 (e) increase the heat of the reaction

**EXERCISE 15-3(c) ANALYSIS:** Given the equilibrium illustrated by the following equation



Will the concentration of  $\text{H}_2$  at equilibrium be increased, decreased, or not affected by the following?

- (a) an increase in concentration of  $\text{H}_2\text{O}$   
 (b) an increase in concentration of  $\text{O}_2$   
 (c) an increase in temperature  
 (d) an increase in pressure  
 (e) addition of a catalyst

**EXERCISE 15-3(d) SYNTHESIS:** If more product forms at lower temperature for a reaction, why not run the reaction at the lowest feasible temperature?

*For additional practice, work chapter problems 15-6, 15-8, 15-10, and 15-12.*

## PART A SUMMARY

### KEY TERMS

- 15-1.1** **Collision theory** describes how reactants are transformed into products. p. 472  
**15-1.2** An **activated complex** is formed at the instant of transformation. The **activation energy** is the energy required to form this complex. pp. 473–474  
**15-2** The **rate of the reaction** is a measure of the time required to transform reactants into products. p. 475  
**15-2.5** A **catalyst** affects the rate of the reaction but does not change the eventual amount of reactants and products. p. 477  
**15-3.1** A **reversible reaction** reaches a **point of equilibrium**. It is referred to as a **dynamic equilibrium**, since the actual reactants and products are constantly changing. pp. 479–480  
**15-3.3** **Le Châtelier's principle** predicts the effect of changing conditions on the eventual distribution of reactants and products. p. 481

### SUMMARY CHARTS

| Increasing the Rate of a Reaction                                  |                  |  |               |
|--|------------------|--|---------------|
| Concentrations   | Temperature      | Catalysts  |               |
| High concentrations of reactants                                   | High temperature | Presence of a catalyst<br>[lowers activation energy ( $E_a$ )] |               |
| The Production of $\text{NH}_3$ from $\text{N}_2$ and $\text{H}_2$ |                  |  |               |
| Effect at Equilibrium  |                  |  |               |
| Change   | $\text{H}_2$     | $\text{N}_2$   | $\text{NH}_3$ |
| Add $\text{N}_2$   | Decrease         | Increase   | Increase      |
| Increase $P$   | Decrease         | Decrease   | Increase      |
| Decrease $V$   | Decrease         | Decrease   | Increase      |
| Lower $T$  | Decrease         | Decrease   | Increase      |
| Add catalyst   | No effect        | No effect  | No effect     |



**PART B**  
**THE QUANTITATIVE ASPECTS**  
**OF REACTIONS AT**  
**EQUILIBRIUM**

**SETTING A GOAL**

- You will learn how to mathematically manipulate reactions that reach a state of equilibrium.

**OBJECTIVES**

- 15-4 (a)** Write the equilibrium constant expression for reactions that take place in the gaseous state. **(b)** Calculate the value of the equilibrium constant given equilibrium concentrations.
- 15-5 (a)** Write equilibrium constant expressions for species in aqueous solution. **(b)** Calculate the value of  $K_a$  or  $K_b$  for a weak acid or base given appropriate data. **(c)** Calculate the pH of a weak acid or base solution given  $K_a$  or  $K_b$ .
- 15-6 (a)** Write the solubility constant expression for a specific ionic compound. **(b)** Calculate the value of the constant from molar solubility data. **(c)** Calculate the solubility of a chemical given its solubility constant.

## 15-4 THE EQUILIBRIUM CONSTANT



**LOOKING AHEAD!** Long before chemists knew anything about collision theory, reaction rates, or activation energy, they realized that the concentrations of reactants and products were distributed in a predictable manner when a reaction reached the point of equilibrium. Our next subject concerns these quantitative aspects of the point of equilibrium. ■

**OBJECTIVES FOR SECTION 15-4**

- (a)** Write the equilibrium constant expression for reactions that take place in the gaseous state. **(b)** Calculate the value of the equilibrium constant given equilibrium concentrations.

### 15-4.1 The Equilibrium Constant Expression

To illustrate how the concentrations of reactants and products relate, we will consider a hypothetical reversible reaction involving  $a$  moles of reactant A combining with  $b$  moles of reactant B to form  $c$  moles of product C and  $d$  moles of product D.



For a reaction at equilibrium, the distribution of reactants and products is given by the following relationship.

$$K_{\text{eq}} = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

Note that the coefficients ( $a$ ,  $b$ ,  $c$ , and  $d$ ) of the substances (A, B, C, and D) become the exponents of the molar concentrations (mol/L) of the same substances. The products are written in the numerator, and the reactants are written in the denominator. This relationship for a particular reaction consists of two parts on each side of the equal sign.  $K_{\text{eq}}$  is called the **equilibrium constant** and has a definite numerical value at a given temperature. The ratio to the right of the equality is called the **equilibrium constant expression**. We will apply this relationship to gas-phase reactions in this section and to certain reactions that occur in aqueous solution in the next section.

### 15-4.2 The Value of the Equilibrium Constant

Using the equilibrium relationship, the distribution of reactants and products at equilibrium can be predicted regardless of initial concentrations. This is illustrated in Table 15-1. In a series of three experiments, we start with an initial concentration of reactants only (expt. 1), an initial concentration of products only (expt. 2), and

**TABLE 15-1** The Value of  $K_{\text{eq}}$ 

For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  at  $450^\circ\text{C}$ ,

$$K_{\text{eq}} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad [X] = \text{concentration in mol/L}$$

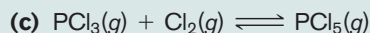
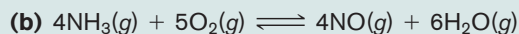
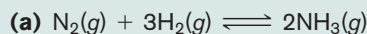
| Expt. | INITIAL CONCENTRATION |                |               | EQUILIBRIUM CONCENTRATION |                |               |                 |
|-------|-----------------------|----------------|---------------|---------------------------|----------------|---------------|-----------------|
|       | $[\text{H}_2]$        | $[\text{I}_2]$ | $[\text{HI}]$ | $[\text{H}_2]$            | $[\text{I}_2]$ | $[\text{HI}]$ | $K_{\text{eq}}$ |
| 1     | 2.000                 | 2.000          | 0             | 0.428                     | 0.428          | 3.144         | 54.0            |
| 2     | 0                     | 0              | 2.000         | 0.214                     | 0.214          | 1.572         | 54.0            |
| 3     | 1.000                 | 1.000          | 1.000         | 0.321                     | 0.321          | 2.358         | 54.0            |

an initial concentration of both reactants and products (expt. 3). By substituting the final equilibrium concentrations of all species in the equilibrium constant expression, a consistent value for the equilibrium constant is obtained for all three cases.

In our first example, we will write the equilibrium constant expressions for three reversible reactions that occur in the gaseous phase.

**EXAMPLE 15-1****Writing Equilibrium Constant Expressions**

Write the equilibrium constant expression for each of the following reactions.

**PROCEDURE**

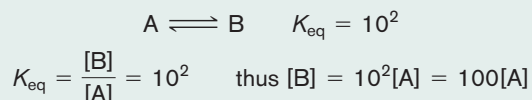
Put the concentrations of products in the numerator and reactants in the denominator. Raise each concentration to the power of the coefficient in the balanced equation.

**SOLUTIONS**

$$\text{(a)} \quad K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \text{(b)} \quad K_{\text{eq}} = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^5} \quad \text{(c)} \quad K_{\text{eq}} = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

**ANALYSIS**

What can we predict, then, about how far a reaction progresses based on the value of  $K_{\text{eq}}$ ? A large value for  $K_{\text{eq}}$  indicates that the numerator is much larger than the denominator in the equilibrium constant expression. This means that the concentrations of products are larger than those of reactants. For example, consider the simple equilibrium



The large value of the equilibrium constant signifies that, for this reaction at the point of equilibrium, the concentration of the product, [B], is 100 times the concentration of the reactant, [A]. That is, the equilibrium lies far to the right. On the other hand, if the value of  $K_{\text{eq}}$  were small (e.g.,  $10^{-2}$ ), then the concentration of the reactant, [A], would be 100 times the concentration of the product, [B], and this equilibrium would lie far to the left.

**SYNTHESIS**

Another useful quantity is called the reaction quotient, given the symbol  $Q$ . It has an expression written the same way as the equilibrium constant expression, except that the values used are the starting concentrations, not the equilibrium concentrations. By comparing the values of  $Q$  and  $K_{\text{eq}}$ , we can determine which way the reaction will move to reach equilibrium. When  $Q < K_{\text{eq}}$ , the product concentrations are too low and the reactant concentrations are too high to be in a state of equilibrium. As a result, the system will produce more product at the expense of reactants. If  $Q > K_{\text{eq}}$ , then the opposite situation

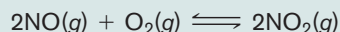
occurs, and the system will move to produce reactant at the expense of product. Should  $Q=K_{\text{eq}}$ , then the system is already at equilibrium and we would expect no relative shifting of concentrations.

The equilibrium constant is calculated from the experimental determination of the distribution of reactants and products at equilibrium. The following two examples illustrate such calculations.

### EXAMPLE 15-2

#### Calculating the Value of $K_{\text{eq}}$

What is the value of  $K_{\text{eq}}$  for the following system at equilibrium?



At a given temperature, the equilibrium concentrations of the gases are  $[\text{NO}] = 0.890$ ,  $[\text{O}_2] = 0.250$ , and  $[\text{NO}_2] = 0.0320$ .

#### PROCEDURE

Substitute the concentrations into the equilibrium constant expression and raise the concentration to the appropriate power.

#### SOLUTION

For this reaction,

$$\begin{aligned} K_{\text{eq}} &= \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \\ &= \frac{[0.0320]^2}{[0.890]^2[0.250]} = \frac{1.024 \times 10^{-3}}{0.198} = \underline{\underline{5.17 \times 10^{-3}}} \end{aligned}$$

#### ANALYSIS

Equilibrium problems are great places to practice your ability to estimate whether the answer you got is reasonable or not. In this problem we see that the equilibrium concentrations of the reactants are considerably higher than the product. This means that the equilibrium position favors reactants. Equilibrium constants for reactant-favored reactions are typically quite small, so our answer is very reasonable.

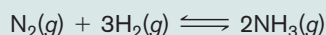
#### SYNTHESIS

What would happen to each of the values, qualitatively, if more oxygen is now added to the system? According to Le Châtelier's principle, the system would shift toward formation of more products. Therefore, the amount of  $\text{NO}_2$  would rise, and the amount of  $\text{NO}$  would fall. The oxygen concentration would fall somewhere in between where it was after the initial equilibrium and where it was after the excess had been added. Though the calculation would be somewhat involved, it is doable once we know the value of the equilibrium constant.

### EXAMPLE 15-3

#### Calculating Equilibrium Concentrations and $K_{\text{eq}}$

For the equilibrium



Complete the table and compute the value of the equilibrium constant.

| Initial Concentrations |                |                 | Equilibrium Concentrations |                |                 |
|------------------------|----------------|-----------------|----------------------------|----------------|-----------------|
| $[\text{H}_2]$         | $[\text{N}_2]$ | $[\text{NH}_3]$ | $[\text{H}_2]$             | $[\text{N}_2]$ | $[\text{NH}_3]$ |
| 0.200                  | 0.200          | 0               | ?                          | ?              | 0.0450          |

#### PROCEDURE

- In a stoichiometry calculation, find the hydrogen and nitrogen concentrations needed to form the 0.0450 mol/L of  $\text{NH}_3$ . (See Section 7-1.)
- Find the  $[\text{H}_2]$  and  $[\text{N}_2]$  remaining at equilibrium by subtracting the concentration that reacted from the initial concentration; that is,

$$[\text{N}_2]_{\text{eq}} = [\text{N}_2]_{\text{initial}} - [\text{N}_2]_{\text{reacted}}$$

- Substitute the concentrations of all compounds present at equilibrium into the equilibrium constant expression and solve to find the value of  $K_{\text{eq}}$ .

**SOLUTION**

1. If 0.0450 mol of  $\text{NH}_3$  is formed, calculate the number of moles of  $\text{N}_2$  that reacted (per liter).

$$0.0450 \text{ mol NH}_3 \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = 0.0225 \text{ mol N}_2 \text{ reacted (per liter)}$$

The number of moles of  $\text{H}_2$  that reacted is

$$0.0450 \text{ mol NH}_3 \times \frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3} = 0.0675 \text{ mol H}_2 \text{ reacted (per liter)}$$

2. At equilibrium

$$[\text{N}_2]_{\text{eq}} = 0.200 - 0.0225 = 0.178$$

$$[\text{H}_2]_{\text{eq}} = 0.200 - 0.0675 = 0.132$$

- 3.

$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.0450)^2}{(0.178)(0.132)^3} = \underline{\underline{4.95}}$$

**ANALYSIS**

This problem may at first seem confusing until we realize that it requires typical stoichiometry calculations. The first part of the problem is much like similar problems we worked in Chapter 7, where we converted the amount of a product to the amount of reactant required. That is, we are given the concentration of  $\text{NH}_3$  and we need to find out the concentrations of reactants that formed the given concentration of  $\text{NH}_3$ . The concentration present at equilibrium of the reactants is simply the concentration left over from the amount that reacted.

**EXAMPLE 15-4****Calculating Equilibrium Concentrations from  $K_{\text{eq}}$** 

In the preceding equilibrium, what is the concentration of  $\text{NH}_3$  at equilibrium if the equilibrium concentrations of  $\text{N}_2$  and  $\text{H}_2$  are 0.22 and 0.14 mol/L, respectively?

**PROCEDURE**

In this example, use the value of  $K_{\text{eq}}$  found in the previous example. The concentration of  $\text{NH}_3$  can be found by substituting the concentrations of the species given and solving for the one unknown.

**SOLUTION**

$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \begin{array}{l} [\text{N}_2] = 0.22 \\ [\text{H}_2] = 0.14 \end{array} \quad K_{\text{eq}} = 4.95$$

$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[0.22][0.14]^3} = 4.95$$

$$[\text{NH}_3]^2 = 2.99 \times 10^{-3}$$

$$[\text{NH}_3] = 5.5 \times 10^{-2} = 0.055$$

Thus the concentration of  $\text{NH}_3 = \underline{\underline{0.055 \text{ mol/L}}}$ .

**ANALYSIS**

This problem requires the use of some simple algebra. That is, we isolate the unknown (i.e.,  $\text{NH}_3$ ) on the left side of the equation and all the known quantities on the right (i.e.,  $K_{\text{eq}}$ ,  $[\text{N}_2]$ , and  $[\text{H}_2]$ ). Notice in this case that the unknown is squared, so the solution requires that we take the square root of the calculated quantity on the right.

**SYNTHESIS**

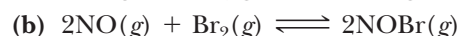
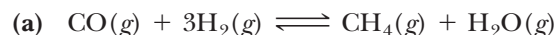
This type of problem could also be solved knowing the initial values of the starting materials, rather than their equilibrium values. In a realistic setting, it is those values that are most readily available. On the other hand, solving that sort of problem introduces complications that require some sophisticated mathematical assumptions and techniques that are beyond the scope of this text. Nevertheless, it's important to know what's possible.

ASSESSING THE  
OBJECTIVES FOR  
SECTION 15-4

**EXERCISE 15-4(a) KNOWLEDGE:** Fill in the blanks.

A gaseous equilibrium can be expressed as a number known as the \_\_\_\_\_ and a ratio of reactants and products known as the \_\_\_\_\_. A small value for  $K_{\text{eq}}$  (e.g.,  $10^{-5}$ ) indicates that \_\_\_\_\_ are favored at equilibrium.

**EXERCISE 15-4(b) KNOWLEDGE:** Write the equilibrium constant expression for the following equilibria.



**EXERCISE 15-4(c) ANALYSIS:** What is the value of  $K_{\text{eq}}$  in part (a) of Exercise 15-4(b) if there are  $2.0 \times 10^{-3}$  mol of CO,  $1.0 \times 10^{-2}$  mol of  $\text{H}_2$ ,  $3.5 \times 10^{-4}$  mol of  $\text{CH}_4$ , and  $5.0 \times 10^{-5}$  mol of  $\text{H}_2\text{O}$  present in a 10.0-L container at equilibrium?

**EXERCISE 15-4(d) ANALYSIS:**

(a) What is the value of  $K_{\text{eq}}$  in part (b) of Exercise 15-4(b) if we start with 4.00 mol of NOBr only in a 20.0-L container, and, at equilibrium, it is found that  $[\text{NOBr}] = 0.10$ ?

(b) Using key from part (a) above, what is the concentration of [NOBr] if  $[\text{NO}] = 0.45$  and  $[\text{Br}_2] = 0.22$  at equilibrium?

**EXERCISE 15-4(e) SYNTHESIS:** Heterogeneous equilibria involve a solid and a gas. An example of such an equilibrium is



The equilibrium constant expression is  $K_{\text{eq}} = [\text{CO}_2]$ . Why don't the concentrations of calcium carbonate and calcium oxide appear in the expression?

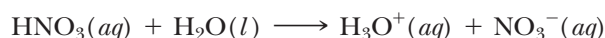
*For additional practice, work chapter problems 15-15, 15-20, 15-25, and 15-30.*

## 15-5 EQUILIBRIA OF WEAK ACIDS AND WEAK BASES IN WATER



**LOOKING AHEAD!** We now return to weak acids, weak bases, and buffer solutions, which we first discussed in Chapter 13. Aqueous solutions of these substances are in equilibria, so they also have an equilibrium constant expression. In these cases the equilibrium occurs in aqueous solution, so these concentrations are the same as the molarity of the species. ■

If one is in a leaky boat and no one bails—down you go. No equilibrium is established between input and output, and the boat fills with water. The reaction of a strong acid in water is analogous to this. That is, no equilibrium occurs, since there is no reverse reaction. As a result, acids such as  $\text{HNO}_3$  are completely ionized in water, which means that the molecular form of the acid does not exist in aqueous solution. In this case, a single arrow indicates a complete reaction.

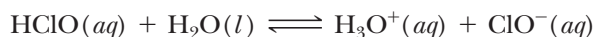
▶ OBJECTIVES FOR  
SECTION 15-5

(a) Write equilibrium constant expressions for species in aqueous solution. (b) Calculate the value of  $K_a$  or  $K_b$  for a weak acid or base given appropriate data. (c) Calculate the pH of a weak acid or base solution given  $K_a$  or  $K_b$ .



### 15-5.1 Equilibrium Constant Expressions for Weak Acids and Weak Bases

The difference between a strong acid and a weak acid lies in the concentration of  $\text{H}_3\text{O}^+$  produced by the acid. A weak acid such as hypochlorous acid ( $\text{HClO}$ ) produces only a small concentration of ions because the ionization is a reversible reaction in which the equilibrium actually lies far to the left. The ionization of  $\text{HClO}$  is represented by the following equation.



The equilibrium constant expression can be written as follows, where the concentrations now represent molarities.

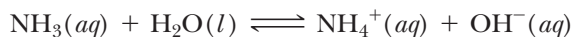
$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{H}_2\text{O}][\text{HClO}]}$$

In this equilibrium, the concentrations of  $\text{H}_3\text{O}^+$ ,  $\text{ClO}^-$ , and  $\text{HClO}$  in aqueous solution can all be varied.  $\text{H}_2\text{O}$  is the solvent, however, and is present in a very large excess compared with the other species. Since the amount of  $\text{H}_2\text{O}$  actually reacting is very small compared with the total amount present, the concentration of  $\text{H}_2\text{O}$  is essentially a constant. The  $[\text{H}_2\text{O}]$  can therefore be included with the other constant,  $K_{\text{eq}}$ , to produce another constant labeled  $K_a$ , which is known as an **acid ionization constant**.

$$K_{\text{eq}}[\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]}$$

In a weak acid solution we essentially have three species (besides water). There are two ions,  $\text{H}_3\text{O}^+$  and the anion of the acid (i.e.,  $\text{ClO}^-$ ) and the acid in molecular form (i.e.,  $\text{HClO}$ ). It is this limited amount of  $\text{H}_3\text{O}^+$  produced that classifies hypochlorous acid as a weak acid.

Ionization of the weak base  $\text{NH}_3$  is represented as



In this case, the three species present are the cation (i.e.,  $\text{NH}_4^+$ ), the  $\text{OH}^-$  ion, and molecular  $\text{NH}_3$ . As in weak acids,  $\text{H}_2\text{O}$  does not appear in the equilibrium constant expression. For this reaction, *the equilibrium constant is labeled  $K_b$ , which is the base ionization constant*.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

### 15-5.2 Determining the Value of $K_a$ or $K_b$

The values of  $K_a$  and  $K_b$  for weak acids and bases are determined experimentally. To calculate  $K_a$  or  $K_b$ , we need to know, or be able to determine from other data, the concentrations of both ions and the nonionized (i.e., molecular) form of the acid or base. In the following two examples, the needed concentrations are not directly given but must be inferred from the amount that ionizes (Example 15-5) or the pH of the solution (Example 15-6). After we illustrate how these constants are calculated, we will discuss their significance and how they are used.

#### EXAMPLE 15-5

##### Calculating $K_a$ from Equilibrium Concentrations

In a 0.20-M solution of  $\text{HNO}_2$ , it is found that 0.009 mol/L of the  $\text{HNO}_2$  ionizes. What are the concentrations of  $\text{H}_3\text{O}^+$ ,  $\text{NO}_2^-$ , and  $\text{HNO}_2$  at equilibrium, and what is the value of  $K_a$ ?



Vinegar contains a weak acid and ammonia, a weak base.

**PROCEDURE**

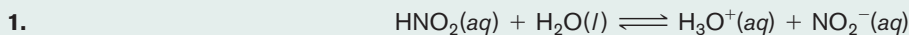
1. Write the equilibrium equation for  $K_a$ . Remember that  $H_2O$  is not included in the expression.
2. Calculate the concentration of nonionized (molecular)  $HNO_2$  present at equilibrium. Remember that the initial concentration given (0.20 M) represents the concentration of nonionized  $HNO_2$  present *plus* the concentration that ionizes. Therefore,  $[HNO_2]$  at equilibrium is the initial concentration minus the concentration that ionizes.

$$[HNO_2]_{eq} = [HNO_2]_{initial} - [HNO_2]_{ionized}$$

3. Note that one  $H_3O^+$  and one  $NO_2^-$  are formed for each  $HNO_2$  that ionizes (from the equation stoichiometry).

$$[H_3O^+]_{eq} = [NO_2^-]_{eq} = [HNO_2]_{ionized}$$

4. Calculate  $K_a$ .

**SOLUTION**

$$2. \quad [HNO_2]_{initial} = 0.20 \quad [HNO_2]_{ionized} = 0.009$$

$$[HNO_2]_{eq} = 0.20 - 0.009 = \underline{0.19}$$

$$3. \quad [H_3O^+]_{eq} = [NO_2^-]_{eq} = \underline{0.009}$$

$$4. \quad K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.009)(0.009)}{0.19} \\ = \underline{4 \times 10^{-4}}$$

**ANALYSIS**

It is important to note that one molecule of acid ionizes to produce one  $H_3O^+$  ion and one anion, which in this case is  $NO_2^-$ . The concentration of the two ions will thus be equal. If you know one, you know the other. It's like having a dozen pairs of shoes. If they are separated, you know there will be one dozen left shoes and one dozen right shoes. Note also that the acidity of the solution is determined only by the concentration of  $H_3O^+$ , not the concentration of the molecular form of the acid.

**SYNTHESIS**

Instead of being given the actual concentrations of the ions, the percent ionization of the acid is sometimes stated. In these cases, the concentrations of the ions are calculated like any other percent problem—by multiplying the percent in decimal form times the original concentration of acid. For example, if a 0.10 M acid is 18% ionized, the concentrations of both ions are  $0.10 \text{ M} \times 0.18 = 0.018 \text{ M}$ , and the concentration of unionized acid is  $0.10 - 0.018 = 0.08 \text{ M}$ . The value of  $K_a$  equals  $[0.018][0.018]/0.08 = 4 \times 10^{-3}$ .

**EXAMPLE 15-6****Calculating  $K_a$  from pH**

A 0.25 M solution of HCN has a pH of 5.00. What is  $K_a$ ?

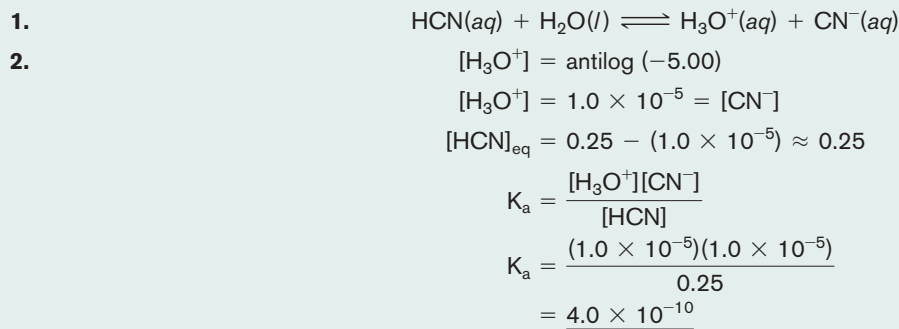
**PROCEDURE**

1. Write the equilibrium reaction.
2. Convert pH to  $[H_3O^+]$ .
3. Note that  $[CN^-] = [H_3O^+]$  at equilibrium.
4. Calculate  $[HCN]$  at equilibrium, which is

$$[HCN]_{eq} = [HCN]_{initial} - [HCN]_{ionized}$$

$$[HCN]_{ionized} = [H_3O^+]_{eq}, \text{ since one } H_3O^+ \text{ is produced at equilibrium for every HCN that ionizes.}$$

5. Use these values to calculate  $K_a$ .

**SOLUTION****ANALYSIS**

Recall that pH is simply a way to express the  $\text{H}_3\text{O}^+$  concentration. If we know the pH, we can calculate  $[\text{H}_3\text{O}^+]$ . If the pH is an integer, it becomes the negative exponent of 10. If it is not an integer, then we need to use a calculator. Refer to Example 13-9 in Chapter 13 for examples of these calculations. Notice also that the concentration of HCN is essentially unchanged. How can some of it ionize yet the original concentration not change? In fact, the amount of HCN that ionizes ( $10^{-5}$  M) is negligible compared with the initial concentration of HCN (0.25 M). Therefore,  $[\text{HCN}]_{\text{eq}} \approx [\text{HCN}]_{\text{initial}}$ . ( $\approx$  means approximately equal). It is like a crowd of about 10,000 people. Ten people more or less in this crowd does not change the overall estimate. For the purposes of these calculations (two significant figures), a number is considered negligible compared with another if it is less than 10% of the larger number. In this case,  $10^{-5}/0.25 \times 100\% = 0.4\%$  ionized.

**SYNTHESIS**

Make a quick prediction based on principles and mathematics. 0.25 M HCN with a pH of 5.0 has a  $K_a = 4 \times 10^{-10}$ . About what would another acid's  $K_a$  be if 0.25 M had a pH equal to 4.0? The same concentration produces a lower pH, indicating more molecules ionized. It is therefore a stronger acid and should have a larger equilibrium constant. Because both the concentration of the  $\text{H}_3\text{O}^+$  and the acid anion are affected at the same time, one power of 10 in pH become two powers of 10 for an equilibrium constant. The value is around  $4 \times 10^{-8}$ .

**15-5.3  $pK_a$  and  $pK_b$** 

The value for  $K_a$  and  $K_b$  can also be expressed as a negative log in same manner as pH. That is

$$pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b$$

Notice that the weaker the acid, the larger the value of  $pK_a$ . For example, if a weak acid had  $K_a = 10^{-4}$ ,  $pK_a = 4.0$ . If an even weaker acid had  $K_a = 10^{-9}$ ,  $pK_a = 9.0$ .  $pK_a$  is often used in organic and biochemistry to indicate relative acid strength and is used in the discussion of buffer solutions that follow.

**TABLE 15-2**  $K_a$  and  $pK_a$  for Some Weak Acids

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} \quad (\text{HX symbolizes a weak acid, X}^- \text{ its conjugate base})$$

| ACID         | FORMULA                           | $K_a$                 | $pK_a$ |                                     |
|--------------|-----------------------------------|-----------------------|--------|-------------------------------------|
| hydrofluoric | HF                                | $6.7 \times 10^{-4}$  | 3.17   | ↓<br>Decreasing<br>acid<br>strength |
| nitrous      | $\text{HNO}_2$                    | $4.5 \times 10^{-4}$  | 3.35   |                                     |
| formic       | $\text{HCHO}_2$                   | $1.8 \times 10^{-4}$  | 3.74   |                                     |
| acetic       | $\text{HC}_2\text{H}_3\text{O}_2$ | $1.8 \times 10^{-5}$  | 4.74   |                                     |
| hypochlorous | HClO                              | $3.2 \times 10^{-8}$  | 7.49   |                                     |
| hypobromous  | HBrO                              | $2.1 \times 10^{-9}$  | 8.68   |                                     |
| hydrocyanic  | HCN                               | $4.0 \times 10^{-10}$ | 9.40   |                                     |

**TABLE 15-3**  $K_b$  and  $pK_b$  for Some Weak Bases

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \quad (\text{B symbolizes a weak base, HB}^+ \text{ its conjugate acid})$$

| BASE          | FORMULA                    | $K_b$                | $pK_b$ |                                  |
|---------------|----------------------------|----------------------|--------|----------------------------------|
| dimethylamine | $(\text{CH}_3)_2\text{NH}$ | $7.4 \times 10^{-4}$ | 3.13   | ↓ Decreasing<br>base<br>strength |
| ammonia       | $\text{NH}_3$              | $1.8 \times 10^{-5}$ | 4.74   |                                  |
| hydrazine     | $\text{N}_2\text{H}_4$     | $9.8 \times 10^{-7}$ | 6.01   |                                  |

### 15-5.4 Using $K_a$ or $K_b$ to Determine pH

Once a value for  $K_a$  or  $K_b$  for a specific weak acid or base is known, we have the ability to calculate the pH of a solution of known concentration of a weak acid (Example 15-7) or a weak base (Example 15-8).

#### EXAMPLE 15-7

#### Calculating the pH of a Solution of a Weak Acid

What is the pH of a 0.155 M solution of HClO?

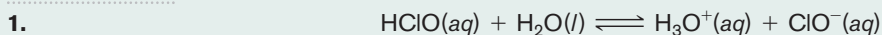
#### PROCEDURE

1. Write the equilibrium involved.
2. Write the appropriate equilibrium constant expression.
3. Let  $x = [\text{H}_3\text{O}^+]$  at equilibrium; since  $[\text{H}_3\text{O}^+] = [\text{ClO}^-]$ ,  $x = [\text{ClO}^-]$ .
4. At equilibrium,  $[\text{HClO}]_{\text{eq}} = [\text{HClO}]_{\text{initial}} - [\text{HClO}]_{\text{ionized}}$ .
5. Using the value for  $K_a$  in Table 15-2, solve for  $x$ .
6. Convert  $x$  to pH.

In summary:

|             | HClO        | $[\text{H}_3\text{O}^+]$ | $[\text{ClO}^-]$ |
|-------------|-------------|--------------------------|------------------|
| initial     | 0.155       | 0                        | 0                |
| equilibrium | $0.155 - x$ | $x$                      | $x$              |

#### SOLUTION



2. 
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = 3.2 \times 10^{-8}$$

3. At equilibrium,  $[\text{H}_3\text{O}^+] = [\text{ClO}^-] = x$ .

4. At equilibrium,  $[\text{HClO}] = 0.155 - x$ .

5. 
$$\frac{(x)(x)}{0.155 - x} = 3.2 \times 10^{-8}$$

The solution of this equation appears to require the quadratic equation. However, a simplification of this calculation is possible. Note that  $K_a$  is a small number, indicating that the degree of ionization is small (the equilibrium lies far to the left). This means that  $x$  is a very small number. Since very small numbers make little or no difference when added to or subtracted from large numbers, they can be ignored with little or no error.

$$0.155 - x \approx 0.155$$

Therefore the expression can now be simplified.

$$\frac{(x)(x)}{0.155 - x} = \frac{x^2}{0.155} = 3.2 \times 10^{-8}$$

$$x^2 = 5.0 \times 10^{-9}$$

To solve for  $x$ , take the square root of each side of the equation.

$$\sqrt{x^2} = \sqrt{5.0 \times 10^{-9}}$$

$$x = [\text{H}_3\text{O}^+] = 7.1 \times 10^{-5}$$

(Note that the  $x$  is indeed much smaller than 0.155.)

6. 
$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.1 \times 10^{-5}) = \underline{4.15}$$

**ANALYSIS**

Finding the pH of a weak acid solution given  $K_a$  is somewhat more mathematically involved than the earlier problems. Students often neglect the important mathematical simplification and assume that the quadratic equation is needed. In fact, it is rarely needed because almost all weak acids are weak enough that we can assume that very little acid or base ionizes. This occurs for  $K_a$  or  $K_b$  values less than about  $10^{-3}$ , which covers most common weak acids and bases. The problem then simply requires the taking of a square root. Sometimes students get confused about which  $x$  to ignore. When  $x$  stands alone, as when it represents a quantity such as  $H_3O^+$ , it is *not* ignored. When it is subtracted from a much large number, it can be ignored.

**SYNTHESIS**

How would one calculate the pH of a 0.01 M ( $10^{-2}$  M) solution of chlorous acid ( $HClO_2$ ,  $K_a = 10^{-2}$ )? If we solved for  $x$  as above,  $x = 10^{-2}$  M. That means it is 100% ionized, which means that the assumption that  $x$  is small compared to  $10^{-2}$  is obviously incorrect. If we use the quadratic,  $x = 0.008$  M, which means that it is 80% ionized. That is more reasonable. See if you can follow the reasoning and calculations.

**EXAMPLE 15-8****Calculating the pH of a Solution of a Weak Base**

What is the pH of a 0.245 M solution of  $N_2H_4$ ?

**PROCEDURE**

1. Write the equilibrium involved.
2. Write the appropriate equilibrium constant expression.
3. Let  $x = [OH^-]$  at equilibrium; since  $[OH^-] = [N_2H_5^+]$ ,  $[N_2H_5^+] = x$ , too.
4. At equilibrium,  $[N_2H_4]_{eq} = [N_2H_4]_{initial} - [N_2H_4]_{ionized}$
5. Using the value for  $K_b$  in Table 15-3, solve for  $x$ .
6. Convert  $x$  to pOH. Convert pOH to pH.

**SOLUTION**

1. 
$$N_2H_4(aq) + H_2O(l) \rightleftharpoons N_2H_5^+(aq) + OH^-(aq)$$
2. 
$$K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = 9.8 \times 10^{-7} \text{ (from Table 15-3)}$$
3. Let  $x = [OH^-] = [N_2H_5^+]$  (at equilibrium)
4.  $[N_2H_4] = 0.245 - x$  (at equilibrium). Since  $K_b$  is very small,  $x$  is very small.  
Therefore,
 
$$0.245 - x \approx 0.245$$
5. 
$$\frac{(x)(x)}{0.245} = 9.8 \times 10^{-7}$$

$$x^2 = 2.4 \times 10^{-7}$$

$$x = 4.9 \times 10^{-4} = [OH^-]$$

$$pOH = -\log [OH^-] = -\log (4.9 \times 10^{-4}) = 3.31$$
6. 
$$pH = 14.00 - pOH = 14.00 - 3.31 = \underline{\underline{10.69}}$$

**ANALYSIS**

This is the same procedure as in Example 15-7, with the appropriate changes made for a base as opposed to an acid. This includes the use of  $K_b$  instead of  $K_a$  and the fact that the  $x$  stands for the hydroxide concentration instead of the hydronium concentration. Therefore, it is pOH that is being calculated directly. A quick conversion yields pH. Certainly, the results seem reasonable. This is a modest concentration of a weak base. A calculated pH value of 10.69 seems to be appropriate for this system.

**SYNTHESIS**

How do these acids and bases compare to those we studied in Chapter 13, when we weren't concerned with equilibrium constants? Consider a comparison between 0.245 M  $N_2H_4$ , the *weak* base in this problem, with 0.245 M NaOH, a *strong* base from Chapter 13. The pH for the  $N_2H_4$  solution is 10.69. The pH for the NaOH solution is 13.39, or nearly a thousand times more concentrated. Why the difference? The pH of the strong base is determined directly from the concentration, so an equilibrium constant is not needed. Any equilibrium lies so far toward producing hydroxide that we assume the two are equal. The pH of the weak base requires the equilibrium expression, where the small value of  $K_b$  makes the pH lower as well.



### 15-5.5 The pH of Buffer Solutions

As mentioned in Chapter 13, buffer solutions are those that resist changes in pH and are made from mixtures of a weak acid (or base) and a salt containing the conjugate base (or acid). They have many important applications, especially in life processes such as maintaining the nearly constant pH of the blood. We can also calculate the pH of buffers using a form of the equation for  $K_a$  outlined previously. In fact, calculations of the pH of buffers are comparatively simple if we rearrange the equilibrium constant expression, as illustrated here with HClO.

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HClO}]}{[\text{ClO}^-]}$$

By taking  $-\log$  of both sides of the equation, we now have

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HClO}]}{[\text{ClO}^-]}$$

Now we substitute pH for  $-\log [\text{H}_3\text{O}^+]$  and  $\text{p}K_a$  for  $-\log K_a$  and invert the ratio of the concentrations which changes the sign of the log.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{ClO}^-]}{[\text{HClO}]}$$

Notice that the  $\text{ClO}^-$  is the base species in the equilibrium and HClO is the acid species. We can thus make this a general equation for calculating the pH of buffers by substituting [acid] for [HClO] and [base] for  $[\text{ClO}^-]$ . *This general equation is known as the Henderson–Hasselbalch equation.*

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad \text{pOH} = \text{p}K_b + \log \frac{[\text{acid}]}{[\text{base}]}$$

Since weak acids and bases are used to make buffers, we are quite safe in assuming that concentrations of the acid and base species present in solution are essentially the same as the originally measured amounts. Also, the conjugate acid or base is added in the form of a salt where one of the ions is not involved in the equilibrium (i.e., the  $\text{Na}^+$  in NaClO). The most effective buffers are made from solutions containing equal molar amounts of acid and base species. In such cases, the ratio of base to acid equals unity. Since  $\log 1 = 0$ , pH equals  $\text{p}K_a$ . *Thus,  $\text{p}K_a$  is sometimes used as a measure of the acid strength and as the pH of the most effective buffer formed from this weak acid.* The pHs of other ratios of acid and base species can be calculated by simply substituting the amounts in moles or the concentrations into the appropriate Henderson–Hasselbalch equation. *Note that this equation is useful only for buffers, not for solutions of weak acids or weak bases alone.*

#### EXAMPLE 15-9

##### Calculating the pH of a Buffer Solution

What is the pH of a buffer solution that is made by dissolving 0.30 mol of  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.50 mol of  $\text{NaC}_2\text{H}_3\text{O}_2$  in enough water to make 1.00 L of solution?

##### PROCEDURE

1. Obtain the value of  $\text{p}K_a$  from Table 15-2.
2. Employ the Henderson–Hasselbalch equation to solve for pH.

##### SOLUTION

In this solution, the concentration of the acid species is  $[\text{HC}_2\text{H}_3\text{O}_2] = 0.30 \text{ mol/L}$ , and the concentration of the base species is  $[\text{C}_2\text{H}_3\text{O}_2^-] = 0.50 \text{ mol/L}$ .

$$\text{pH} = 4.74 + \log \frac{[0.50]}{[0.30]} = 4.74 + 0.22 = \underline{\underline{4.96}}$$

## ANALYSIS

The buffer capacity of a system relates to the original concentration of the acid and base species in the solution. In this case the buffer capacity of the base is 0.50 mol/L. If any more than 0.50 mol/L of  $\text{H}_3\text{O}^+$  is added to the system, the base of the buffer is used up and the pH decreases rapidly. If any more than 0.30 mol/L of  $\text{OH}^-$  is added to the system, the buffering capacity of the acid is used up and the pH rises dramatically. For example, if we added 0.60 mol/L of HCl to the system, the buffer could react with 0.50 mol/L of that amount. The 0.10 mol/L of excess  $\text{H}_3\text{O}^+$  would lower the pH to 1.0.

## SYNTHESIS

Reread Making It Real, “The pH Balance in the Blood,” in Chapter 13. This is a very important biological concept because metabolism occurs in a very narrow pH range, so the blood is very heavily buffered. The normal pH of blood is 7.4, yet the  $pK_a$  of carbonic acid is 6.4. Using the Henderson–Hasselbalch equation, we can see what this means. The pH of this buffer would be 7.4 if the concentration of bicarbonate ion is 10 times the concentration of carbonic acid, as shown below. Mathematically, we are saying  $[\text{HCO}_3^-] = 10[\text{H}_2\text{CO}_3]$

$$\begin{aligned} \text{pH} &= pK_a + \log B/A = 6.4 + \log [\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = \\ &6.4 + \log 10[\text{H}_2\text{CO}_3]/[\text{H}_2\text{CO}_3] = 6.4 + \log 10 = 6.4 + 1.0 = 7.4 \end{aligned}$$

What this tells us is that our blood is 10 times more buffered against the addition of acid than base. In fact, more acid (e.g., lactic acid from exercise) enters our blood than base, so this works out well.



## Buffers and Swimming Pool Chemistry



Control of pH in a swimming pool is essential.

in a pool must be closely monitored on a daily basis by some lucky person.

First, the pool must have the proper content of chlorine, which is usually in the form of hypochlorous acid (HOCl), which destroys bacteria and keeps the pool safe. The most common source of chlorine is sodium hypochlorite (bleach) added as a 10% solution. Sodium hypochlorite dissolves to produce the hypochlorite ion, which undergoes basic hydrolysis (reaction 1). By itself this solution would produce a swimming pool with a pH of around 10 because of hydrolysis of the  $\text{ClO}^-$  ion. This is way too alkaline. The pH is lowered to about 7.5 by adding hydrochloric acid or sodium bisulfate (reaction 2). At  $\text{pH} = 7.5$ ,  $\text{pH} = pK_a$  for this system, which means that equal molar amounts of HOCl and  $\text{OCl}^-$  are present (reaction 3). Recall that this is a buffer solution, so the pH is stabilized around 7.5 even if some acid or base enters the pool. However, if the pH does drop below 7.2, the water can sting the eyes and cause corrosion of metal pipes. Sodium

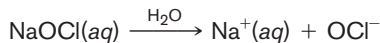
When we take a refreshing dive into a swimming pool, we may not appreciate the fact that maintenance of this pleasure requires application of some

serious chemistry.

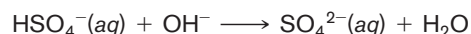
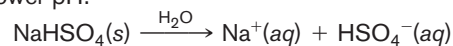
The balance of chemicals

carbonate is added until the pH returns to 7.5 (reaction 4). If it rises above 7.8, the pool may become cloudy and scaling (i.e., deposits of  $\text{CaCO}_3$ ) may occur. The pool manager adds more sodium bisulfate to bring the pH down. The reactions that we have discussed are illustrated by the equations below.

1. Add NaOCl:



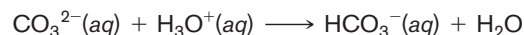
2. Lower pH:



3. Buffer equilibrium ( $\text{pH} = pK_a = 7.5$ )



4. Raise pH:  $\text{Na}_2\text{CO}_3(s) \xrightarrow{\text{H}_2\text{O}} 2\text{Na}^+(aq) + \text{CO}_3^{2-}(aq)$



A good clean pool needs even more help. The presence of humans in the pool and their fluids (perspiration, etc.) produce ammonia. Ammonia reacts with HOCl to produce chloramines (i.e.,  $\text{NH}_2\text{Cl}$ ). If “the pool smells like chlorine,” the smell is actually due to chloramines. It is removed by “shocking” the pool by adding another special chemical. If algae form, the pool becomes green and slimy, but another chemical clears it up.

Next time you are invited to take a dip in a nice swimming pool, remember how chemistry, work, and lots of money make it all possible as well as pleasant.

ASSESSING THE  
OBJECTIVES FOR  
SECTION 15-5

**EXERCISE 15-5(a) KNOWLEDGE:** Write the equilibrium involved and the equilibrium constant expression of an aqueous solution of formic acid ( $\text{HCHO}_2$ ). Write the equilibrium involved and the equilibrium constant expression of an aqueous solution of the hypothetical weak nitrogen base  $\text{NX}_3$ .

**EXERCISE 15-5(b) KNOWLEDGE:** The concentration of  $\text{H}_3\text{O}^+$  in a 0.10-M solution of a weak acid is  $1.3 \times 10^{-3}\text{M}$ . What are the concentrations of each species in the equilibrium expression? What is the weak acid from those listed in Table 15-2?

**EXERCISE 15-5(c) KNOWLEDGE:** A buffer is made by dissolving an equal number of moles of the weak base  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_2\text{NH}_2^+\text{Br}^-$ . If  $K_b = 7.4 \times 10^{-4}$ , what is the pH of the solution?

**EXERCISE 15-5(d) ANALYSIS:** What is the pH of a 0.10 M solution of  $\text{HCHO}_2$ ? (Refer to Table 15-2.)

**EXERCISE 15-5(e) ANALYSIS:** What is the pH of a buffer made by mixing 0.068 mol of  $\text{NH}_3$  and 0.049 mol of  $\text{NH}_4\text{Cl}$  in 2.0 L of solution? (Refer to Table 15-3.)

**EXERCISE 15-5(f) SYNTHESIS:** A 0.25 M solution of a hypothetical weak nitrogen base ( $\text{NX}_3$ ) is 1.0% ionized. What is  $K_b$ ?

**EXERCISE 15-5(g) SYNTHESIS:** If you wished to construct a buffer solution of  $\text{pH} = 7.0$  using compounds from Table 15-2, what would be the best choice? What ratio of anion to cation would produce the correct pH?

*For additional practice, work chapter problems 15-35, 15-39, 15-45, 15-51, and 15-56.*

## 15-6 SOLUBILITY EQUILIBRIA



**LOOKING AHEAD!** We mentioned in Chapters 5 and 12 that all salts have a specific solubility in water. In fact, saturated solutions of salts demonstrate a dynamic equilibrium between the solid salt and the ions in solution. This is reexamined in this section. ■

▶ OBJECTIVES FOR  
SECTION 15-6

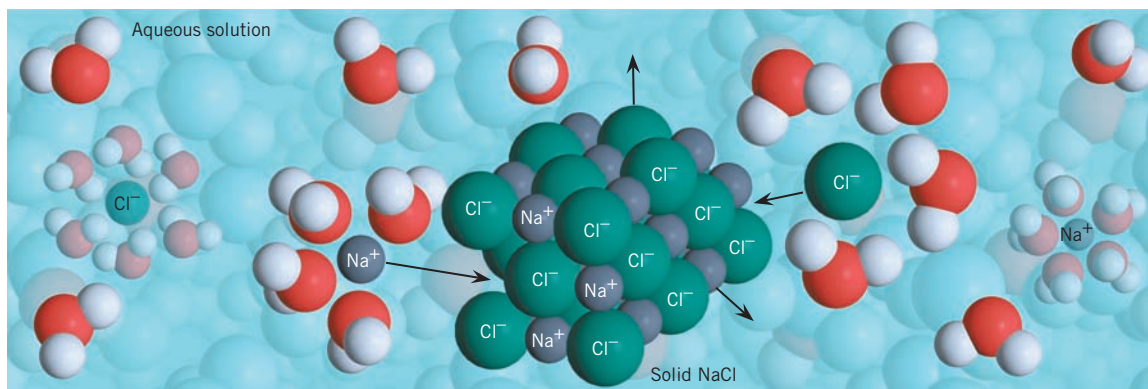
(a) Write the solubility constant expression for a specific ionic compound. (b) Calculate the value of the constant from molar solubility data. (c) Calculate the solubility of a chemical given its solubility constant.

Passing a kidney stone is an event that one does not easily forget. It can be as painful as childbirth. The most common type of kidney stone is composed of calcium oxalate ( $\text{CaC}_2\text{O}_4$ ), which can be deposited as a solid in the kidney in a typical precipitation reaction. Fortunately, a little knowledge of the equilibrium involved in the formation of kidney stones and an appropriate diet can help prevent their formation in the first place. We will return to kidney stones shortly.

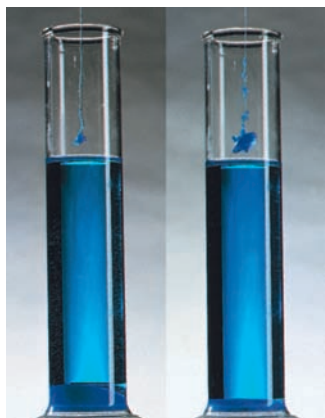
First we will review what happens when a salt such as  $\text{NaCl}$  is added to water. As discussed in Chapter 12, if enough solid is added to the water, the solution eventually becomes saturated. At this point it appears that the solution process has stopped. Instead, we find that the rate of solution of the salt is equal to the rate of deposition of the solid from the ions in solution and we have a dynamic equilibrium situation. (See Figure 15-13.) This is illustrated by the equilibrium shown below.



A common but interesting chemical phenomenon that is often displayed at science fairs is the science (and art) of crystal growing. Crystal growing demonstrates the principle of equilibrium. If a comparatively large crystal of a compound such as blue



**FIGURE 15-13 Solubility and Equilibrium** At equilibrium, the rate at which ions are dissolving equals the rate at which ions are forming the solid.

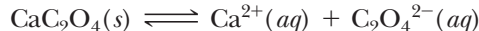


**FIGURE 15-14 Crystal Growth** After the  $\text{CuSO}_4$  crystal on the left was suspended in the solution for a few days, it grew larger.

$\text{CuSO}_4$  is suspended in a saturated solution of that compound, the small crystals at the bottom get smaller and the large one grows larger. The concentrations of  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  in solution remain constant, as does the total mass of solid crystals. The changing size of the crystals, however, indicates that an equilibrium exists in which the identities of ions in the solid and dissolved states are changing. (See Figure 15-14.) This phenomenon occurs because small crystals, with their greater surface area, dissolve faster than large crystals. Thus, although the total mass of the crystals remains constant, the unequal rate of solution favors solution of small crystals and precipitation on the large crystal.

### 15-6.1 The Solubility Product

Now consider the equilibrium between solid calcium oxalate and its ions in solution.



The extent of the solubility of this compound can be represented by an equilibrium constant known as the **solubility product constant ( $K_{\text{sp}}$ )** or simply the **solubility product**. In this case the constant expression is

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

It is set up like any other equilibrium constant expression except that the solid (on the left) is not included. The reason for this is that the concentration of a solid is a constant. *So, as long as at least some solid is present, how much solid is present is not relevant to the concentration of ions in solution.* Another example of a solubility product involves the solution of lead(II) chloride.



Notice that the  $[\text{Cl}^-]$  concentration is squared because there are two chlorides in the equilibrium equation.

The equilibrium constant expressions can be written for other salts, as illustrated in Example 15-10.

#### EXAMPLE 15-10

##### Writing the Equilibrium Constant Expressions for $K_{\text{sp}}$

Write the equilibrium constant expressions ( $K_{\text{sp}}$ ) for a solution of (a)  $\text{Ag}_2\text{CrO}_4$ , (b)  $\text{Fe}(\text{OH})_3$ , and (c)  $\text{Ca}_3(\text{PO}_4)_2$ .

##### PROCEDURE

Write the equations for the solution of the salts in water. The ionic solid is the reactant, and the aqueous ions are the products. It may be necessary to review Chapter 4 and specifically Table 4-2 to determine the identity of the ions formed from the compounds.

- (a)  $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$   
 (b)  $\text{Fe}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq})$   
 (c)  $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$

**SOLUTION**

- (a)  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$     (c)  $K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$   
 (b)  $K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3$

**ANALYSIS**

As ionic compound formulas involve cations and anions with charges of 3 or less, there are relatively few forms the solubility product can take:

| Salt Formula                                     | Solubility Product   |
|--|--|
| MX   | $K_{\text{sp}} = [\text{M}^+][\text{X}^-]$   |
| $\text{MX}_2$ or $\text{M}_2\text{X}$            | $K_{\text{sp}} = [\text{M}^{2+}][\text{X}^-]^2$ or $K_{\text{sp}} = [\text{M}^+]^2[\text{X}^{2-}]$           |
| $\text{MX}_3$ or $\text{M}_3\text{X}$            | $K_{\text{sp}} = [\text{M}^{3+}][\text{X}^-]^3$ or $K_{\text{sp}} = [\text{M}^+]^3[\text{X}^{3-}]$           |
| $\text{M}_2\text{X}_3$ or $\text{M}_3\text{X}_2$ | $K_{\text{sp}} = [\text{M}^{3+}]^2[\text{X}^{2-}]^3$ or $K_{\text{sp}} = [\text{M}^{2+}]^3[\text{X}^{3-}]^2$ |

Any of the compounds you'll run into will have one of these forms.

**SYNTHESIS**

For even the most difficult problems that chemists are likely to encounter, writing the reaction that is occurring is typically the first step. But since many reactions are equilibrium reactions, what you write as the reactant and what you write as the product are not always clear-cut. Any one of the reactions above could be written in the opposite direction and still be a valid chemical equation. The equilibrium expression would then simply be the reverse of the one we've already written, and the equilibrium constant would be the inverse of the reported value. Because there is no natural restriction on how we need to write a reaction, we have to agree to a convention that all chemists will follow. The convention for solubility products is to write the solid compound first, dissolving into its component ions.

**15-6.2 The Value of  $K_{\text{sp}}$** 

The values for  $K_{\text{sp}}$  are determined from molar solubility data, as illustrated in Examples 15-11 and 15-12.

**EXAMPLE 15-11****Determining  $K_{\text{sp}}$  from Solubility Data**

The molar solubility of AgCl is  $1.3 \times 10^{-5}$  mol/L. What is the value of  $K_{\text{sp}}$  for AgCl?

**PROCEDURE**

Write the equation for the solution of AgCl and the expression for  $K_{\text{sp}}$ .



Notice from the stoichiometry of the equilibrium that for every mole of AgCl that dissolves, one mole of  $\text{Ag}^+$  and one mole of  $\text{Cl}^-$  are formed. Therefore, the concentration of each ion is equal to the amount that dissolves, or the molar solubility.

**SOLUTION**

$$\begin{aligned} \text{solubility} &= 1.3 \times 10^{-5} \text{ mol/L} = [\text{Ag}^+] = [\text{Cl}^-] \\ [1.3 \times 10^{-5}][1.3 \times 10^{-5}] &= \underline{\underline{1.7 \times 10^{-10}}} \end{aligned}$$

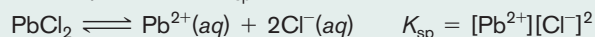


**EXAMPLE 15-12****Determining  $K_{sp}$  from Solubility Data**

What is the value of  $K_{sp}$  for  $PbCl_2$  if the molar solubility of this compound is  $3.9 \times 10^{-2}$  mol/L?

**PROCEDURE**

Write the solution equilibrium and the expression for  $K_{sp}$ .



Notice from the stoichiometry of the solution that for each mole of  $PbCl_2$  that dissolves, it produces one mole of  $Pb^{2+}$  and two moles of  $Cl^{-}$ . Therefore, the concentration of  $Pb^{2+}$  is equal to the actual moles/L that dissolve (i.e., the solubility), but the concentration of  $Cl^{-}$  is twice the solubility.

**SOLUTION**

$$[Pb^{2+}] = 3.9 \times 10^{-2} \quad [Cl^{-}] = 2 \times 3.9 \times 10^{-2} = 7.8 \times 10^{-2}$$

$$K_{sp} = [3.9 \times 10^{-2}] [7.8 \times 10^{-2}]^2 = (3.9 \times 10^{-2})(6.1 \times 10^{-3}) = \underline{\underline{2.4 \times 10^{-4}}}$$

**ANALYSIS**

Notice that the 2 in front of  $Cl^{-}$  is used twice—once to multiply the concentration by 2 and again to raise the concentration to the second power. What would it be for a hypothetical chemical  $M_2X_3$ , whose molar solubility is 0.10 mol/l? The 2 and the 3 would each be used twice:  $(2 \times 0.10)^2 \times (3 \times 0.10)^3 = 1.1 \times 10^{-3}$ .

**SYNTHESIS**

Unlike  $K_a$  for acids, the solubility of two different salts cannot be compared directly by simply observing the value of  $K_{sp}$ . In setting up the expression for  $K_a$ , the equilibrium constant expressions for weak acids were all the same. The equilibrium constant expressions for salts, however, take on various forms depending on the stoichiometry of the salts. For example, two salts,  $MX$  and  $MY_2$ , may have the same solubility (e.g.,  $10^{-2}$  mol/L) but very different values for  $K_{sp}$ . For  $MX$ ,  $K_{sp} = 1 \times 10^{-4}$  and for  $MY_2$ ,  $K_{sp} = 4 \times 10^{-6}$ .

**EXAMPLE 15-13****Determining Molar Solubility from  $K_{sp}$** 

What is the molar solubility of  $CaC_2O_4$ ? For  $CaC_2O_4$ ,  $K_{sp} = 2.1 \times 10^{-9}$ .

**PROCEDURE**

Write the solution equilibrium for  $CaC_2O_4$  and the expression for  $K_{sp}$ .



Notice that the number of moles of  $Ca^{2+}$  in solution is equal to the number of moles of  $C_2O_4^{2-}$  and both are equal to the molar solubility. We will let  $x$  = the molar solubility.

**SOLUTION**

If  $x$  = the molar solubility, then at equilibrium  $[Ca^{2+}] = [C_2O_4^{2-}] = x$ .

Thus  $[x][x] = K_{sp} = 2.1 \times 10^{-9}$ .

Taking the square root of  $K_{sp}$ , the molar solubility is  $\underline{\underline{4.6 \times 10^{-5}$  mol/L}.

**ANALYSIS**

When one dozen pairs of shoes dissociate, they form one dozen right shoes and one dozen left shoes. One dozen pairs produces two dozen shoes. Likewise, one mole of  $CaC_2O_4$  produces one mole of  $Ca^{2+}$  and one mole of  $C_2O_4^{2-}$ . To extend this to the abstract,  $x$  moles of  $CaC_2O_4$  dissociate into  $x$  moles of  $Ca^{2+}$  and  $x$  moles of  $C_2O_4^{2-}$ .

**SYNTHESIS**

Consider a more complex case where you are asked to calculate the molar solubility of a salt such as  $PbI_2$ . In this case,  $x$  would equal the concentration of  $Pb^{2+}$ , as in this example, but the concentration of  $I^{-}$  would be  $2x$ . The solution has  $4x^3$  equal to  $K_{sp}$ . See if you can set this up.

### 15-6.3 $K_{sp}$ and the Formation of Precipitates

Now we return to the formation of calcium oxalate kidney stones as described at the beginning of this section. Why does calcium oxalate precipitate from an aqueous solution such as the bloodstream? In a complex system such as in our blood,  $\text{Ca}^{2+}$  ion and  $\text{C}_2\text{O}_4^{2-}$  ion originate from many sources, so they are not exactly equal. However, whenever the product of the concentrations of the two ions is equal to  $K_{sp}$ , the solution is saturated and at equilibrium. In Example 15-14 we have calculated the concentration of oxalate that is present in a saturated solution with a specific calcium ion concentration. The answer represents the maximum amount of that ion that can be present without formation of solid calcium oxalate. If the concentration of  $\text{Ca}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  is such that the product of their concentrations is greater than the value for  $K_{sp}$ , the system is not at equilibrium. *To reestablish equilibrium, the concentration of the ions must decrease by coming together to form a precipitate.* So how does one use this information to avoid calcium oxalate kidney stones? A stone (precipitate) will not form if the product of the ion concentrations is equal to or less than  $K_{sp}$ . There are three ways to accomplish this. (1) Lower the concentration of both ions by dilution. In other words, drink plenty of water. This is always a good idea. (2) Lower the concentration of  $\text{Ca}^{2+}$  ion. This is not a good idea.  $\text{Ca}^{2+}$  is also incorporated into teeth and bones. If we lower the  $\text{Ca}^{2+}$  ion concentration too much, the solubility equilibrium involving bones may be affected and cause bone tissue to dissolve (osteoporosis). We don't want to avoid kidney stones by having brittle bones. (3) Lower the concentration of oxalate ion. Many foods such as celery, spinach, and beets have relatively high amounts of oxalate salts. If one is susceptible to these types of kidney stones, the best advice is to drink plenty of water and limit high-oxalate foods (which also include chocolate, unfortunately).

#### EXAMPLE 15-14

##### Determining the Concentrations of Ions in a Saturated Solution

What is the maximum oxalate ion concentration in a solution where  $[\text{Ca}^{2+}] = 4.4 \times 10^{-4} \text{ mol/L}$ ?

##### PROCEDURE

Solve for  $[\text{C}_2\text{O}_4^{2-}]$  in the expression for  $K_{sp}$ .

##### SOLUTION

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

$$[\text{C}_2\text{O}_4^{2-}] = K_{sp}/[\text{Ca}^{2+}] = 2.1 \times 10^{-9}/4.4 \times 10^{-4} = 4.8 \times 10^{-6} \text{ M}$$

If the concentration of oxalate were any higher than the calculated value, a precipitate of  $\text{CaC}_2\text{O}_4$  would form.

##### ANALYSIS

It is important to note that the concentrations of ions do not have to be the same for a precipitate to form. The critical point is that if the ion product, set up like the equilibrium constant expression, exceeds the value of  $K_{sp}$  a precipitate forms. In fact, as you can see from the expression, the higher the concentration of oxalate ion, the lower the concentration of calcium ion that can be tolerated before a solid forms. Also, it does not matter what other ions may be present. For example, the  $\text{Ca}^{2+}$  may be in solution from a variety of compounds and the oxalate may have entered the blood in solution as sodium oxalate.

##### SYNTHESIS

This concept can also be used in conjunction with pH. Most hydroxides of metals have very low solubilities. Since one of the ions produced in solution is the  $\text{OH}^-$  ion, addition of acid to the solution will affect the solubility. This is because the added  $\text{H}^+$  reacts with  $\text{OH}^-$  to form water (neutralization). According to Le Châtelier's principle, removing the  $\text{OH}^-$  ion in the equilibrium leads to a shift of the equilibrium to the right. Therefore, most metal hydroxides are more soluble at lower pH's than they are at higher pH's. Water companies make use of this fact to treat hard water by increasing the pH of the water at the processing plant. Increasing the pH, along with adding "flocculants," causes metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , which cause hard water in many locales, to precipitate out as solid hydroxides. This solid is then allowed to settle, and is removed.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 15-6

**EXERCISE 15-6(a) KNOWLEDGE:** Write the solubility constant expression for  $\text{Mg}_3(\text{PO}_4)_2$ .

**EXERCISE 15-6(b) ANALYSIS:** The solubility of  $\text{Mg}(\text{OH})_2$  is  $1.3 \times 10^{-4}$  mol/L. What is the value of  $K_{\text{sp}}$ ?

**EXERCISE 15-6(c) ANALYSIS:** What is the molar solubility of barium carbonate? For  $\text{BaCO}_3$ ,  $K_{\text{sp}} = 8.1 \times 10^{-9}$ .

**EXERCISE 15-6(d) ANALYSIS:** What is the  $\text{Mg}^{2+}$  concentration in a solution with  $\text{pH} = 10.00$ ? Use  $K_{\text{sp}}$  for  $\text{Mg}(\text{OH})_2$  from the Exercise 15-6(b).

**EXERCISE 15-6(e) SYNTHESIS:** Which compound is more soluble in mol/L,  $\text{CuI}$  ( $K_{\text{sp}} = 1.1 \times 10^{-12}$ ) or  $\text{Ni}(\text{OH})_2$  ( $K_{\text{sp}} = 2.0 \times 10^{-15}$ )? Would the addition of acid to either of these solutions affect the solubility?

For additional practice, work chapter problems 15-62 and 15-66.

PART B  
SUMMARY

## KEY TERMS

- 15-4.1** The **equilibrium constant ( $K_{\text{eq}}$ )** has a specific value. The **equilibrium constant expression** is a fraction related to the equilibrium involved. p. 485
- 15-5.1** The equilibrium constant expression for a weak acid is known as the **acid ionization constant ( $K_{\text{a}}$ )** and for a base is known as the **base ionization constant ( $K_{\text{b}}$ )**. p. 490
- 15-5.5** The **Henderson–Hasselbalch equation** is used to calculate the pH of a buffer solution. p. 495
- 15-6.1** The solubility of an ionic compound in water can be expressed as a **solubility product constant ( $K_{\text{sp}}$ )** or simply **solubility product**. p. 498

## SUMMARY CHARTS

## Equilibrium Constant Expressions

| Gases   | Weak Acid in Water  | Ionic Compound in Water  |
|---|---|--|
| $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$ | $\text{HX}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-(\text{aq})$ | $\text{MX}_2 \rightleftharpoons \text{M}^{2+}(\text{aq}) + 2\text{X}^-(\text{aq})$ |
| $K_{\text{eq}} = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]}$                      | $K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$                                     | $K_{\text{sp}} = [\text{M}^{2+}][\text{X}^-]^2$                                    |

## CHAPTER SUMMARY

This chapter concerns several important chemistry topics, such as how reactions take place, the rates at which they occur, and the point of equilibrium in reversible reactions. **Collision theory** tells us that reactions take place through collisions of molecules. The **rate of a reaction** is determined by the frequency of these collisions and the **activation energy** of the reaction. There are several things that influence these two factors and thus

affect the rate of the reaction. These are: (1) The magnitude of the *activation energy*. Each set of potential reactants requires a different amount of energy to form the **activated complex** that leads to the formation of products. If collisions do not have the necessary kinetic energy, no products form. (2) The *temperature*. (3) The *concentration of reactants*. (4) The *particle size* in the case of heterogeneous reactions. (5) A **catalyst**.

**Reversible reactions** often reach a **point of equilibrium** where measurable concentrations of reactants and products coexist. In fact, a **dynamic equilibrium** exists because both the forward and reverse reactions are occurring at the same rate. The point of equilibrium can be influenced by reaction conditions. However, changes in these reaction conditions have a predictable effect on the point of equilibrium, which is correlated by **Le Châtelier's principle**. The factors that can shift the point of equilibrium include (1) *concentration*, (2) *pressure*, and (3) *temperature*.

For exothermic reactions, an increase in temperature leads to a decrease in the proportion of products. Just the opposite occurs for an endothermic reaction. Many important industrial reactions do not take place readily, or even at all, without a catalyst present. A catalyst brings a reaction mixture to the point of equilibrium faster but does not change the actual point of equilibrium.

The distribution of concentrations of reactants and products can be predicted. This is done using a numerical value ( $K_{\text{eq}}$ ) called the **equilibrium constant**, which

is equal to a ratio of reactants and products constructed from the balanced equation and known as the **equilibrium constant expression**.

The value of the equilibrium constant at a given temperature is obtained by experimental measurements of the distribution of reactants and products at equilibrium. The constant and the initial concentrations can then be used to calculate the concentration of a given gas or ion at equilibrium.

The equilibrium of weak acids and bases can also be expressed in terms of an equilibrium constant expression. The **acid ionization constants** for weak acids ( $K_{\text{a}}$ ) and the **base ionization constants** for weak bases ( $K_{\text{b}}$ ) are useful for calculation of the pH of these solutions. We are also able to use equilibrium constants to calculate the pH of buffers. The **Henderson–Hasselbalch equation** can be used to calculate the pH of buffer solutions. The solubility of salts in water is determined by the equilibrium constant  $K_{\text{sp}}$ , which is known as the **solubility product constant** or simply the **solubility product**.  $K_{\text{sp}}$  can be calculated from solubility data, and vice versa.

|         |   | OBJECTIVES       |                |                    |
|---------|---|------------------|----------------|--------------------|
| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES         | EXERCISES      | CHAPTER PROBLEMS   |
| 15-1    | Describe on a molecular level how a chemical reaction takes place.                                      |                  | 1a, 1c         | 2, 4               |
|         | Create an energy diagram for an exothermic or endothermic reaction.                                     |                  | 1b, 1c         | 8, 9               |
| 15-2    | List the factors that affect the rate of a chemical reaction.   |                  | 2a, 2b         |                    |
| 15-3    | Describe systems that reach a point of equilibrium.   |                  | 3a, 3b, 3d     | 18                 |
|         | Using Le Châtelier's principle, list the conditions that can affect the point of equilibrium.           |                  | 3c             | 11, 13             |
| 15-4    | Write the equilibrium constant expression for reactions that take place in the gaseous state.           | 15-1             | 4a, 4b, 4e     | 15, 16             |
|         | Calculate the value of the equilibrium constant given equilibrium concentrations.                       | 15-2, 15-3, 15-4 | 4c, 4d         | 20, 22, 24, 26, 29 |
| 15-5    | Write equilibrium constant expressions for species in aqueous solution.                                 |                  | 5a             | 35, 36, 37         |
|         | Calculate the value of $K_{\text{a}}$ or $K_{\text{b}}$ for a weak acid or base given appropriate data. | 15-5, 15-6       | 5b, 5f         | 41, 42             |
|         | Calculate the pH of a weak acid or base solution given $K_{\text{a}}$ or $K_{\text{b}}$ .               | 15-7, 15-8, 15-9 | 5c, 5d, 5e, 5g | 46, 48, 50, 52, 57 |
| 15-6    | Write the solubility constant expression for a specific ionic compound.                                 | 15-10            | 6a             | 60, 61             |
|         | Calculate the value of the constant from molar solubility data.   | 15-11, 15-12     | 6b             | 63, 64, 65         |
|         | Calculate the solubility of a chemical given its solubility constant.                                   | 15-13, 15-4      | 6c, 6d, 63     | 67, 68, 69         |

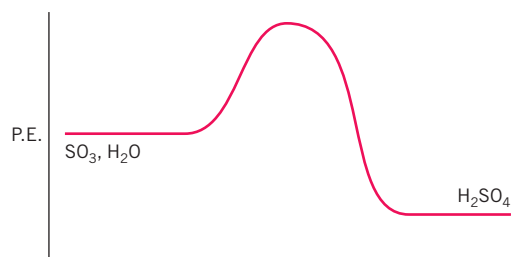
## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

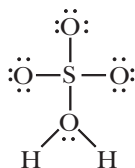
## EXERCISES

**15-1(a)** Chemical reactions occur because of collisions between reactant molecules. In order for a reaction to take place, molecules must collide in the proper orientation and with a minimum amount of energy, known as the activation energy. An activated complex forms at the point of maximum potential energy.

**15-1(b)**



**15-1(c)**



To form the product molecule, a hydrogen must transfer from the oxygen in the water molecule to another oxygen. Sulfuric acid has two  $\text{—O—H}$  bonds.

**15-2(a)** The rate of appearance of a product as a function of time is a measure of the rate of the reaction. At higher temperatures, more molecules can overcome this energy barrier, so the rate of the reaction increases. Increasing the concentration of colliding molecules increases the rate of the reaction. The presence of a catalyst does not change the distribution of products, but it increases the rate of the reaction.

**15-2(b)** (a) Cooling the body slows the rate of metabolism, which means organs like the brain can go longer without oxygen. This increases the time that blood flow can be interrupted before damage occurs. (b) Pure oxygen increases the concentration of a reactant of combustion. This increases the rate of the reaction and the amount of heat generated. (c) Manganese dioxide acts as a catalyst, which increases the rate of the reaction. (d) Enzymes are biological catalysts. They are necessary to break down sugars or to cause thousands of other chemical reactions in the human body.

**15-3(a)** Reactions that are reversible may reach a point of equilibrium where the concentrations of reactants and products remain constant. The point of equilibrium may be affected by a change of concentrations of reactants, a change of temperature, and a change of pressure (in a gaseous system).

**15-3(b)** A catalyst does not increase the amount of product formed (b). It just produces it faster. It also does not change the heat of the reaction (e).

**15-3(c)** (a) increased (b) decreased (c) increased (d) decreased (e) not affected

**15-3(d)** Recall that all reactions slow as the temperature decreases. We reach a point where the reaction stops as the temperature is lowered. The temperature must be raised for the reaction to proceed, even though the yield of product is reduced.

## PART B

## EXERCISES

**15-4(a)** A gaseous equilibrium can be expressed as a number known as the equilibrium constant and a ratio of reactants and products known as the equilibrium constant expression. A small value for  $K_{sp}$  (e.g.,  $10^{-5}$ ) indicates that reactants are favored at equilibrium.

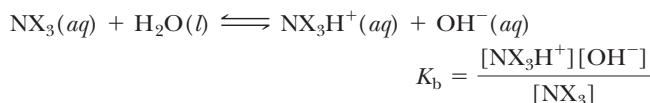
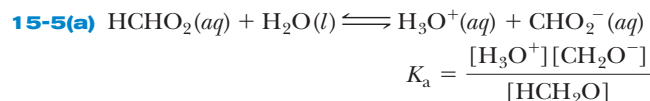
**15-4(b)**

$$\begin{aligned}
 \text{(a)} \quad K_{eq} &= \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \\
 \text{(b)} \quad K_{eq} &= \frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]}
 \end{aligned}$$

$$\begin{aligned}
 \text{15-4(c)} \quad K_{eq} &= \frac{\left[\frac{3.5 \times 10^{-4} \text{ mol}}{10.0 \text{ L}}\right] \left[\frac{5.0 \times 10^{-5} \text{ mol}}{10.0 \text{ L}}\right]}{\left[\frac{2.0 \times 10^{-3} \text{ mol}}{10.0 \text{ L}}\right] \left[\frac{1.0 \times 10^{-2} \text{ mol}}{10.0 \text{ L}}\right]^3} \\
 &= \frac{17.5 \times 10^{-11}}{2.0 \times 10^{-13}} = \underline{880}
 \end{aligned}$$

**15-4(d)** (a)  $K_{eq} = 20$  (b)  $[\text{NOBr}] = 0.94 \text{ mol/L}$

**15-4(e)** The concentration (mol/L) of a pure solid or liquid is essentially a constant, just like its density (g/mL). Pressure and temperature have little effect on the volume of a liquid or solid. On the other hand, the concentration of a gas is a variable very much dependent on the temperature and pressure. Only variables appear in the equilibrium constant expression. As long as  $\text{CaCO}_3$  and  $\text{CaO}$  are present, the distribution of reactants and products at equilibrium depends only on the concentration of  $\text{CO}_2$ .





$$15-5(b) \quad [H_3O^+] = [\text{anion}] = 1.3 \times 10^{-3}$$

$$\frac{(1.3 \times 10^{-3})(1.3 \times 10^{-3})}{0.10} = 1.7 \times 10^{-5}$$

$$[\text{Acid}] = 0.10 - 0.0013 = 0.10$$

This  $K_a$  is closest to acetic acid ( $HC_2H_3O_2$ ).

$$15-5(c) \quad pK_b = 3.13$$

$$pOH = pK_b + \log \frac{[\text{acid}]}{[\text{base}]}$$

for equi molar amounts of acid and base,

$$pOH = pK_b + \log 1$$

$$pOH = 3.13 \quad \underline{pH = 10.87}$$

$$15-5(d) \quad \text{From Table 15-2 for } HCHO_2, K_a = 1.8 \times 10^{-4}.$$

Let  $x = [H_3O^+] = [CHO_2^-]$  at equilibrium. Then

$$[HCHO_2] = 0.10 - x \approx 0.10 \text{ at equilibrium.}$$

$$\frac{x^2}{0.10} = 1.8 \times 10^{-4} \quad x^2 = 1.8 \times 10^{-5} \quad x = 4.2 \times 10^{-3}$$

$$pH = -\log(4.2 \times 10^{-3}) = \underline{2.38}$$

$$15-5(e) \quad \text{The base species is } NH_3: [\text{base}] = 0.068 \text{ mol}/2.0 \text{ L}$$

The acid species is  $NH_4^+$ :  $[\text{acid}] = 0.049 \text{ mol}/2.0 \text{ L}$

(The  $Cl^-$  is a spectator ion and is not part of the equilibrium.)

$$pOH = 4.74 + \log \frac{(0.049 \text{ mol}/2.0 \text{ L})}{(0.068 \text{ mol}/2.0 \text{ L})} = 4.74 - 0.14 = 4.60$$

$$pH = 14.00 - 4.60 = \underline{9.40}$$

$$15-5(f) \quad [OH^-] = [NX_3H^+] = 0.0025, [NX_3] = 0.25$$

$$K_b = 2.5 \times 10^{-5}$$

**15-5(g)** Try to match the pH to the  $pK_a$ . The closest is hypochlorous acid, with a  $pK_a = 7.5$ . The two compounds should therefore be  $HClO$  and its salt,  $NaClO$  (as an example). Use the Henderson–Hasselbalch equation to determine the ratio of the two.  $7.0 = 7.5 + \log [ClO^-]/[HClO]$

$$\log [ClO^-]/[HClO] = -0.5$$

$$[ClO^-]/[HClO] \approx 1/3$$

A 3:1 mole ratio of  $HClO$  to  $NaClO$  will buffer a solution at  $pH = 7.0$

$$15-6(a) \quad K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2$$

$$15-6(b) \quad K_{sp} = [1.3 \times 10^{-4}][2.6 \times 10^{-4}]^2 = 8.8 \times 10^{-12}$$

$$15-6(c) \quad x^2 = 8.1 \times 10^{-9} \quad x = 9.0 \times 10^{-5}$$

$$15-6(d) \quad [Mg^{2+}][OH^-]^2 = 8.8 \times 10^{-12} \quad [Mg^{2+}] = K_{sp}/[OH^-]^2$$

If  $pH = 10.00$ ,  $pOH = 4.00$ ,  $[OH^-] = 1.0 \times 10^{-4}$

$$[Mg^{2+}] = 8.8 \times 10^{-12}/(1.0 \times 10^{-4})^2 = 8.8 \times 10^{-4} \text{ mol/L}$$

**15-6(e)** You cannot compare  $K_{sp}$  values directly. Calculate solubilities.

$$CuI: K_{sp} = [Cu^+][I^-] \quad 1.1 \times 10^{-12} = x^2$$

$$x = 1.1 \times 10^{-6} \text{ mol/L}$$

$$Ni(OH)_2: K_{sp} = [Ni^{2+}][OH^-]^2 \quad 2.0 \times 10^{-15} = 4x^3$$

$$x = 7.9 \times 10^{-6} \text{ mol/L}$$

$Ni(OH)_2$  is marginally more soluble despite the smaller  $K_{sp}$ . However, because it contains  $OH^-$ , it is susceptible to pH. Decreasing the pH decreases the  $OH^-$  concentration and increases the solubility of the compound.

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

### Collision Theory and Reaction Rates

#### (SECTIONS 15-1 AND 15-2)

**15-1.** Explain why all collisions between reactant molecules do not lead to products.

**15-2.** The equation



represents a reaction in which the mechanism of the forward reaction involves a collision between the two reactant molecules. Describe the probable orientation of the molecules in this collision.

**15-3.** Explain the following facts from your knowledge of collision theory and the factors that affect the rates of reactions.

- The rates of chemical reactions approximately double for each  $10^\circ\text{C}$  rise in temperature.
- Eggs cook more slowly in boiling water at higher altitudes where water boils at temperatures less than  $100^\circ\text{C}$ .
- $H_2$  and  $O_2$  do not start to react to form  $H_2O$  except at very high temperatures (unless initiated by a spark).
- Wood burns explosively in pure  $O_2$  but slowly in air, which is about 20%  $O_2$ .
- Coal dust burns faster than a single lump of coal.

- Milk sours if left out for a day or two but will last two weeks in the refrigerator.
- $H_2$  and  $O_2$  react smoothly at room temperature in the presence of finely divided platinum.

**15-4.** Explain the following facts from your knowledge of collision theory and the factors that affect the rates of reactions.

- A wasp is lethargic at temperatures below  $65^\circ\text{F}$ .
- Charcoal burns faster if you blow on the coals.
- A 0.10 M boric acid solution ( $[H_3O^+] = 7.8 \times 10^{-6}$ ) can be used for eyewash, but a 0.10 M hydrochloric acid solution ( $[H_3O^+] = 0.10$ ) would cause severe damage.
- To keep apple juice from fermenting to apple cider, the apple juice must be kept cold.
- Coal does not spontaneously ignite at room temperature, but white phosphorus does.
- Potassium chlorate decomposes at a much lower temperature when mixed with  $MnO_2$ .

### Equilibrium and Le Châtelier's Principle

#### (SECTION 15-3)

**15-5.** Explain the point of equilibrium in terms of reaction rates.

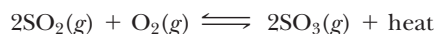
**15-6.** In the hypothetical reaction between  $A_2$  and  $B_2$ , when was the rate of the forward reaction at a maximum? In the same reaction, when was the rate of the reverse reaction at a maximum? (Refer to Figure 15-12.)

**15-7.** Give a reason, besides reaching a point of equilibrium, why certain reactions do not go to completion (100% to the right).

**15-8.** Compare the activation energy for the reverse reaction with that for the forward reaction in Figure 15-3. Which are easier to form, reactants from products or products from reactants? Which system would come to equilibrium faster, a reaction starting with pure products or one starting with pure reactants?

**15-9.** Consider an endothermic reaction that comes to a point of equilibrium such as shown in Figure 15-4. Which is greater, the activation energy for the forward or for the reverse reaction? Which system would come to equilibrium faster, a reaction starting with pure products or one starting with pure reactants?

**15-10.** The following equilibrium represents an important industrial process to produce sulfur trioxide, which is then converted to sulfuric acid. More sulfuric acid is manufactured on a worldwide bases by this process than any other chemical. The production of sulfur trioxide from sulfur dioxide is aided by a catalyst. Sulfur dioxide is produced from the combustion of elemental sulfur or sulfur compounds. The reaction is run at about  $400^\circ\text{C}$ .



Determine the direction in which the equilibrium will be shifted by the following changes.

- increasing the concentration of  $\text{O}_2$
- increasing the concentration of  $\text{SO}_3$
- decreasing the concentration of  $\text{SO}_2$
- decreasing the concentration of  $\text{SO}_3$
- compressing the reaction mixture
- removing the catalyst
- How will the yield of  $\text{SO}_3$  be affected by raising the temperature to  $750^\circ\text{C}$ ?
- How will the yield of  $\text{SO}_3$  be affected by lowering the temperature to  $0^\circ\text{C}$ ? How will this affect the rate of formation of  $\text{SO}_3$ ?

**15-11.** Consider the equilibrium



How will this system at equilibrium be affected by the following changes?

- increasing the concentration of  $\text{O}_2$
- removing all of the  $\text{H}_2\text{O}$  as it is formed
- increasing the concentration of  $\text{NO}$
- compressing the reaction mixture
- increasing the volume of the reaction container
- increasing the temperature
- decreasing the concentration of  $\text{O}_2$
- adding a catalyst

**15-12.** The following equilibrium takes place at high temperatures.



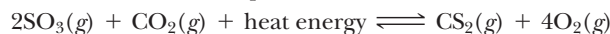
How will the concentration of  $\text{NO}$  at equilibrium be affected by these changes?

- increasing  $[\text{N}_2]$
- decreasing  $[\text{H}_2]$
- compressing the reaction mixture
- decreasing the volume of the reaction container

(e) decreasing the temperature

(f) adding a catalyst

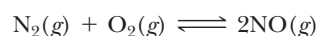
**15-13.** Consider the equilibrium



How will the concentration of  $\text{CS}_2$  at equilibrium be affected by these changes?

- decreasing the volume of the reaction vessel
- adding a catalyst
- increasing the temperature
- increasing the original concentration of  $\text{CO}_2$
- removing some  $\text{O}_2$  as it forms

**15-14.** Fortunately for us, the major components of air,  $\text{N}_2$  and  $\text{O}_2$ , do not react under ordinary conditions. The reaction shown is endothermic.



Would the formation of  $\text{NO}$  in an automobile be affected by these changes?

- a lower pressure
- a lower temperature
- a lower concentration of  $\text{O}_2$

## The Equilibrium Constant Expression

### (SECTION 15-4)

**15-15.** Write the equilibrium constant expression for each of the following equilibria.

- $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$
- $\text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + 4\text{H}_2(g)$
- $4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$
- $\text{CH}_4(g) + \text{Cl}_2(g) \rightleftharpoons \text{CH}_3\text{Cl}(g) + \text{HCl}(g)$

**15-16.** Write the equilibrium constant expression for each of the following equilibria.

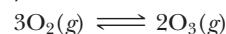
- $3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$
- $\text{N}_2(g) + 2\text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$
- $\text{C}_2\text{H}_2(g) + 2\text{H}_2(g) \rightleftharpoons \text{C}_2\text{H}_6(g)$
- $4\text{H}_2(g) + \text{CS}_2(g) \rightleftharpoons \text{CH}_4(g) + 2\text{H}_2\text{S}(g)$

**15-17.** For the hypothetical reaction  $A_2 + B_2 \rightleftharpoons 2AB$ ,  $K_{\text{eq}} = 1.0 \times 10^8$ , are reactants or products favored at equilibrium?

**15-18.** For the hypothetical reaction  $2C + 3B \rightleftharpoons 2D + F$ ,  $K_{\text{eq}} = 5 \times 10^{-7}$ , are reactants or products favored at equilibrium?

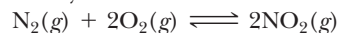
**15-19.** For the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ ,  $K_{\text{eq}} = 45$  at a given temperature, are reactants or products favored at equilibrium?

**15-20.** Given the system



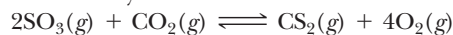
at equilibrium,  $[\text{O}_2] = 0.35$  and  $[\text{O}_3] = 0.12$ . What is  $K_{\text{eq}}$  for the reaction under these conditions?

**15-21.** Given the system



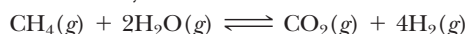
at a given temperature, there are  $1.25 \times 10^{-3}$  mol of  $\text{N}_2$ ,  $2.50 \times 10^{-3}$  mol of  $\text{O}_2$ , and  $6.20 \times 10^{-4}$  mol of  $\text{NO}_2$  in a 1.00-L container. What is  $K_{\text{eq}}$  for this reaction at this temperature?

**15-22.** Given the system



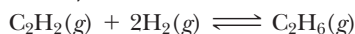
what is  $K_{\text{eq}}$  if, at equilibrium,  $[\text{SO}_3] = 2.0 \times 10^{-2}$  mol/L,  $[\text{CO}_2] = 4.5 \times 10^{-3}$  mol/L,  $[\text{CS}_2] = 6.2 \times 10^{-4}$  mol/L, and  $[\text{O}_2] = 1.0 \times 10^{-4}$  mol/L?

**15-23.** Given the system



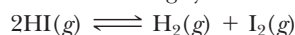
at equilibrium, we find 2.20 mol of  $\text{CO}_2$ , 4.00 mol of  $\text{H}_2$ , 6.20 mol of  $\text{CH}_4$ , and 3.00 mol of  $\text{H}_2\text{O}$  in a 30.0-L container. What is  $K_{\text{eq}}$  for the reaction? (*Hint:* Convert amount and volume to concentration.)

**15-24.** Given the system



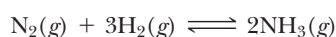
at equilibrium, we find 296 g of  $\text{C}_2\text{H}_6$  present along with 3.50 g of  $\text{H}_2$  and 21.0 g of  $\text{C}_2\text{H}_2$  in a 400-mL container. What is  $K_{\text{eq}}$ ? (*Hint:* Convert amount and volume to concentration.)

**\*15-25.** Consider the following system:



- If we start with  $[\text{HI}] = 0.60$ , what would  $[\text{H}_2]$  and  $[\text{I}_2]$  be if all the HI reacts?
- If we start with  $[\text{HI}] = 0.60$  and  $[\text{I}_2] = 0.20$ , what would  $[\text{H}_2]$  and  $[\text{I}_2]$  be if all the HI reacts?
- If we start with only  $[\text{HI}] = 0.60$  and 0.20 mol/L of HI reacts, what are  $[\text{HI}]$ ,  $[\text{I}_2]$ , and  $[\text{H}_2]$  at equilibrium?
- From the information in (c), calculate  $K_{\text{eq}}$ .
- What is the  $K_{\text{eq}}$  for the reverse reaction? How does this value differ from the value given in Table 15-1?

**\*15-26.** In the reaction



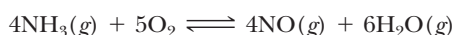
initially 1.00 mol of  $\text{N}_2$  and 1.00 mol of  $\text{H}_2$  are mixed in a 1.00-L container. At equilibrium, it is found that  $[\text{NH}_3] = 0.20$ .

- What are the concentrations of  $\text{N}_2$  and  $\text{H}_2$  at equilibrium?
- What is the  $K_{\text{eq}}$  for the system at this temperature?

**\*15-27.** At a given temperature,  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  are mixed. The initial concentration of each is 0.50 mol/L. At equilibrium, the concentration of  $\text{N}_2$  is 0.40 mol/L.

- Calculate the concentrations of  $\text{H}_2$  and  $\text{NH}_3$  at equilibrium.
- What is the  $K_{\text{eq}}$  at this temperature?

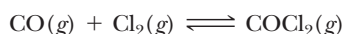
**\*15-28.** At the start of the reaction



$[\text{NH}_3] = [\text{O}_2] = 1.00$ . At equilibrium, it is found that 0.25 mol/L of  $\text{NH}_3$  has reacted.

- What concentration of  $\text{O}_2$  reacts?
- What are the concentrations of all species at equilibrium?
- Write the equilibrium constant expression and substitute the proper values for the concentrations of reactants and products.

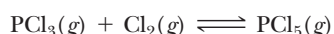
**\*15-29.** At the start of the reaction



$[\text{CO}] = 0.650$  and  $[\text{Cl}_2] = 0.435$ . At equilibrium, it is found that 10.0% of the CO has reacted. What are  $[\text{CO}]$ ,  $[\text{Cl}_2]$ , and  $[\text{COCl}_2]$  at equilibrium? What is  $K_{\text{eq}}$ ?

### Calculations Involving $K_{\text{eq}}$ (SECTION 15-4)

**15-30.** For the reaction



$K_{\text{eq}} = 0.95$  at a given temperature. If  $[\text{PCl}_3] = 0.75$  and  $[\text{Cl}_2] = 0.40$  at equilibrium, what is the concentration of  $\text{PCl}_5$  at equilibrium?

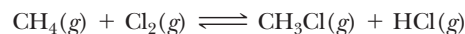
**15-31.** At a given temperature,  $K_{\text{eq}} = 46.0$  for the reaction

$$4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$$

At equilibrium,  $[\text{HCl}] = 0.100$ ,  $[\text{O}_2] = 0.455$ , and  $[\text{H}_2\text{O}] = 0.675$ . What is  $[\text{Cl}_2]$  at equilibrium?

**15-32.** Using the value for  $K_{\text{eq}}$  calculated in problem 15-23, find the concentration of  $\text{H}_2\text{O}$  at equilibrium if, at equilibrium,  $[\text{CH}_4] = 0.50$ ,  $[\text{CO}_2] = 0.24$ , and  $[\text{H}_2] = 0.20$ .

**\*15-33.** For the following equilibrium,  $K_{\text{eq}} = 56$  at a given temperature.



At equilibrium,  $[\text{CH}_4] = 0.20$  and  $[\text{Cl}_2] = 0.40$ . What are the equilibrium concentrations of  $\text{CH}_3\text{Cl}$  and  $\text{HCl}$  if they are equal?

**\*15-34.** Using the equilibrium in problem 15-20, calculate the equilibrium concentration of  $\text{O}_3$  if the equilibrium concentration of  $\text{O}_2$  is 0.80 mol/L.

### Equilibria of Weak Acids and Weak Bases

#### (SECTION 15-5)

**15-35.** Write the expression for  $K_a$  or  $K_b$  for each of the following equilibria. Where necessary, complete the equilibrium.

- $\text{HBrO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{BrO}^-$
- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_3^-$
- $\text{HSO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{_____} + \text{SO}_3^{2-}$
- $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{_____}$
- $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{_____}$

**15-36.** Write the expression for  $K_a$  or  $K_b$  for each of the following equilibria. Where necessary, complete the equilibrium.

- $\text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OH}^-$
- $\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$
- $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{_____}$
- $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{_____} + \text{HPO}_4^{2-}$

**15-37.** A 0.10 M solution of a weak acid HX has a pH of 5.0. A 0.10 M solution of another weak acid HB has a pH of 5.8. Which is the weaker acid? Which has the larger value for  $K_a$ ?

**15-38.** A hypothetical weak acid HZ has a  $K_a$  of  $4.5 \times 10^{-4}$ . Rank the following 0.10 M solutions in order of increasing pH: HZ,  $\text{HC}_2\text{H}_3\text{O}_2$ , and  $\text{HClO}$ .

**15-39.** In a 0.20 M solution of cyanic acid,  $\text{HOCN}$ ,  $[\text{H}_3\text{O}^+] = [\text{OCN}^-] = 6.2 \times 10^{-3}$ .

- What is  $[\text{HOCN}]$  at equilibrium?
- What is  $K_a$ ?
- What is the pH?

**15-40.** A 0.58 M solution of a weak acid (HX) is 10.0% dissociated.

- Write the equilibrium equation and the equilibrium constant expression.
- What are  $[\text{H}_3\text{O}^+]$ ,  $[\text{X}^-]$ , and  $[\text{HX}]$  at equilibrium?
- What is  $K_a$ ?
- What is the pH?

**15-41.** Nicotine (Nc) is a nitrogen base in water (similar to ammonia). Write the equilibrium equation illustrating this base behavior. In a 0.44 M solution of nicotine,  $[\text{OH}^-] = [\text{NcH}^+] = 5.5 \times 10^{-4}$ . What is  $K_b$  for nicotine? What is the pH of the solution?

**15-42.** In a 0.085 M solution of carboic acid,  $\text{HC}_6\text{H}_5\text{O}$ , the pH = 5.48. What is  $K_a$ ?

**15-43.** Novocaine (Nv) is a nitrogen base in water (similar to ammonia). Write the equilibrium equation. In a 1.25 M solution of novocaine,  $\text{pH} = 11.46$ . What is  $K_b$ ?

**15-44.** In a 0.300 M solution of chloroacetic acid ( $\text{HC}_2\text{Cl}_3\text{O}_2$ ),  $[\text{HC}_2\text{Cl}_3\text{O}_2] = 0.277 \text{ M}$  at equilibrium. What is the  $\text{pH}$ ? What is  $K_a$ ?

**15-45.** What is the  $\text{pH}$  of a 0.65 M solution of  $\text{HBrO}$ ?

**15-46.** What is the  $\text{pH}$  of a 1.50 M solution of  $\text{HNO}_2$ ?

**15-47.** What is  $[\text{OH}^-]$  in a 0.55 M solution of  $\text{NH}_3$ ?

**15-48.** What is  $[\text{H}_3\text{O}^+]$  in a 0.25 M solution of  $\text{HC}_2\text{H}_3\text{O}_2$ ?

**15-49.** What is the  $\text{pH}$  of a 1.00 M solution of  $(\text{CH}_3)_2\text{NH}$ ?

**15-50.** What is the  $\text{pH}$  of a 0.567 M solution of  $\text{N}_2\text{H}_4$ ?

**15-51.** What is the  $\text{pH}$  of a buffer made by mixing 0.45 mol of  $\text{NaCN}$  and 0.45 mol of  $\text{HCN}$  in 2.50 L of solution?

**15-52.** What is the  $\text{pH}$  of a buffer made by dissolving 1.20 mol of  $\text{NH}_3$  and 1.20 mol of  $\text{NH}_4\text{ClO}_4$  in 13.5 L of solution?

**15-53.** What is the  $\text{pH}$  of a buffer made by dissolving 0.20 mol of  $\text{KBrO}$  and 0.60 mol of  $\text{HBrO}$  in 850 mL of solution? What is the  $\text{pH}$  if the solution is diluted to 2.00 L?

**15-54.** What is the  $\text{pH}$  of a buffer solution made by mixing 0.044 mol of  $\text{HCHO}_2$  with 0.064 mol of  $\text{KCHO}_2$  in 1.00 L of solution?

**15-55.** What is the  $\text{pH}$  of a buffer solution made by mixing 0.058 mol of  $\text{HClO}$  and 5.50 g of  $\text{Ca}(\text{ClO})_2$  in a certain amount of water?

**15-56.** What is the  $\text{pH}$  of a buffer made by mixing 1.50 g of  $\text{N}_2\text{H}_4$  with 1.97 g of  $\text{N}_2\text{H}_5^+\text{Cl}^-$  in 2.00 L of solution?

**15-57.** What is the  $\text{pH}$  of a buffer that contains 150 g of  $\text{HNO}_2$  and 150 g of  $\text{LiNO}_2$ ?

**\*15-58.** A buffer of  $\text{pH} = 7.50$  is desired. Which two of the following compounds should be dissolved in water in equimolar amounts to provide this buffer solution:  $\text{HNO}_2$ ,  $\text{HClO}$ ,  $\text{HCN}$ ,  $\text{NaNO}_2$ ,  $\text{NH}_3$ ,  $\text{KCN}$ ,  $\text{KClO}$ ,  $\text{NH}_4\text{Cl}$ ?

**\*15-59.** A buffer of  $\text{pH} = 9.25$  is desired. Which two of the following compounds should be dissolved in water in equimolar amounts to provide this buffer solution:  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{HClO}$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{KC}_2\text{H}_3\text{O}_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaClO}$ ,  $\text{N}_2\text{H}_5\text{Br}$ ?

### Solubility Equilibria (SECTION 15-6)

**15-60.** Write the expression of  $K_{\text{sp}}$  for the following salts: (a)  $\text{FeS}$ , (b)  $\text{Ag}_2\text{S}$ , (c)  $\text{Zn}(\text{OH})_2$ .

**15-61.** Write the expression for  $K_{\text{sp}}$  for the following salts: (a)  $\text{PbCO}_3$ , (b)  $\text{Bi}_2\text{S}_3$ , (c)  $\text{PbI}_2$ .

**15-62.** What is the value of  $K_{\text{sp}}$  for copper(I) iodide if the molar solubility is  $2.2 \times 10^{-6} \text{ mol/L}$ ?

**15-63.** What is the value of  $K_{\text{sp}}$  for magnesium carbonate ( $\text{MgCO}_3$ ) if a saturated solution contains 0.287 g/L?

**15-64.** What is the value of  $K_{\text{sp}}$  for  $\text{Ca}(\text{OH})_2$  if the molar solubility is  $1.3 \times 10^{-2} \text{ mol/L}$ ?

**\*15-65.** What is the value of  $K_{\text{sp}}$  for  $\text{Cr}(\text{OH})_3$  if the molar solubility is  $3 \times 10^{-8} \text{ mol/L}$ ?

**15-66.** What is the molar solubility of  $\text{AgI}$ ? For  $\text{AgI}$ ,  $K_{\text{sp}} = 8.3 \times 10^{-17}$ .

**\*15-67.** Lead(II) fluoride is present in the earth as the mineral fluorite. It is considered insoluble in water. What is the molar solubility of lead(II) fluoride? For  $\text{PbF}_2$ ,  $K_{\text{sp}} = 4.1 \times 10^{-8}$ .

**15-68.** The concentration of  $\text{Ag}^+$  ion in a solution is  $7 \times 10^{-6} \text{ M}$ , and the concentration of  $\text{Br}^-$  is  $8 \times 10^{-7} \text{ M}$ . Will a precipitate of  $\text{AgBr}$  form? For  $\text{AgBr}$ ,  $K_{\text{sp}} = 7.7 \times 10^{-13}$ .

**15-69.** The concentration of  $\text{Ag}^+$  in a solution is 0.012 M, and the concentration of  $\text{SO}_4^{2-}$  is 0.050 M. Will a precipitate of  $\text{Ag}_2\text{SO}_4$  form? For  $\text{Ag}_2\text{SO}_4$ ,  $K_{\text{sp}} = 1.4 \times 10^{-5}$ .

### General Problems

**15-70.** In a given gaseous equilibrium, chlorine reacts with ammonia to produce nitrogen trichloride and hydrogen chloride.

(a) Write the balanced equation illustrating this equilibrium.

(b) Write the expression for  $K_{\text{eq}}$ .

(c) How is the equilibrium concentration of ammonia affected by an increase in pressure?

(d) How is the equilibrium concentration of ammonia affected by the addition of some chlorine gas?

(e) The value of  $K_{\text{eq}}$  for this reaction is  $2.4 \times 10^{-9}$ . Are there more products or reactants present at equilibrium?

(f) If the equilibrium concentrations of chlorine = 0.10 M, nitrogen trichloride =  $2.0 \times 10^{-4} \text{ M}$ , and hydrogen chloride =  $1.0 \times 10^{-3} \text{ M}$ , what is the equilibrium concentration of ammonia?

**15-71.** In a given gaseous equilibrium, acetylene ( $\text{C}_2\text{H}_2$ ) reacts with  $\text{HCl}$  to form  $\text{C}_2\text{H}_4\text{Cl}_2$ .

(a) Write the balanced equation illustrating this equilibrium.

(b) Write the expression for  $K_{\text{eq}}$ .

(c) How does an increase in pressure affect the equilibrium concentration of  $\text{C}_2\text{H}_4\text{Cl}_2$ ?

(d) The reaction is exothermic. How does an increase in temperature affect the value of  $K_{\text{eq}}$ ? How does it affect the equilibrium concentration of  $\text{HCl}$ ?

(e) At a given temperature at equilibrium,  $[\text{C}_2\text{H}_2] = 0.030$ ,  $[\text{HCl}] = 0.010$ , and  $[\text{C}_2\text{H}_4\text{Cl}_2] = 0.60$ . What is the value of  $K_{\text{eq}}$ ?

(f) What does the value of  $K_{\text{eq}}$  tell us about the point of equilibrium at this temperature?

**15-72.** Dinitrogen oxide (nitrous oxide) decomposes to its elements in a gaseous equilibrium reaction.

(a) Write the balanced equation illustrating this equilibrium.

(b) Write the expression for  $K_{\text{eq}}$ .

(c) How does an increase in pressure affect the equilibrium concentration of nitrogen?

(d) If the reaction is exothermic, how does a decrease in temperature affect the equilibrium concentration of dinitrogen oxide?

(e) At a given temperature, 0.10 mol of dinitrogen oxide is placed in a 1.00-L container. At equilibrium, it is found that 1.5% of the dinitrogen oxide has decomposed. What is the value of  $K_{\text{eq}}$ ?

**15-73.** Nitrogen dioxide is in a gaseous equilibrium with dinitrogen tetroxide.

(a) Write the balanced equation illustrating this reaction. Show nitrogen dioxide as the reactant and dinitrogen tetroxide as the product.

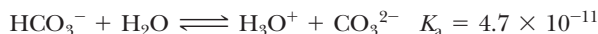
(b) Write the expression for  $K_{\text{eq}}$ .

(c) How does an increase in pressure affect the concentration of nitrogen dioxide at equilibrium?

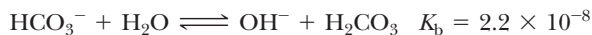
(d) At equilibrium at a given temperature, it is found that there are 10.0 g of nitrogen dioxide and 12.0 g of dinitrogen tetroxide in a 2.50-L container. What is the value of  $K_{\text{eq}}$ ?



**15-74.** The bicarbonate ion ( $\text{HCO}_3^-$ ) can act as either an acid or a base in water. For the acid reaction



For the base reaction



- Based on the values of  $K_a$  and  $K_b$ , is a solution of  $\text{NaHCO}_3$  acidic or basic?
- How is bicarbonate of soda used medically?
- Write the reaction that occurs when sodium bicarbonate reacts with stomach acid ( $\text{HCl}$ ).
- Can sodium bisulfate act in the same way toward acids as sodium bicarbonate does?

**\*15-75.** Given 0.10 M solutions of the compounds  $\text{KOH}$ ,  $\text{NaCl}$ ,  $\text{HNO}_2$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HCHO}_2$ , and  $\text{N}_2\text{H}_4$ , rank them in order of increasing pH.

**15-76.** What is the pH of a buffer that is made by mixing 265 mL of 0.22 M  $\text{HC}_2\text{H}_3\text{O}_2$  with 375 mL of 0.12 M  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ ?

**\*15-77.** What is the pH of a buffer made by adding 0.20 mol of  $\text{NaOH}$  to 1.00 L of a 1.00 M solution of  $\text{HC}_2\text{H}_3\text{O}_2$ ? Assume no volume change. (*Hint:* First consider the partial neutralization of  $\text{HC}_2\text{H}_3\text{O}_2$  by  $\text{NaOH}$ .)

**\*15-78.** What is the value of  $K_{sp}$  for  $\text{Mg}(\text{OH})_2$  if the pH of a saturated solution is equal to 10.50?

**\*15-79.** What is the pH of a saturated solution of  $\text{Fe}(\text{OH})_2$ ? For  $\text{Fe}(\text{OH})_2$ ,  $K_{sp} = 1.6 \times 10^{-14}$ .

**15-80.** Aqueous solutions of barium salts are very poisonous, yet we ingest barium sulfate as a contrasting agent for X-rays of the intestinal tract. What is the  $\text{Ba}^{2+}$  concentration in a saturated solution of  $\text{BaSO}_4$ ? What is the mass of  $\text{BaSO}_4$  present in one liter of solution? For  $\text{BaSO}_4$ ,  $K_{sp} = 1.1 \times 10^{-10}$ .

## STUDENT WORKSHOP

### Equilibrium and Le Châtelier's Principle

**Purpose:** To examine the effect of changes in concentration on the amounts of reactants and products of a reaction at equilibrium. (Work in groups of three or four. Estimated time: 25 min.)

In order to illustrate the interplay of chemicals involved in establishing equilibrium, play this little game. You'll require two dozen interlocking blocks (such as Lego<sup>®</sup>) in two colors. You'll assemble "molecules" based on the equation:



(In other words, the "reaction" is a block of each color combining together to form a product)

**The equilibrium condition is that there must be the same number of AB molecules as the total number of A's and B's.**

(Real equilibria work on the mathematical relationship between the concentrations of all reactants and products (i.e.,  $K_a$ ), but this serves as an easy way to illustrate the point.)

- Begin with 12 A and 12 B. How many AB's must you produce to establish equilibrium?
- Perturb the system by adding an additional 6 A's from the reserve. How must things alter to reestablish equilibrium?

3. Now take away 3 AB's. What has to happen?

4. Add 9 B's. How does the equilibrium shift?

5. Add 6 AB's. What are the new values for each chemical species?

Fill in the following chart for each of the changes:

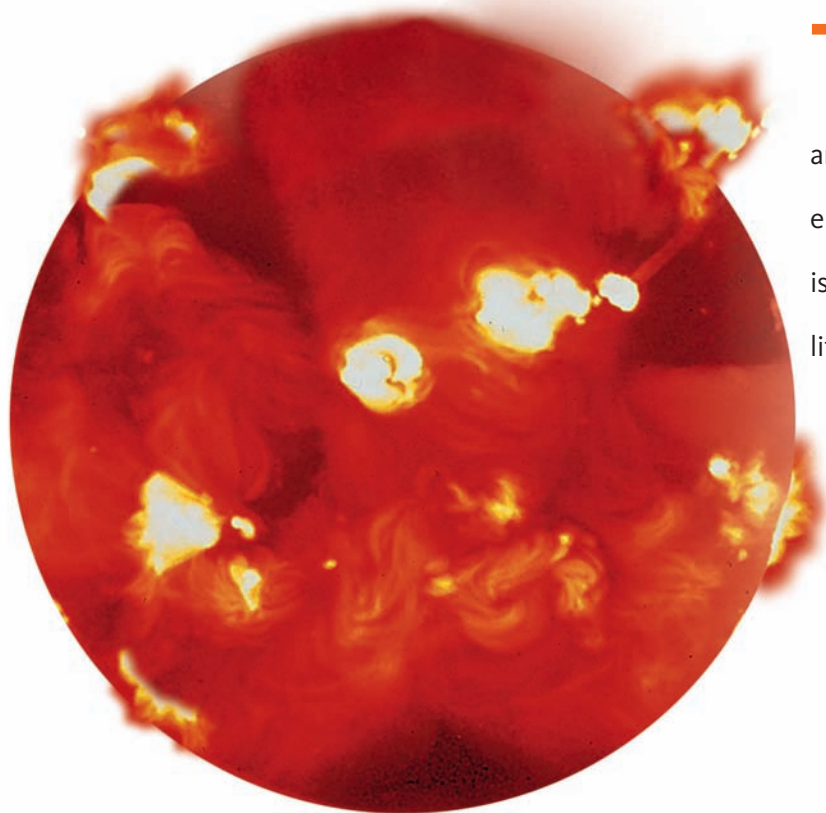
| Initial |       | Shift<br>←, → |       | Equilibrium |       |       |
|---------|-------|---------------|-------|-------------|-------|-------|
| A       | B     | AB            | #     | A           | B     | AB    |
| 12      | 12    | 0             | 8-    | 4           | 4     | 8     |
| _____   | _____ | _____         | _____ | _____       | _____ | _____ |
| _____   | _____ | _____         | _____ | _____       | _____ | _____ |
| _____   | _____ | _____         | _____ | _____       | _____ | _____ |
| _____   | _____ | _____         | _____ | _____       | _____ | _____ |

- In what other ways can you alter the equilibrium position?
- How would the dynamics change if the equation were  $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$ ?



# CHAPTER 16

## Nuclear Chemistry



**T**he sun is the source of life. Deep in its interior, nuclear reactions are occurring that liberate energy. This energy is transmitted to us as light. It is the source of the energy that makes life possible.

**PART A**  
**NATURALLY OCCURRING**  
**RADIOACTIVITY**

**16-1** Radioactivity

**16-2** Rates of Decay of Radioactive  
Isotopes

**16-3** The Effects of Radiation

 **MAKING IT REAL**

*Radioactivity and Smoke Detectors*

**16-4** The Detection and Measurement  
of Radiation

**PART B**  
**INDUCED NUCLEAR**  
**CHANGES AND THEIR USES**

**16-5** Nuclear Reactions

**16-6** Applications of Radioactivity

**16-7** Nuclear Fission and Fusion

 **MAKING IT REAL**

*Revisiting the Origin of the Elements*

**SETTING THE STAGE** In July 1945, the most powerful explosion yet produced by the human race shook the New Mexico desert. The first nuclear bomb had been detonated, and our world would never be the same—the nuclear age was now upon us. But the dawn of this age actually began quite innocently 49 years earlier. At that time, there was certainly no intent to launch the human race in a radical new direction. In 1896, a French scientist named Henri Becquerel was investigating how sunlight interacted with a uranium mineral called pitchblende. He suspected that sunlight caused pitchblende to give off the mysterious “X-rays” that had been discovered the previous year by Wilhelm Roentgen. X-rays, a high-energy form of light, were known to penetrate the covering of photographic plates, thus exposing the film. One cloudy day, Becquerel was unable to do an experiment, but he left the uranium on top of unexposed film in a photographic plate. Several days later, he developed the film anyway and discovered that the part underneath the sample of pitchblende was exposed. Obviously, the uranium had spontaneously emitted some form of radiation that had nothing to do with sunlight. It was this discovery that marked the true beginning of the nuclear age.

Since we first discussed the atom in Chapter 2, we have addressed the results of interactions of the electrons that reside outside a tiny but comparatively massive nucleus. Interactions of electrons account for the way atoms of an element combine chemically with other atoms. Now we turn our attention to the nucleus, which is composed of two types of particles, neutrons and protons, both called nucleons. Also recall that elements are composed of isotopes. Isotopes of a specific element are those atoms that have the same number of protons but different numbers of neutrons.

As we will see, most natural nuclear processes transform one element into another. Deep in castle dungeons around 600 years ago, alchemists thought, or at least hoped, that they could accomplish this feat. Actually, it wasn't just any element they wanted to produce—it was gold. The synthesis of one element from another never happened at that time, but it wasn't long into the nuclear age that this was actually accomplished. Beginning with a simple experiment by Lord Rutherford in the early 1900s and extending to the use of huge accelerators today, humans have been transforming the elements.

In Part A, we examine in more detail the changes that can occur in the nucleus of a particular isotope as a result of the radiation that Becquerel first observed. In Part B, we will see how human intervention has produced results that range from the fear of nuclear bombs to the hope of nuclear medicine.

## PART A NATURALLY OCCURRING RADIOACTIVITY

### SETTING A GOAL

- You will learn of the different types of radiation and how it affects surrounding matter.

### OBJECTIVES

- 16-1** Write balanced nuclear equations for the five types of radiation.
- 16-2** Using half-lives, estimate the time needed for various amounts of radioactive decay to occur.
- 16-3** Describe how the three natural types of radiation affect matter.
- 16-4** Describe the common methods whereby radiation is detected and the units used to measure the amount of radiation.

### OBJECTIVE FOR SECTION 16-1

Write balanced nuclear equations for the five types of radiation.

## 16-1 RADIOACTIVITY

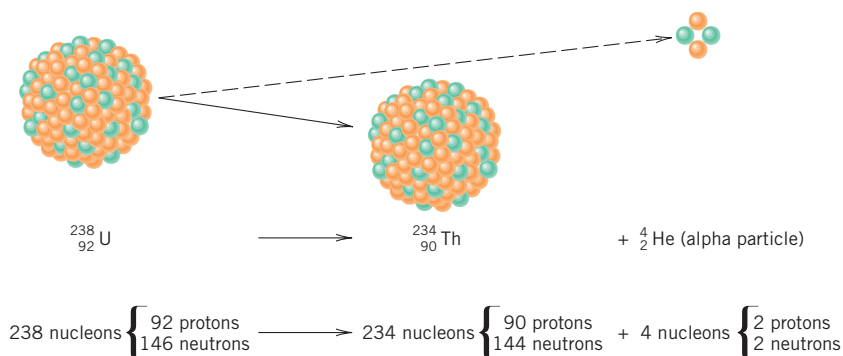


**LOOKING AHEAD!** It was a monumental discovery that one element could change into another through natural processes. We will look closely at the nature of those changes in this section. ■

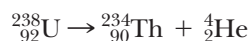
The radiation process discovered by Becquerel was more complex than originally thought. The term *radioactive* was first suggested by Marie Curie to describe elements that spontaneously emit **radiation** (*particles or energy*). Marie Curie and her husband, Pierre Curie, pursued the observation of Becquerel and discovered several more naturally **radioactive isotopes** of elements besides uranium (thorium, polonium, and radium). Lord Rutherford later identified three types of natural radiation. We will look at these three processes individually, as well as two additional processes since discovered.

### 16-1.1 Alpha ( $\alpha$ ) Particles

The first nuclear change that was identified involved the emission of a helium nucleus from the nucleus of a heavy isotope. *The emitted helium nucleus, composed of two protons and two neutrons but no electrons, is referred to as an alpha ( $\alpha$ ) particle.* This process is conveniently illustrated by a nuclear equation. A **nuclear equation** shows the initial nucleus to the left of the reaction arrow and the product nuclei or particles to the right of the arrow. Just as chemical equations are balanced, so are nuclear equations. Nuclear equations are balanced by having the same totals of positive charges (the numbers that are subscripts on the left of the symbol) and mass numbers (the numbers that are superscripts on the left of the symbol) on both sides of the equation. The emission of an alpha particle by  $^{238}\text{U}$  is illustrated in Figure 16-1 and represented by the following nuclear equation.



**FIGURE 16-1** Alpha Radiation An alpha particle is a helium nucleus emitted from a larger nucleus.



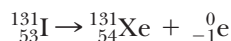
Note that the loss of four nucleons from the original (parent) nucleus leaves the remaining (daughter) nucleus with 234 nucleons ( $238 - 4 = 234$ ); the loss of two

protons leaves 90 protons in the daughter nucleus ( $92 - 2 = 90$ ). Because a nucleus with 90 protons is an isotope of thorium, one element has indeed changed into another.

### 16-1.2 Beta ( $\beta$ ) Particles

A second form of radiation involves the emission of an electron from the nucleus. *An electron emitted from the nucleus is known as a beta ( $\beta$ ) particle.*

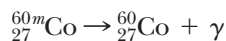
*In effect, beta particle emission changes a neutron in a nucleus into a proton.* This causes the atomic number of the isotope to increase by 1 while the mass number remains constant. This type of radiation is illustrated in Figure 16-2 and represented by the following nuclear equation.



Notice that, as with alpha radiation, the sum of the atomic masses and the atomic numbers on both sides of the arrow are the same.

### 16-1.3 Gamma ( $\gamma$ ) Rays

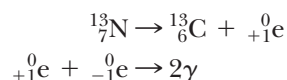
*A third type of radioactive decay involves the emission of a high-energy form of light called a gamma ( $\gamma$ ) ray.* Like all light, gamma rays travel at  $3.0 \times 10^{10}$  cm/sec (186,000 mi/sec). This type of radiation may occur alone or in combination with alpha or beta radiation. The following equation illustrates gamma ray emission.



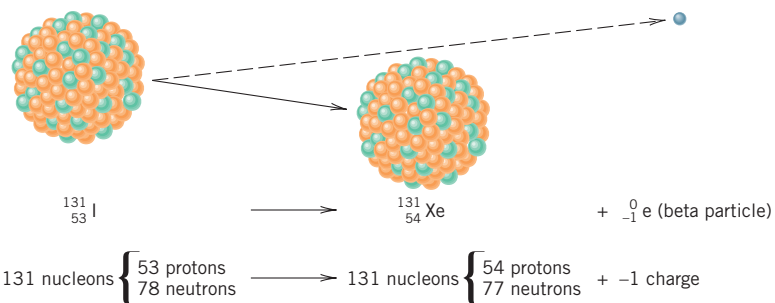
Gamma radiation alone does not result in a change in either the mass number or the atomic number of the isotope. In the equation shown above, the *m* stands for *metastable*, which means that the isotope is in a high-energy state. A nucleus in a metastable, or high-energy, state may emit energy in the form of gamma radiation. The product nucleus has the same identity but is then in a lower energy state.

### 16-1.4 Positron Particles and Electron Capture

This type of radiation is not among the three types of naturally occurring radiation but is found in a few artificially produced isotopes. A **positron ( ${}_{+1}^0\text{e}$ ) particle** is an electron with a positive charge rather than a negative charge. *In effect, positron emission changes a proton into a neutron.* As a result, the product nucleus has the same mass number but a lower atomic number. A positron is known as a form of *antimatter* because, when it comes in contact with normal matter (e.g., a negatively charged electron), the two particles annihilate each other, producing two gamma rays that travel in exactly opposite directions.



Another nuclear process, known as **electron capture**, involves *the capture of an inner-shell electron by the nucleus.* This process is very rare in nature but is more common in artificially produced elements. When an isotope captures an orbital electron, the effect is the same as positron emission. *That is, a proton changes into a neutron.* Electron capture is detected by the X-rays that are emitted as outer electrons fall into the inner shell, where there is a vacancy due to the captured electron. In most cases, gamma rays are also emitted by the product nuclei. Electron capture is illustrated by the following nuclear equation.

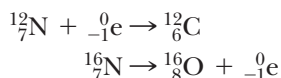


**FIGURE 16-2 Beta Radiation** A beta particle is an electron emitted from a nucleus.

### 16-1.5 The Mode of Decay

Why one isotope is stable and another is not is a somewhat involved topic. We can, however, make some simple observations. Notice that the atomic masses of most of the lighter elements in the periodic table are about double their atomic numbers. That is because the most common isotopes of these elements have equal numbers of protons and neutrons, or nearly so (e.g.,  ${}^4\text{He}$ ,  ${}^{16}\text{O}$ ,  ${}^{40}\text{Ca}$ ,  ${}^{32}\text{S}$ ). The heavier elements, however, tend to have more neutrons than protons in their most common and stable isotopes.

Notice that an isotope, such as  ${}^{14}\text{C}$ , has eight neutrons and six protons, so it has two more neutrons than its common stable isotope  ${}^{12}\text{C}$ . Such an isotope is radioactive, and we might expect it to decay by a process that would increase the number of protons and decrease the number of neutrons. This would be accomplished if a neutron turned into a proton. That process is beta particle emission. The result of this radiation is a change to a more stable neutron/proton ratio (e.g.,  ${}^{14}_7\text{N} + {}^0_{-1}\text{e}$ ). Isotopes that have excess protons (e.g.,  ${}^{10}\text{C}$ ) also tend to be radioactive but decay by positron emission (or electron capture). The result of this radiation is a change of a proton into a neutron and, again, a more stable nucleus with a better neutron/proton ratio (e.g.,  ${}^{10}_5\text{B} + {}^0_{+1}\text{e}$ ). For example, consider the four known isotopes of nitrogen— ${}^{12}\text{N}$ ,  ${}^{14}\text{N}$ ,  ${}^{15}\text{N}$ , and  ${}^{16}\text{N}$ .  ${}^{12}\text{N}$  decays by electron capture to form the stable isotope  ${}^{12}\text{C}$ .  ${}^{14}\text{N}$  and  ${}^{15}\text{N}$  are stable.  ${}^{16}\text{N}$  decays by beta particle emission to form the stable isotope  ${}^{16}\text{O}$ .



Since the heaviest stable element is bismuth, isotopes heavier than bismuth must all lose both mass and charge to become stable. This is alpha particle emission.

The five types of radiation that have been discussed are summarized in Table 16-1.

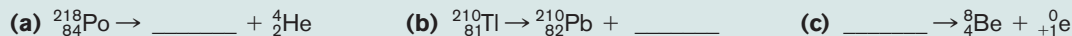
**TABLE 16-1** Types of Radiation

| RADIATION          | MASS NUMBER | CHARGE | IDENTITY                  |
|--------------------|-------------|--------|---------------------------|
| alpha ( $\alpha$ ) | 4           | +2     | helium nucleus            |
| beta ( $\beta$ )   | 0           | -1     | electron (out of nucleus) |
| gamma ( $\gamma$ ) | 0           | 0      | light energy              |
| positron           | 0           | +1     | positive electron         |
| electron capture   | 0           | -1     | electron (into nucleus)   |

#### EXAMPLE 16-1

##### Writing Equations for Nuclear Decay

Complete the following nuclear equations



##### PROCEDURE

For the missing isotope or particle:

- Find the total number of nucleons; it is the same on both sides of the equation.
- Find the total charge or atomic number; it is also the same on both sides of the equation.
- If what's missing is the isotope of an element, find the symbol of the element that matches the atomic number from the list of elements inside the front cover.

##### SOLUTION

- (a) Nucleons:  $218 = x + 4$ , so  $x = 214$   
Atomic number:  $84 = y + 2$ , so  $y = 82$



From the inside cover, the element having an atomic number of 82 is Pb. The isotope is



(b) Nucleons:  $210 = 210 + x$ , so  $x = 0$

Atomic number:  $81 = 82 + y$ , so  $y = -1$

An electron or beta particle has negligible mass (compared with a nucleon) and a charge of  $-1$ .



(c) Nucleons:  $x = 8 + 0$ , so  $x = 8$

Atomic number:  $y = 4 + 1$ , so  $y = 5$

From the inside cover, the element with an atomic number of 5 is B. The isotope is



### ANALYSIS

Radioactive particles are either emitted (alpha particles, beta particles, positrons) and are therefore found on the product side of a nuclear equation, or absorbed (electrons by electron capture) and therefore appear on the reactant side of the equation. Each one has a symbol and a specific charge (lower left) and mass (upper left) associated with that symbol. Referring to Table 16-1, can you write the symbol for each?  ${}^4_2\alpha$  for alpha,  ${}^0_{-1}\beta$  for beta,  ${}^0_{+1}\text{e}$  for a positron, and  ${}^0_{-1}\text{e}$  for an electron being captured. ( ${}^0_0\gamma$  for gamma radiation can be included, but it doesn't affect the mathematics.) Once the equation is completed, confirm that the superscripts on both sides of the arrow add up to the same value and that the subscripts do likewise.

### SYNTHESIS

Recall that we can predict what type of emission may occur based on the ratio of protons to neutrons in an isotope. Each element on the periodic table with an atomic number less than bismuth has at least one stable isotope (except Pm and Tc). Furthermore, the stable isotopes have atomic masses very close to their average atomic masses listed on the periodic table. If the mass number of a particular isotope is very much above this number, we would predict beta particle emission. If, on the other hand, the mass number is very much below average, we would predict positron emission (or electron capture). For very large isotopes (ones larger than bismuth), alpha emission, which lowers the size of the nucleus, is the most common form of radiation.

## ASSESSING THE OBJECTIVE FOR SECTION 16-1

**EXERCISE 16-1(a) KNOWLEDGE:** Fill in the blanks.

There are five types of \_\_\_\_\_.

1. An alpha particle is a \_\_\_\_\_ nucleus.
2. A beta particle is an \_\_\_\_\_.
3. A gamma ray is a high-energy form of \_\_\_\_\_.
4. A positron is a \_\_\_\_\_ \_\_\_\_\_ \_\_\_\_\_.
5. Electron capture has the same effect on a nucleus as \_\_\_\_\_ emission.

**EXERCISE 16-1(b) ANALYSIS:** Write the radioactive isotope that leads to the indicated nucleus and particle or ray.

- (a) \_\_\_\_\_  $\rightarrow$   ${}^{87}_{38}\text{Sr}$  + beta particle      (d) \_\_\_\_\_ + electron capture  $\rightarrow$   ${}^{123}_{51}\text{Sb}$   
 (b) \_\_\_\_\_  $\rightarrow$   ${}^{223}_{87}\text{Fr}$  + alpha particle      (e) \_\_\_\_\_  $\rightarrow$   ${}^{137}_{55}\text{Cs}$  + gamma ray  
 (c) \_\_\_\_\_  $\rightarrow$   ${}^{54}_{26}\text{Fe}$  + positron

**EXERCISE 16-1(c) SYNTHESIS:** Predict the mode of decay (beta particle or positron particle) if appropriate for the following isotopes: (a)  ${}^{14}\text{O}$ , (b)  ${}^{45}\text{Ca}$ , and (c)  ${}^{32}\text{S}$ .

For additional practice, work chapter problems 16-1, 16-16, and 16-18.

**OBJECTIVE FOR SECTION 16-2**

Using half-lives, estimate the time needed for various amounts of radioactive decay to occur.

**16-2 RATES OF DECAY OF RADIOACTIVE ISOTOPES**

**LOOKING AHEAD!** Uranium is a naturally occurring element, but it is radioactive. Why hasn't it all decayed by now? Why some radioactive elements are still present on this ancient Earth is the subject of this section. ■

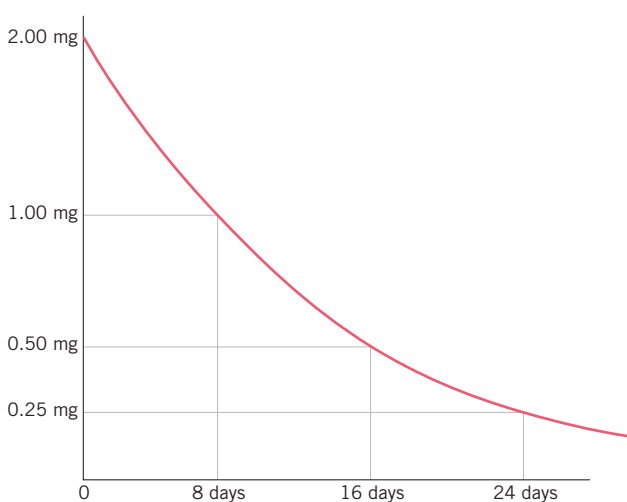
**16-2.1 Half-Life**

The heaviest element in the periodic table with at least one stable isotope is bismuth (#83). All elements heavier than bismuth have no stable isotopes (i.e., all isotopes are radioactive). Some heavy elements, such as uranium, still exist in the earth in significant amounts, however, because they have very long “half-lives.” The **half-life ( $t_{1/2}$ ) of a radioactive isotope is the time required for one-half of a given sample to decay.** There are also many isotopes lighter than bismuth that are also radioactive. Each radioactive isotope has a specific and constant half-life. Unlike the rate of chemical reactions, the half-life of an isotope is independent of conditions such as temperature, pressure, and whether the element is in the free state or part of a compound. The half-lives of radioactive isotopes vary from billions of years to fractions of a second. The half-lives and modes of decay of several radioactive isotopes are listed in Table 16-2.

**TABLE 16-2** Half-Lives

| ISOTOPE                  | $t_{1/2}$                | MODE OF DECAY    | PRODUCT                  |
|--------------------------|--------------------------|------------------|--------------------------|
| ${}_{92}^{238}\text{U}$  | $4.5 \times 10^9$ years  | $\alpha, \gamma$ | ${}_{90}^{234}\text{Th}$ |
| ${}_{94}^{242}\text{Pu}$ | $3.76 \times 10^5$ years | $\alpha$         | ${}_{92}^{238}\text{U}$  |
| ${}_{90}^{234}\text{Th}$ | 24.1 days                | $\beta$          | ${}_{91}^{234}\text{Pa}$ |
| ${}_{88}^{226}\text{Ra}$ | 1620 years               | $\alpha$         | ${}_{86}^{222}\text{Rn}$ |
| ${}_{6}^{14}\text{C}$    | 5760 years               | $\beta$          | ${}_{7}^{14}\text{N}$    |
| ${}_{53}^{131}\text{I}$  | 8.0 days                 | $\beta, \gamma$  | ${}_{54}^{131}\text{Xe}$ |
| ${}_{85}^{218}\text{At}$ | 1.3 seconds              | $\alpha$         | ${}_{83}^{214}\text{Bi}$ |

**FIGURE 16-3**  
**Radioactive Decay** The graph illustrates the progress of the decay of iodine-131.



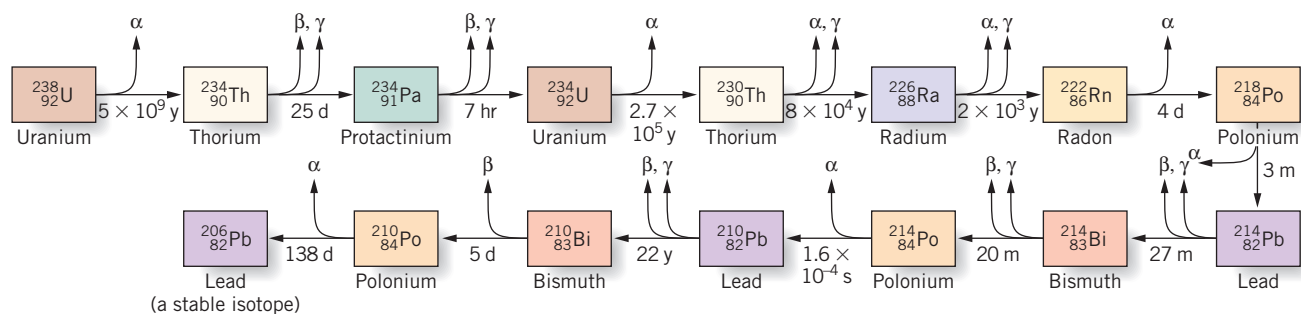
From Table 16-2, notice that  ${}^{131}\text{I}$  has a half-life of 8 days. If one started with 10.00 mg of  ${}^{131}\text{I}$ , there would be 5.00 mg left after 8 days. After 16 days (two half-lives), half of the amount present after 8 days would be left, which is 2.50 mg (1/4 of the original amount). After three half-lives, one-half of that would remain, which is 1.25 mg (1/8 of the original amount). A similar calculation is shown in Example 16-2.

The decay of an isotope is illustrated graphically in Figure 16-3.

**16-2.2 Radioactive Decay Series**

${}_{92}^{238}\text{U}$  has a half-life of  $4.5 \times 10^9$  years. Since that is roughly the age of Earth, about one-half of the  ${}_{92}^{238}\text{U}$  originally present when Earth formed from hot gases and dust is still present. (Half of what is now present will decay in another 4.5 billion years.)

Note in Table 16-2 that when  ${}_{92}^{238}\text{U}$  decays, it forms an isotope ( ${}_{90}^{234}\text{Th}$ ) that also decays (very rapidly compared with  ${}_{92}^{238}\text{U}$ ). The  ${}_{91}^{234}\text{Pa}$  formed from the decay of  ${}_{90}^{234}\text{Th}$  also decays and so forth, until finally the stable isotope,  ${}_{82}^{206}\text{Pb}$ , is formed. This is known as the  ${}_{92}^{238}\text{U}$  radioactive decay series. A **radioactive decay series** starts with a naturally occurring radioactive isotope



**FIGURE 16-4** Radioactive Decay Series This series starts with  $^{238}\text{U}$  and ends with  $^{206}\text{Pb}$ .

with a half-life near the age of Earth. (If it was very much shorter, there wouldn't be any left.) The series ends with a stable isotope. (See Figure 16-4.) There are at least two other naturally occurring decay series: the  $^{235}\text{U}$  series, which ends with  $^{207}\text{Pb}$ , and the  $^{232}\text{Th}$  series, which ends with  $^{208}\text{Pb}$ . As a result of the  $^{238}\text{U}$  decay series, where uranium is found in rocks, we also find other radioactive isotopes as well as lead. In fact, by examining the ratio of  $^{238}\text{U}$  to  $^{206}\text{Pb}$  in a rock, its age can be determined. For example, a rock from the moon showed that about half of the original  $^{238}\text{U}$  had decayed to  $^{206}\text{Pb}$ . This meant that the rock was formed about  $4.5 \times 10^9$  years ago.

### EXAMPLE 16-2

#### Calculating the Time to Decay

If we started with 4.0 mg of  $^{14}\text{C}$ , how long would it take until only 0.50 mg remained?

#### PROCEDURE

Find the half-life of  $^{14}\text{C}$  from Table 16-2 and calculate the amount remaining after each half-life.

#### SOLUTION

After each half-life, the amount is reduced by one-half.

$$\begin{aligned} \text{After 5760 years, } \frac{1}{2} \times 4.0 \text{ mg} &= 2.0 \text{ mg remaining} \\ \text{After another 5760 years, } \frac{1}{2} \times 2.0 \text{ mg} &= 1.0 \text{ mg remaining} \\ \text{After another 5760 years, } \frac{1}{2} \times 1.0 \text{ mg} &= 0.50 \text{ mg remaining} \\ \text{Total time} &= 17,280 \text{ years} \end{aligned}$$

Therefore, in 17,280 years, 0.50 mg remains.

#### ANALYSIS

It is often wrongly assumed that the half of a sample decays in the first half-life and the second half in the second half-life. In other words, it would all be gone in two half-lives. Note that each half-life starts with the amount remaining from the previous decay. If we started with one mole of particles ( $6.02 \times 10^{23}$ ), it would, theoretically, take 79 half-lives before every single particle decayed. In practice, our ability to detect isotopes fails long before the concentration falls that low.

#### SYNTHESIS

It is calculations like these that allow us to determine the age of objects containing radioactive particles. The natural amount of an isotope is established, and then, by detecting how much is left in a sample, we can calculate how many half-lives the sample has undergone. By working down, we can estimate the amount of time since the object was formed. We will give examples of such calculations later in this chapter.

### EXAMPLE 16-3

#### Calculating the Amount of Isotope Remaining

$^{103}\text{Pd}$  has a half-life of 17 days and is used to treat prostate cancer. A titanium capsule containing the isotope remains in the body after treatment. If  $10.0 \mu\text{g}$  ( $1 \mu\text{g} = 10^{-6} \text{g}$ ) is inserted into the prostate gland, how much of the radioactive isotope remains after 68 days?

**PROCEDURE**

Calculate how much would remain after each half-life. Determine the number of half-lives in 68 days (i.e.,  $68/7 = 4$ ).

**SOLUTION**

$$\begin{aligned} \text{After one half-life } & \frac{1}{2} \times 10.0 \mu\text{g} = 5.00 \mu\text{g} \\ \text{After two half-lives } & \frac{1}{2} \times 5.00 \mu\text{g} = 2.50 \mu\text{g} \\ \text{After three half-lives } & \frac{1}{2} \times 2.50 \mu\text{g} = 1.25 \mu\text{g} \\ \text{After four half-lives } & \frac{1}{2} \times 1.25 \mu\text{g} = 0.625 \mu\text{g} \end{aligned}$$

**ANALYSIS**

After four half-lives,  $0.625 \mu\text{g}$  remains, which means that in a little over two months only 6.25% of the radioactive isotope is still present. Even if the time period doesn't work out to exactly round numbers of half-lives, the amount can be estimated. (There are also specific equations that will allow us to calculate it directly, but they are beyond our scope.)

**SYNTHESIS**

In most cases, chemical reactions occur because two individual molecules collide. In other cases, there may be just one molecule involved in the reaction but some external energy source, such as heat or light, initiates the reaction. But a nuclear decay reaction is unique in that it involves just a single type of atom, and the impetus for the reaction comes internally from the atom itself. This is why the rate at which the reaction occurs, measured by the half-life, is not dependent on concentration, temperature, pressure, or any other external factor. Half-life is an innate function of the isotope itself.

**ASSESSING THE OBJECTIVE FOR SECTION 16-2**

**EXERCISE 16-2(a) KNOWLEDGE:** Which isotopes decay faster: ones with large half-lives or ones with small half-lives?

**EXERCISE 16-2(b) ANALYSIS:** What percent of an isotope has decayed after three half-lives?

**EXERCISE 16-2(c) ANALYSIS:** After 36.0 minutes, it was found that  $4.0 \mu\text{g}$  remains of a sample of a radioactive isotope that originally weighed  $64 \mu\text{g}$ . What is the half-life of the isotope?

**EXERCISE 16-2(d) SYNTHESIS:** Why is it not possible to isolate a pure sample of a radioactive substance?

*For additional practice, work chapter problems 16-20 and 16-22.*

**OBJECTIVE FOR SECTION 16-3**

Describe how the three natural types of radiation affect matter.

**16-3 THE EFFECTS OF RADIATION**

**LOOKING AHEAD!** We tend to fear the effects of radiation. Certainly, it may cause cancer and sickness, but this same radiation can save lives when used in medical diagnosis or cancer treatment. How radiation interacts with matter is our next subject. ■

A generation grew up with a deep fear of radiation as a result of a possible nuclear holocaust. Although the threat of nuclear bombs remains, we now see radiation in a more positive light because of all the medical applications that are in common use. The same radiation that we fear so much is also used to shrink cancerous tumors, treat other diseases, and diagnose illnesses that would otherwise go undetected.

**16-3.1 Generation of Heat**

Nuclear decay is a process in which a nucleus spontaneously gives off high-energy particles (alpha or beta) or high-energy light (gamma). The interaction of these fast-

moving particles or light waves with surrounding matter eventually results in increased velocity for all molecules in the area. In other words, the temperature increases. In fact, much of the heat generated in the interior of Earth and other planets is a direct result of natural radiation from decaying isotopes. The presence of radioactive isotopes in waste from nuclear power plants makes these materials extremely hot. In most cases the wastes must be stored in water continuously so that they do not melt.

### 16-3.2 Formation of Ions and Free Radicals

Radiation also interacts with matter to cause ionization. *Besides producing heat, collisions of radioactive particles or rays leave a trail of ions along their path, so this type of radiation is sometimes referred to as ionizing radiation.* The formation of ions is caused by the removal of an electron from a neutral molecule.

If high-energy particles or rays collide with an  $\text{H}_2\text{O}$  molecule, an electron may be ejected from the molecule, leaving an  $\text{H}_2\text{O}^+$  ion behind. The ion is chemically reactive and can be very destructive to biological molecules involved in life processes. If the molecule that is ionized is a large, complex molecule that is part of a cell in a living system, the ionization causes damage, mutation, or even eventual destruction of the cell.

Another important effect of radiation is the creation of free radicals. **Free radicals are neutral atoms or neutral parts of molecules that have unpaired electrons.** For example, the  $\text{H}_2\text{O}^+$  ion is formed from radiation. The  $\text{H}_2\text{O}^+$  ion can break into an  $\text{H}^+$  ion and a neutral OH free radical as shown below.



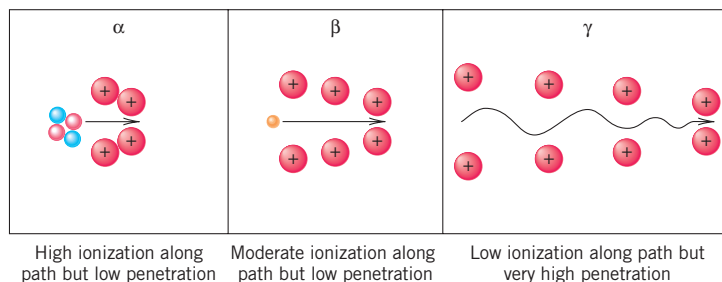
Free radicals such as OH are particularly destructive to living cells.

### 16-3.3 Ionization and Types of Radiation

As shown in Figure 16-5, an alpha particle causes the most ionization and is the most destructive along its path. However, these particles do not travel more than a few centimeters in air before they acquire two electrons to become an ordinary helium atom. They can be stopped by a piece of paper. The danger of alpha emitters (such as uranium and plutonium) is that they can be ingested through food or inhaled into the lungs, and eventually accumulate in bones. There, in intimate contact with the blood-producing cells of the bone marrow, they slowly damage the surrounding tissue at the molecular level. Ultimately, the radiation can cause certain cells to become abnormal. Rapid reproduction of these altered cells in the bone marrow causes the type of cancer commonly referred to as leukemia.

Beta radiation is less ionizing along its path than alpha radiation but is more penetrating. Still, a thin sheet of metal such as aluminum will stop most beta radiation. This type of radiation can cause damage to surface tissue such as skin and eyes but does not reach internal organs unless ingested. In the past, countries tested nuclear devices in the atmosphere. This produced large quantities of  $^{90}\text{Sr}$  (a beta emitter with a half-life of 28 years). Strontium is an alkaline earth metal like calcium, a major component of bones. Strontium can substitute for calcium, accumulate in the bones, and eventually cause leukemia and bone cancer. Good sense finally prevailed on the major atomic powers, and atmospheric testing of nuclear weapons has not occurred to any extent for many years.

The radiation from each radioactive isotope also has a specific energy. The energy of the emitted particles or rays is also important in the amount of ionization or free radical formation that occurs.



**FIGURE 16-5 Ionization and Penetration** Gamma radiation has the most penetrating power of the three types of radiation.



Lead aprons are worn to protect workers from X-rays and gamma rays.



MAKING

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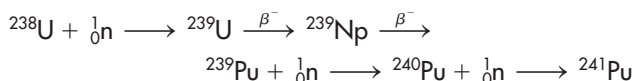
REAL

## Radioactivity and Smoke Detectors



Smoke detectors make use of a synthetic element.

It all starts in the reactor with  $^{238}\text{U}$ , the most abundant isotope of uranium. The neutrons produced in the reactor form  $^{241}\text{Pu}$  in the following steps.



Most of the  $^{241}\text{Pu}$  ( $t_{1/2} = 14$  days) has decayed to  $^{241}\text{Am}$  ( $t_{1/2} = 432$  years) by the time the extraction occurs. It is quite expensive, though. It is produced by the U.S.

We don't usually think of the presence in our home of radioactive isotopes as a good thing. However, an isotope of Americium ( $^{241}\text{Am}$ ) in smoke detectors has saved many lives. Americium is a rather new element on the periodic table.  $^{243}\text{Am}$  ( $t_{1/2} = 7370$  years) was first discovered in 1945 in airborne dust particles after the first atomic bombs. The isotope used in smoke detectors is a by-product of nuclear reactors. It is formed from the decay of

$^{241}\text{Pu}$ , which is extracted from

Atomic Energy Commission, where it sells for about \$1500 per gram. However, since only 0.2 mg of  $^{241}\text{Am}$  (as the compound  $\text{AmO}_2$ ) is used in each unit, 5000 smoke detectors can be made from one gram of the isotope. That amount of Americium produces about  $3 \times 10^4$  decays/second.

Smoke detectors work on simple principles. The  $^{241}\text{Am}$  decays by alpha particle emission. The alpha particles ( $^4\text{He}$ ) ionize the major molecules of air ( $\text{N}_2$  and  $\text{O}_2$ ) to form  $\text{N}_2^+$  and  $\text{O}_2^+$  ions. These ions form between plates of two electrodes that are connected to a battery or house current. The ions serve as a conduction pathway between the two electrodes and complete a circuit. When smoke drifts in between the two electrodes, it absorbs the alpha particles, so fewer ions are formed. When the detector senses the circuit is disrupted, the alarm sounds.

Are smoke detectors safe? The answer is yes. Alpha particles have a short range of a few centimeters at most, so they stay within the confines of the detector. The detectors themselves do not have enough radioactivity to pose a problem to the environment. The current necessary for continual operation is very small, so a 9-volt battery should last at least six months.

Modern smoke detectors are life-saving devices that are the direct product of the nuclear age. We are glad to have them.

### ASSESSING THE OBJECTIVE FOR SECTION 16-3

**EXERCISE 16-3(a) KNOWLEDGE:** Fill in the blanks.

Radiation causes \_\_\_\_\_ as well as the formation of \_\_\_\_\_ along its path. The most ionizing type of radiation is \_\_\_\_\_, whereas the most penetrating is \_\_\_\_\_.

**EXERCISE 16-3(b) ANALYSIS:** Which of the following is an ion that may be formed from radiation and which is a free radical?



**EXERCISE 16-3(c) SYNTHESIS:** The heat in Earth's interior that forms the lava in volcanoes is due to radiation. Explain how radiation causes heating.

*For additional practice, work chapter problems 16-26 and 16-27.*

## 16-4 THE DETECTION AND MEASUREMENT OF RADIATION

### ▶ OBJECTIVE FOR SECTION 16-4

Describe the common methods whereby radiation is detected and the units used to measure the amount of radiation.



**LOOKING AHEAD!** How do we know how much radiation we are absorbing? Since we can't see it or feel it, we must have some method of measuring radiation. The detection and measurement of radiation are obviously important in understanding the danger or the benefit. ■

### 16-4.1 Film Badges and Radon Detectors

Becquerel first discovered radiation by noticing that it exposed photographic film. This is still an important method of both detecting and measuring radiation. Film badges are worn by anyone who works near a source of radiation. (See Figure 16-6.) When the film is developed, the degree of darkening is proportional to the amount of radiation absorbed. Different filters are used so that the amount of each type of radiation received (alpha, beta, or gamma) can be measured.

An application of the film badge is used in radon detectors.  $^{222}\text{Rn}$  is a radioactive isotope formed as part of the natural decay series starting with  $^{238}\text{U}$ . Because radon is a noble gas, it can escape from the ground into the air. In certain areas of the United States where there is a significant amount of uranium in the soil, radon may accumulate in basements or other enclosed areas through foundation cracks. When inhaled, radon is usually exhaled unchanged, causing no harm. Its half-life, however, is only 10.82 days, which means that some actually does undergo radioactive decay when it is inhaled. If so, it decays to  $^{218}\text{Po}$ , which stays in the lungs because polonium is a solid. This is also a highly radioactive isotope that then decays in the lungs and may cause damage. When left in a basement, the detector measures the number of radon disintegrations. After a specified time, the detector is sent to a laboratory, where the film is developed and the amount of radiation from radon is determined.



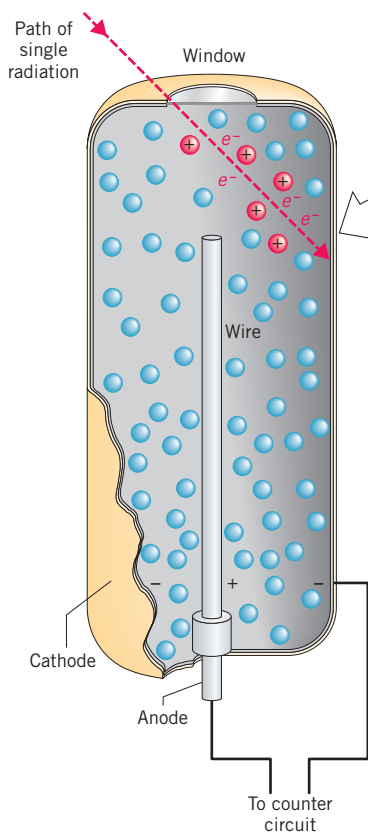
**FIGURE 16-6** Film Badges and Radon Detector

These devices are used to detect radiation.

### 16-4.2 Geiger and Scintillation Counters

As mentioned in the previous section, radiation causes ionization. Ionization is also used to measure radiation in the **Geiger counter**. The Geiger counter is composed of a long metal tube with a thin membrane at one end that allows all types of radiation to penetrate. The metal tube is filled with a gas such as argon at low pressure. A metal wire in the center of the tube is positively charged. When a radioactive particle enters the tube, it causes ionization. The electrons from this ionization move quickly to the positive electrode, causing a pulse of electricity to flow. This pulse is amplified and causes a light to flash, produces an audible “beep,” or registers on a meter in some unit such as “counts per minute.” (See Figure 16-7.)

A third type of radiation detector is a **scintillation counter**. Certain compounds such as zinc sulfide are known as phosphors. When radiation strikes a phosphor, a tiny flash of light is emitted in a process known as *fluorescence*. The flash of light is converted into a pulse of electricity that can be counted in the same manner as in the Geiger counter.



**FIGURE 16-7** The Geiger Counter This device measures radiation by the ionization it causes.

### 16-4.3 Radiation and the Human Body

How much radiation a person receives and how it affects the human body are matters of great importance. As a result, various units of measurement have been devised. The first measure of radiation simply relates to the number of disintegrations (counts) that occur in a specified time interval. This is known as the sample's activity. This unit is known as the **curie** (named after Madame Curie). It is defined as the decay rate of one gram of radium. The milli- and microcuries refer to smaller and more meaningful measures of radiation.

$$1 \text{ curie (Ci)} = 1.0 \times 10^{10} \text{ counts/s}$$

$$1 \text{ millicurie (mCi)} = 1.0 \times 10^7 \text{ counts/s}$$

$$1 \text{ microcurie } (\mu\text{Ci}) = 1.0 \times 10^4 \text{ counts/s}$$

The **becquerel** (Bq) is 1 disintegration per second and is used to measure very low levels of activity.

An important unit of radiation specifically refers to how different types of radiation affect the human body. The unit that describes the effect on the human body is the **rem** (roentgen equivalent in man). Other units used for this measure are **millirems** (mrem) ( $1 \text{ mrem} = 10^{-3} \text{ rems}$ ) and **sieverts** (Sv) ( $1 \text{ Sv} = 100 \text{ rems}$ ). Sieverts and millisieverts ( $10^{-3} \text{ Sv}$ ) are the SI units and are now used in most standard publications, although millirems are more convenient to describe common amounts of radiation equivalents.

When one is exposed to various types of radiation, the total amount of radiation in rems or sieverts becomes a critical number. Our natural environment provides what is referred to as background radiation. It comes from radon in the air; radiation from the sun and outer space, known as cosmic rays; and radioactive elements in rocks and in concrete. Even TV and smoking provide a small amount of radiation exposure. Although the amount varies geographically, on the average we absorb about 300 mrem annually from background radiation. Modern X-rays vary from about 20 mrem for dental to over 1000 mrem for certain extensive diagnostic X-rays of the intestines.

The amount of radiation the average person absorbs in one year is a concern. Those who live in higher altitudes or fly frequently in airplanes receive more cosmic radiation than those who stay at sea level. People who work in the nuclear industry, such as hospitals or nuclear power plants, receive extra radiation and must wear film badges to measure the rems of radiation received. The federal government puts the health limit at 5000 mrem (5 rems) as the maximum amount one should receive in one year.

Although the amount of cumulative radiation can be dangerous, it is far more dangerous to receive a large dose of radiation at one time. Over a period of time, the body can recover to a certain extent. If one receives a dose of 100 rems at one exposure, radiation sickness occurs. A sharp reduction of white blood cells occurs along with nausea, vomiting, and fatigue. Above 300 rem, hair loss and severe infection may occur because of the absence of white blood cells.

Doses above 500 rem cause death in 50% of those who have received that amount of radiation. This is known as the  $LD_{50}$ , *the dose that is fatal to one-half of those receiving that amount*. A dose above 600 rems is considered fatal to all humans within a few weeks.

### ASSESSING THE OBJECTIVE FOR SECTION 16-4

**EXERCISE 16-4(a) KNOWLEDGE:** Fill in the blanks.

Three major ways in which radiation is measured are the \_\_\_\_\_ badge, the \_\_\_\_\_ counter, and the \_\_\_\_\_ counter. The major unit used to measure the total amount of radiation is the \_\_\_\_\_. The major units that measure the amount of radiation received by a person are the \_\_\_\_\_ and the \_\_\_\_\_. The amount of radiation that is fatal to half of those that receive it is known as the \_\_\_\_\_.

**EXERCISE 16-4(b) SYNTHESIS:** Radiation causes fluorescence. Historically, this was put to use in a common item that almost everyone wore. Do you know what it was?

*For additional practice, work chapter problems 16-28 and 16-29.*

### PART A SUMMARY

#### KEY TERMS

- 16-1** **Radiation** refers to the particles or light energy. **Radioactive isotopes** spontaneously emit radiation. p. 512
- 16-1.1** **Alpha particles ( $\alpha$ )** are helium nuclei emitted from a nucleus. A **nuclear equation** illustrates changes in the nucleus. p. 512
- 16-1.2** **Beta particles ( $\beta$ )** are electrons emitted from a nucleus. p. 513
- 16-1.3** **Gamma rays ( $\gamma$ )** are composed of high-energy light from a nucleus. p. 513
- 16-1.4** **Positrons** are positively charged electrons. Positron emission and **electron capture** both decrease the nuclear charge of the emitting nucleus by 1. p. 513
- 16-2.1** The **half-life ( $t_{1/2}$ )** of an isotope is the time required for one-half of a sample to decay. p. 516
- 16-2.2** A **radioactive decay series** relates to the isotopes formed between a long-lived isotope and a stable isotope of lead. p. 516
- 16-3.2** **Ionizing radiation** is responsible for the production of ions. **Free radicals** are also formed as a result of radiation. p. 519
- 16-4.2** **Geiger counters** and **scintillation counters** are used to detect radiation. p. 521
- 16-4.3** The **curie** and **becquerel** are units that relate to the number of disintegrations. The **rem**, **mrem**, and **sievert** are units that relate to the effect of radiation on humans. p. 522
- 16-4.3** The  $LD_{50}$  relates to the amount of radiation fatal to one-half of victims. p. 523

#### SUMMARY CHART

| Effect of Type of Radiation on an Isotope |                        |                     |                    |                                |
|---|------------------------|---------------------|--------------------|--------------------------------|
|   | Alpha ( $\alpha$ )     | Beta ( $\beta$ )    | Gamma ( $\gamma$ ) | Positron (or Electron Capture) |
| Identity                                  | ${}^4_2\text{He}^{2+}$ | ${}_{-1}^0\text{e}$ | light energy       | ${}_{+1}^0\text{e}$            |
| Effect on                                 | mass $-4$              | mass $0$            | mass $0$           | mass $0$                       |
| Isotope                                   | charge $-2$            | charge $+1$         | charge $0$         | charge $-1$                    |

**PART B**  
**INDUCED NUCLEAR**  
**CHANGES AND THEIR USES**

**SETTING A GOAL**

- You will learn how we have applied synthetic nuclear reactions to develop a wide range of nuclear processes.

**OBJECTIVES**

- 16-5** Write balanced nuclear equations for the synthesis of specific isotopes by nuclear reactions.
- 16-6** List and describe the beneficial uses of radioactivity.
- 16-7 (a)** Identify the differences between nuclear fission and natural radioactivity. **(b)** Differentiate between nuclear fission and nuclear fusion.

► **OBJECTIVE FOR SECTION 16-5**

Write balanced nuclear equations for the synthesis of specific isotopes by nuclear reactions.

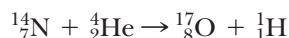
## 16-5 NUCLEAR REACTIONS



**LOOKING AHEAD!** Elements spontaneously change into other elements by emitting alpha or beta particles. But can scientists do the same thing? Our next topic involves the accomplishment of changing one element into another. ■

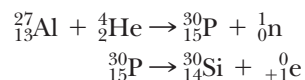
### 16-5.1 Transmutation

**Transmutation** of an element is the conversion of that element into another. The first example of transmutation was discovered by Ernest Rutherford in 1919; earlier, he had proposed the nuclear model of the atom. Rutherford found that bombarding  $^{14}\text{N}$  atoms with alpha particles caused a nuclear reaction that produced  $^{17}\text{O}$  and a proton. This nuclear reaction is illustrated by the nuclear equation



Note that the total number of nucleons is conserved by the reaction ( $14 + 4$  on the left =  $17 + 1$  on the right). The total charge is also conserved during the reaction ( $7 + 2$  on the left =  $8 + 1$  on the right). Both the number of nucleons and the total charge must be balanced (the same on both sides of the equation) in a nuclear reaction.

Over a decade later, Irène Curie, daughter of Pierre and Marie Curie, and her husband, Frédéric Joliot, produced an isotope of phosphorus that was radioactive. This was the first artificially induced radioactivity, for which Curie and Joliot received the 1935 Nobel Prize in chemistry. The radioactive isotope formed was  $^{30}\text{P}$ , which decays to  $^{30}\text{Si}$  as illustrated by the following nuclear equations.



### 16-5.2 Particle Accelerators

Because the nucleus has a positive charge and many of the bombarding nuclei (except neutrons) also have a positive charge (e.g.,  $^4_2\text{He}$ ,  $^1_1\text{H}$ ,  $^2_1\text{H}$ ), the particles must have a high energy (velocity) to overcome the natural repulsion between these two like charges. From the collision of the nucleus and the particle, a high-energy nucleus is formed. As a result, another particle (usually a neutron) is then emitted by the nucleus to carry away excess energy from the collision. This is analogous to a head-on collision of two cars, where fenders, doors, and bumpers come flying off after impact. The nucleus-particle collision is illustrated in Figure 16-8.

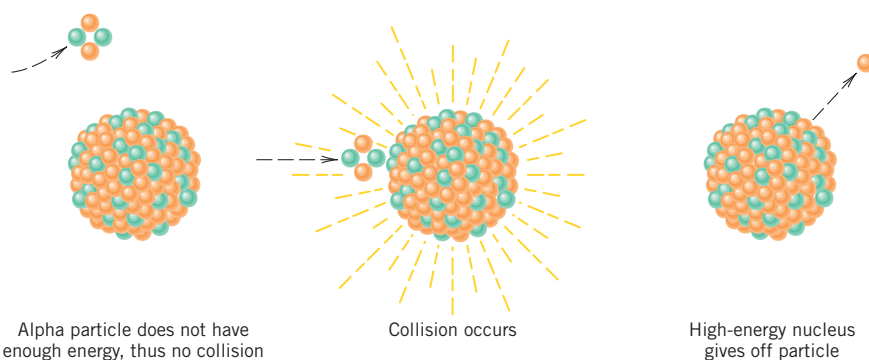
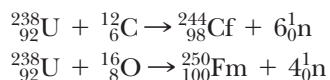


The invention of particle accelerators, which increase the velocity and energy of nuclei and subatomic particles, opened the door to vast possibilities for artificial nuclear reactions. The larger accelerators also allow studies of collisions so powerful that the colliding nuclei are blasted apart. From these experiments, scientists have glimpsed the most basic composition of matter. These accelerators are large and expensive. Completed in the early

1970s, the Fermi National Accelerator in Batavia, Illinois, has a circumference of about 6 miles and cost \$245 million. A huge accelerator, known as the *Superconducting Super Collider* (SSC), was about one-third completed in Texas and would have had a circumference of 52 miles. The cost of about \$12 billion was considered too much, however, so it was canceled by the U.S. Congress. CERN, the largest accelerator, is in Switzerland and is known as the *Giant Hydron Collider* (GHC). It is hoped it will create conditions that have not occurred since the big bang. (See Figure 16-9.)

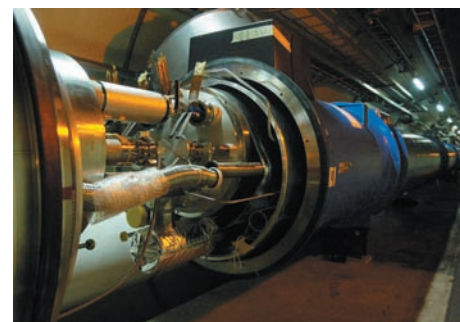
### 16-5.3 Synthetic Heavy Elements

The use of particle accelerators has made possible the extension of the periodic table past element number 94, plutonium. Elements number 95 through the last element reported, number 118, have been synthesized by means of particle accelerators. In 1995 elements number 110 and 111 and in 1996 number 112 were reported as being synthesized by scientists in Darmstadt, Germany. More recently, scientists at the Joint Institute for Nuclear Research in Dubna, Russia, reported the synthesis of elements number 113, 115, and 116. In late 2006, the same team reported the synthesis of three atoms of element number 118. Before these elements take their place on the periodic table, the experiments must be duplicated at other facilities. The following nuclear reactions illustrate the formation of two heavy elements.



**FIGURE 16-8** Collision of an Alpha Particle with a Nucleus

Alpha particles must have sufficient energy to overcome the repulsion of the target nucleus for a collision to take place.

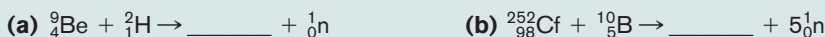


**FIGURE 16-9** CERN Accelerator This is the largest accelerator in use today.

#### EXAMPLE 16-4

##### Writing Equations for Nuclear Reactions

Complete the following nuclear equations.



##### PROCEDURE

Complex nuclear equations are balanced in the same manner as discussed in Example 16-1. Determine the missing isotope or particle by recalling that the total mass and the total charge are the same on both sides of the equation.

##### SOLUTION

(a) Nucleons:  $9 + 2 = x + 1$ , so  $x = 10$

Atomic number:  $4 + 1 = y + 0$ , so  $y = 5$

From the list of elements, we find that the element is boron (atomic number 5). The isotope is



(b) Nucleons:  $252 + 10 = x + (5 \times 1)$ , so  $x = 257$ .

Atomic number:  $98 + 5 = y + (5 \times 0)$ , so  $y = 103$

From the list of elements, the isotope is



### ANALYSIS

The new nuclear symbol for this set of exercises is the neutron,  ${}^1_0\text{n}$ , which can be emitted when two particles collide. Notice that the elemental species that are involved in the reactions have a degree of redundancy to them. Along with the symbol, the atomic number is reported, in the lower left corner. These values can be determined by the symbols themselves, so their inclusion is not critical but is convenient.

### SYNTHESIS

Notice that the product of each of these reactions, along with the daughter particle, is one or more neutrons. These high-energy particles are themselves potential reactants in nuclear transmutations [see Exercise 16-5(b) in Assessing the Objective for Section 16-5]. Neutrons, which have no charge, are not affected by repulsion of a nucleus as are alpha particles or other nuclei. Therefore, because it takes less energy for a neutron to collide with a nucleus, reactions initiated by neutrons can take place under less extreme conditions than those that require a particle accelerator.

## ASSESSING THE OBJECTIVE FOR SECTION 16-5

**EXERCISE 16-5(a) KNOWLEDGE:** When completing a nuclear reaction, what must be balanced?

**EXERCISE 16-5(b) ANALYSIS:** Fill in the blanks in the following equations.

- (a)  ${}^{51}_{23}\text{V} + {}^2_1\text{H} \rightarrow \underline{\hspace{2cm}} + {}^1_1\text{H}$   
 (b)  ${}^{235}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^{90}_{38}\text{Sr} + \underline{\hspace{2cm}} + 2{}^1_0\text{n}$   
 (c)  ${}^{246}_{96}\text{Cm} + \underline{\hspace{2cm}} \rightarrow {}^{254}_{102}\text{No} + 4{}^1_0\text{n}$

**EXERCISE 16-5(c) SYNTHESIS:** The formation of element 118 was first reported in 1999. It was a fraudulent claim, however, so the report was withdrawn. In late 2006, the formation of three atoms of element 118 was again reported by reliable scientists who had previously reported the discovery of elements 113, 114, 115, and 116. Element 118 was made by bombarding  ${}^{249}\text{Cf}$  with  ${}^{48}\text{Ca}$ . The new element had 176 neutrons. It decayed almost immediately by giving off three alpha particles one at a time.

- (a) Write the nuclear equation showing the formation of element 118 and the three products of the alpha particle decays.  
 (b) Do you think  ${}^{48}\text{Ca}$  is radioactive? If so, how would it decay?  
 (c) If enough of element 118 could be produced, what would be its physical state at room temperature?

*For additional practice, work chapter problems 16-30 and 16-32.*

## ▶ OBJECTIVE FOR SECTION 16-6

List and describe the beneficial uses of radioactivity.

## 16-6 APPLICATIONS OF RADIOACTIVITY



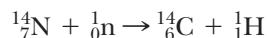
**LOOKING AHEAD!** Despite their horrible reputation, radioactive isotopes have a huge number of beneficial applications. How we use radioactivity to date artifacts, make our food healthier, and help diagnose and even cure our illnesses is the subject of this section. ■

The benefits of the nuclear age are awesome. Heart scans tell us whether bypass surgery is indicated. Radiation treatments have saved thousands of lives and prolonged many thousands of others. The shelf-life of perishable food has been extended by weeks. These and other uses have far outweighed the dangers from the misuse of

radioactivity. We will begin our discussion of how radioactivity improves our lives with how we use a naturally produced radioactive isotope to date artifacts.

### 16-6.1 Carbon Dating

Perhaps one of the most interesting applications of radioactive isotopes is the dating of wood or other carbon-containing substances that were once alive.  $^{14}\text{C}$  dating is effective in dating artifacts that are from about 1000 to about 50,000 years old.  $^{14}\text{C}$  is a radioactive isotope with a half-life of 5760 years. It is produced in the stratosphere by a nuclear reaction involving *cosmic rays* (a variety of radiation and particles) from the sun.



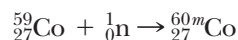
The  $^{14}\text{C}$  then mixes with the normal and stable isotopes of carbon in the form of carbon dioxide. Carbon dioxide is taken up by living systems and, through photosynthesis, becomes part of the carbon structure of the organism. As long as the carbon-based system is alive, the ratio of  $^{14}\text{C}$  to normal carbon is the same as in the atmosphere. When the system dies, the amount of  $^{14}\text{C}$  in the organism begins to decrease. By comparing the amount of radiation from  $^{14}\text{C}$  in the artifact with that in living systems, the age can be determined. (See Example 16-2.)

The procedure can analyze carbon-containing objects like wood, cloth, and bone that are as much as 50,000 years old before the levels become too low to detect, and it is accurate to within 30 years or so even for very old samples. Some famous examples include dating the Shroud of Turin to around A.D. 1300 and the “Ice-Man,” found near the Italian–Austrian border in 1991, to around 3300 B.C.

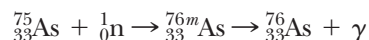
Besides  $^{14}\text{C}$  dating, the decay of other isotopes (e.g.,  $^{40}\text{K}$ ) can be studied to determine the age of rocks that were formed from molten material millions of years ago.

### 16-6.2 Neutron Activation Analysis

Most naturally occurring isotopes are not radioactive. **Neutron activation analysis** is a process whereby stable isotopes are made radioactive by absorption of neutrons in a nuclear reactor. An example is the production of  $^{60}\text{Co}$ , which is used in cancer therapy, from a stable isotope of cobalt.



Another application of neutron activation concerns the analysis of arsenic in human hair. Arsenic compounds can be used as a slow poison, but arsenic accumulates in human hair in minute amounts. By subjecting the human hair to neutron bombardment, the stable isotope of arsenic is changed to a metastable nucleus.



The amount of gamma radiation from the metastable arsenic can be measured and is proportional to the amount of arsenic present. The method is very sensitive to even trace amounts of arsenic.

### 16-6.3 Food Preservation

In a very simple procedure, many types of food can be irradiated with gamma radiation, which kills bacteria and other microorganisms that cause food spoilage without changing the taste or appearance of the food. This increases the shelf-life of food before decay sets in. For example, mold begins to form on strawberries, even when refrigerated, in just a few days. After irradiation, the same strawberries can be stored for two weeks without decay. (See Figure 16-10.) There has been some buyer resistance to irradiated foods. The public worries that irradiation somehow may make the food radioactive. The procedure is perfectly safe, however, and as public apprehension declines, we will probably see more and more irradiated foods at the grocery store.



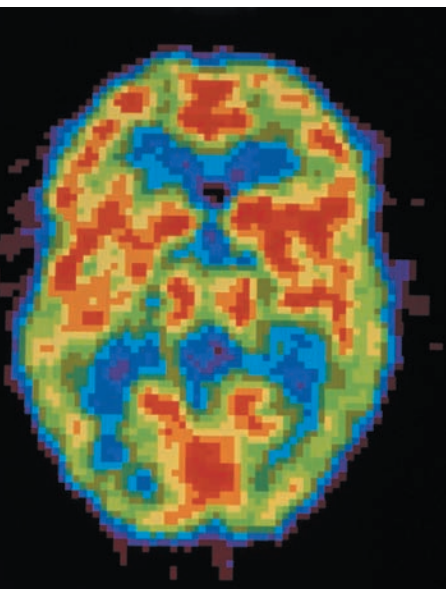
The Shroud of Turin was dated to the fourteenth century.



**FIGURE 16-10**  
**Irradiated Strawberries** The strawberries at the top are moldy after a few days. Those on the bottom have been irradiated and are still fresh after two weeks.



**FIGURE 16-11**  $^{60}\text{Co}$  Radiation Treatment A beam of gamma rays can be used to destroy cancerous tissue.



**FIGURE 16-12** PET Scan This PET scan of the brain reveals areas of activity during sleep.

### 16-6.4 Medical Therapy

$^{60}\text{Co}$  gamma radiation can be focused into a narrow beam. Although gamma radiation destroys healthy as well as malignant cells, healthy cells recover faster. By focusing the beam at different angles on tumors located within the body, the gamma rays can be concentrated on the tumor. (See Figure 16-11.) This treatment has many unpleasant side effects because of the destruction of normal, healthy cells.

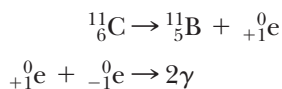
A procedure known as *brachytherapy* is used increasingly in the treatment of prostate cancer. Tiny “seeds” of  $^{103}\text{Pd}$  ( $t_{1/2} = 17$  days) or  $^{125}\text{I}$  ( $t_{1/2} = 8$  days) inside a titanium capsule are implanted in the cancerous gland. As these isotopes decay by electron capture, they release low-energy X-rays, which destroy prostate tissue but penetrate only about 1 cm into the surrounding tissue. Since the radiation has a localized effect, nearby organs are minimally affected. The radiation lasts only a few months because of the short half-lives, so the seeds are left permanently in place. Although there are several other radioactive isotopes used in therapies, the greatest application of these isotopes is in diagnosis.

### 16-6.5 Medical Diagnosis

Today, hardly any large hospital could be without its nuclear medicine division. We have come to rely on the use of radioactive isotopes to help diagnose many diseases and conditions. Various radioactive isotopes can be injected into the body, and their movement through the body or where they accumulate can be detected outside the body with radiation detectors.  $^{59}\text{Fe}$  is used to measure the rate of formation and lifetime of red blood cells.  $^{99m}\text{Tc}$  is used to image the brain, heart, and other organs.  $^{131}\text{I}$  is used to detect thyroid malfunction and can also be used for the treatment of thyroid tumors.  $^{24}\text{Na}$  is used to study the circulatory system.

One of the more useful (and expensive) tests is known as a *PET* (*positron emission tomography*) scan, which produces an image of a two-dimensional slice through a portion of the body. The body is injected with a compound (e.g., glucose) containing a radioactive isotope such as  $^{11}\text{C}$ . The glucose containing this isotope of carbon is metabolized along with glucose produced by the body containing the stable isotope  $^{12}\text{C}$ . The parts of the brain that are particularly active in metabolism of glucose will display increased radioactivity. Abnormal glucose metabolism in the brain can then be detected, which may indicate a tumor or Alzheimer’s disease. This diagnostic procedure is considered noninvasive compared to surgery. (See Figure 16-12.)

The  $^{11}\text{C}$  decays by positron emission.



Almost immediate annihilation of the positron by an electron leads to two gamma rays that exit the body in exactly opposite directions. Scintillation counters are positioned around the body to detect these two gamma rays and ignore others from background radiation. Computers are then used to translate the density and location of the gamma rays into two-dimensional images.

#### ASSESSING THE OBJECTIVE FOR SECTION 16-6

**EXERCISE 16-6(a) KNOWLEDGE:** Fill in the blanks.

Both naturally occurring and synthetic radioactive isotopes find many uses. The decay of carbon-\_\_\_\_\_ can be used to date many carbon-containing fossils. Medically useful radioactive isotopes can be prepared by \_\_\_\_\_ activation. Food can be preserved by radiation with \_\_\_\_\_. PET scans make use of isotopes that emit \_\_\_\_\_.



**EXERCISE 16-6(b) ANALYSIS:** The most commonly used isotope in PET scans is  $^{18}\text{F}$ , with a half-life of 110 min compared to  $^{11}\text{C}$ , with a half-life of 20 min. These isotopes must be synthesized in a nearby cyclotron because of their short half-lives. What isotope would  $^{16}\text{O}$  be bombarded with to produce  $^{18}\text{F}$ ? What isotope would be used to produce  $^{11}\text{C}$  if it was bombarded with protons?

**EXERCISE 16-6(c) SYNTHESIS:**

(a) Why can't a fossil that is over 50,000 years old be dated by normal carbon dating?

(b) Why does adding a neutron to a stable isotope often produce a radioactive isotope?

For additional practice, work chapter problems 16-25 and 16-42.

## 16-7 NUCLEAR FISSION AND FUSION



**LOOKING AHEAD!** In 1938, a discovery was made that at first suggested massive destruction and, later, on the positive side, inexpensive energy. The discovery was the atomic bomb and then the control of its process in nuclear power plants. The nuclear process that produces this power is the next topic. ■

### OBJECTIVES FOR SECTION 16-7

(a) Identify the differences between nuclear fission and natural radioactivity. (b) Differentiate between nuclear fission and nuclear fusion.

### 16-7.1 The Atomic Bomb

In 1934, two Italian physicists, Enrico Fermi and Emilio Segré, attempted to expand the periodic table by bombarding  $^{238}\text{U}$  with neutrons to produce neutron-rich isotopes that would decay by beta particle emission to form elements with atomic numbers greater than 92 (the last element on the periodic table at the time).



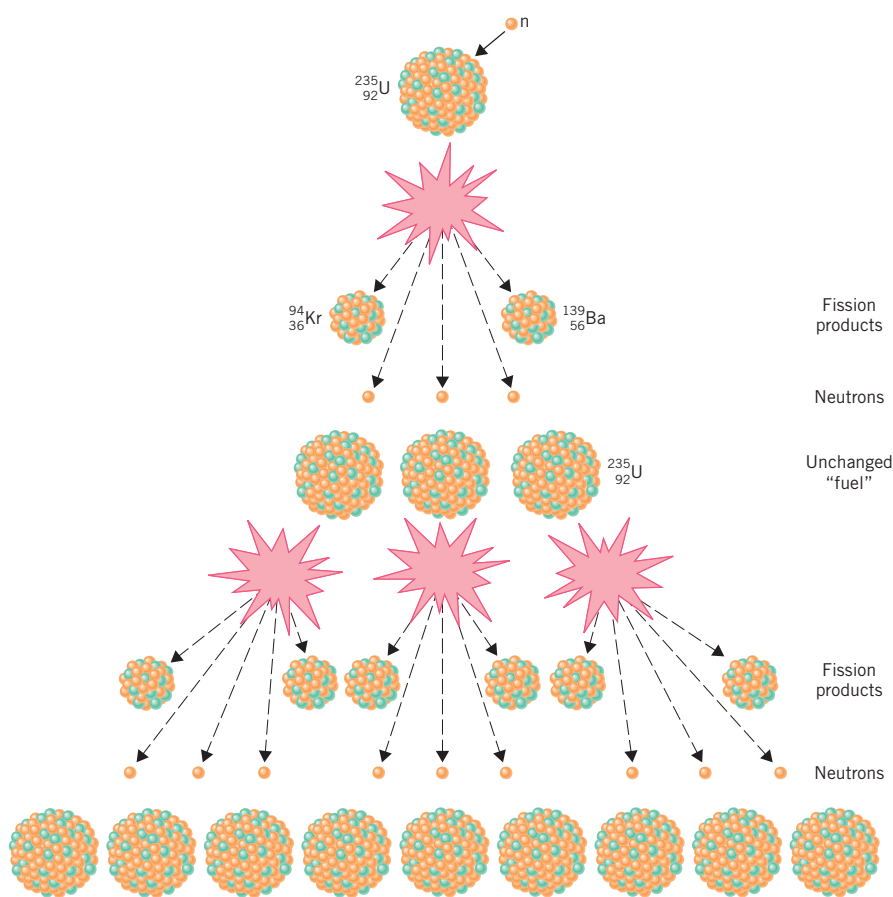
The experiment seemed to work, but they were perplexed by the presence of several radioactive isotopes produced in addition to the presumed element number 93. In 1938, these experiments were repeated by two German scientists, Otto Hahn and Fritz Strassman. They were able to identify the excess radioactivity as coming from isotopes such as barium, lanthanum, and cerium, which had about half the mass of the uranium isotope. Two other German physicists, Lise Meitner and Otto Frisch, were able to show that the rare isotope of uranium ( $^{235}\text{U}$ , 0.7% of naturally occurring uranium) was undergoing fission into roughly two equal parts after absorbing a neutron. **Fission** is the splitting of a large nucleus into two smaller nuclei of similar size. It should be noted that there are a variety of products from the fission of  $^{235}\text{U}$  in addition to those represented by the following equation. (See Figure 16-13.)



Two points about this reaction had monumental consequences for the world, and scientists in Europe and America were quick to grasp their meaning in a world about to go to war.

1. Comparison of the masses of the product nuclei with that of the original nucleus indicated that a significant amount of mass was lost in the reaction. According to Einstein's equation ( $E = mc^2$ ), the lost mass must be converted to a tremendous amount of energy. Fission of a few kilograms of  $^{235}\text{U}$  all at once could produce energy equivalent to tens of thousands of tons of the conventional explosive TNT.
2. What made the rapid fission of a large sample of  $^{235}\text{U}$  feasible was the potential for a chain reaction. A nuclear chain reaction is a reaction that is self-sustaining. The reaction generates the means to trigger additional reactions. Note in Figure 16-13 that the reaction of one original neutron caused three to be released. These three neutrons cause the release of nine neutrons and





**FIGURE 16-13 Fission and Chain Reactions** In fission, one neutron produces two fragments of the original atom and an average of three neutrons. These three neutrons can cause additional fission reactions and lead to a chain reaction.

is encased in long rods called fuel elements. Cadmium bars are raised and lowered among the fuel elements to control the rate of fission by absorbing excess neutrons. If the cadmium bars are lowered all the way, the fission process can be halted altogether. In normal operation, the bars are raised just enough so that the fission reaction occurs at the desired level. Energy released by the fission and by the decay of radioactive products formed from the fission is used to heat water, which circulates among the fuel elements. This water, which is called the primary coolant, becomes very hot (about 300°C) without boiling because it is under high pressure. The water heats a second source of water, changing it to steam. The steam from the secondary coolant is cycled outside of the containment building, where it is used to turn a turbine that generates electricity.

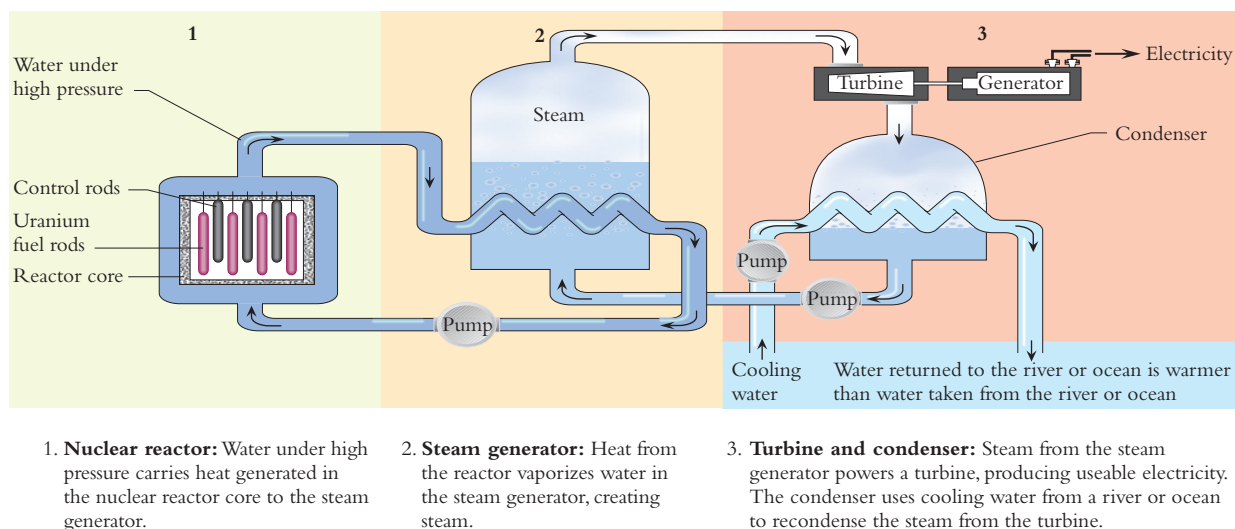
Perhaps the greatest advantage of nuclear energy is that it does not pollute the air with oxides of sulfur and carbon as conventional power plants do. Sulfur oxides have been implicated as a major cause of acid rain. It also seems likely that large amounts of carbon dioxide in the atmosphere are leading to significant changes in the weather as a result of the greenhouse effect. Another advantage is that nuclear power does not deplete the limited supply of fossil fuels (oil, coal, and natural gas), which are also used to make plastics and fertilizers. Until the tragedy in Chernobyl, Ukraine, in April 1986, there had been no loss of human life from the use of nuclear energy to generate electricity. At the current time, about 28 countries produce electricity through nuclear power. The United States currently generates about 20% and France about 80% of their electricity from nuclear power. (See Figure 16-15.) Proponents of nuclear power feel that if the proper systems were used with adequate safeguards and backups, catastrophic accidents would be avoided. In fact, new designs of nuclear power plants solve many of the legitimate concerns of citizens. A safe reactor would be one that shuts itself down in case of an emergency and would not overheat or explode. (Such an explosion would be a conventional explosion,

so forth. If a given densely packed “critical mass” of  $^{235}\text{U}$  is present, the whole mass of uranium can undergo fission in an instant, with a quick release of energy in the form of radiation.

Unfortunately, the world thus entered the nuclear age in pursuit of a bomb. In the early 1940s a massive secret effort—the Manhattan Project—began research into producing “the atomic bomb.” The first nuclear bomb was exploded over Alamogordo Flats in New Mexico on July 16, 1945. This bomb and the bomb exploded over Nagasaki, Japan, were made of  $^{239}\text{Pu}$ , which is a synthetic fissionable isotope. The bomb exploded over Hiroshima, Japan, was made of  $^{235}\text{U}$ .

## 16-7.2 Nuclear Power

This enormously destructive device, however, can be tamed. The chain reaction can be controlled by absorbing excess neutrons with cadmium bars. A typical nuclear reactor is illustrated in Figure 16-14. In a reactor core, uranium in the form of pellets



**FIGURE 16-14 A Nuclear Reactor** Nuclear energy is converted to heat energy, the heat energy to mechanical energy, and the mechanical energy to electrical energy.

not an atomic explosion.) Experts from several countries are also currently planning a relatively safe reactor that will use as a fuel the  $^{239}\text{Pu}$  salvaged from dismantled nuclear bombs of the United States and of the former Soviet Union. This reactor would be highly efficient, converting about 50% of the heat generated into electricity, compared with an efficiency of about 33% for a typical commercial nuclear power plant.

The disadvantages have been made painfully obvious. The catastrophic explosion (which was conventional, not nuclear) and subsequent fire in reactor 4 in Chernobyl, Ukraine, in 1986 dispersed more dangerous radiation into the environment than all the atmospheric bomb tests by all nations put together. (See Figure 16-16.) The surroundings for at least 30 mi around the plant, and even farther downwind, are still uninhabitable. The reactor itself has been entombed in concrete and must remain so for hundreds of years. The extent of the damage is still being assessed. The number of actual deaths is also a matter of controversy. Estimates range from less than 100 to several thousand. At a minimum, many lives will probably be shortened by exposure to the radiation. In the United States, an accident at Three Mile Island, Pennsylvania, in March 1979 took more than 14 years to clean up at a cost greater than \$1 billion. Fortunately, there was very little release of radioactivity and no loss of life in this accident.

In both of these accidents, a core meltdown did not occur. A meltdown would occur if the temperature of the reactor core exceeded  $1130^\circ\text{C}$ , the melting point of uranium. Theoretically, the mass of molten uranium, together with all the highly radioactive decay products, could accumulate on the floor of the reactor, melt through the many feet of protective concrete, and eventually reach groundwater. If this happened, vast amounts of deadly radioactive wastes could be spread through the groundwater into streams and lakes.



**FIGURE 16-15 A Nuclear Power Plant** In such plants, the nuclear energy of uranium is converted into electrical energy.



**FIGURE 16-16 The Chernobyl Reactor** The explosion of this reactor spread radioactive debris for miles around.

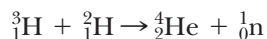
The type of accident that occurred in Ukraine is unlikely in most of the world's commercial reactors. Unlike reactors in the former Soviet Union, these reactors are surrounded by an extremely strong structure, called a containment building, made of reinforced concrete. These buildings should contain an explosion such as occurred at Chernobyl. The reactors in the United States are built to withstand the collision of a jet airliner and 300 mi/hr winds. Also, most reactors do not contain graphite, which is highly combustible and led to the prolonged fire in Chernobyl that spread so much radioactivity into the atmosphere. There is one reactor similar to the Ukrainian reactors, in Hanford, Washington, but it has been shut down indefinitely. It should be noted that bomb-grade uranium is at least 90%  $^{235}\text{U}$ , while that used in nuclear reactors is 2–3%  $^{235}\text{U}$ . The uranium used in nuclear reactors could not be used for a bomb.

A growing problem in the use of nuclear energy involves used, or spent, fuel. Originally, used fuel was to be processed at designated centers where the unused fuel could be separated and reused and the radioactive wastes disposed of. However, problems in transportation of this radioactive material and the danger of theft of the  $^{239}\text{Pu}$  that is produced in a reactor have hindered solution of the problem. ( $^{239}\text{Pu}$  is also fissionable and could be used in a nuclear bomb.) Currently, spent fuel elements, which must be replaced every four years, are being stored at the reactor sites. These fuel rods are not only highly radioactive but remain extremely hot and must be continually cooled. It is estimated that they will remain dangerously radioactive for at least 1000 years. This is a problem that must soon be resolved. Current plans in the United States are to store the waste in Yucca Flats in Nevada, although this has not been done yet.

Because of the accidents, new regulations regarding safeguards have made the cost of a new nuclear power plant considerably higher than that of a conventional power plant using fossil fuels. As a result, no new nuclear plants are planned in the United States in the immediate future. However, due to the higher prices of oil, that situation may soon change.

### 16-7.3 Nuclear Fusion

In the late 1930s, another source of nuclear energy was proposed by Hans Bethe. This involved fusing small nuclei together rather than splitting large ones. It was even suggested that this was the major source of energy in the universe because it powered the sun and the stars. *This reaction involves the fusion, or bringing together, of two small nuclei.* An example of a fusion reaction is



( ${}^3_1\text{H}$  is called tritium; it is a radioactive isotope of hydrogen.)

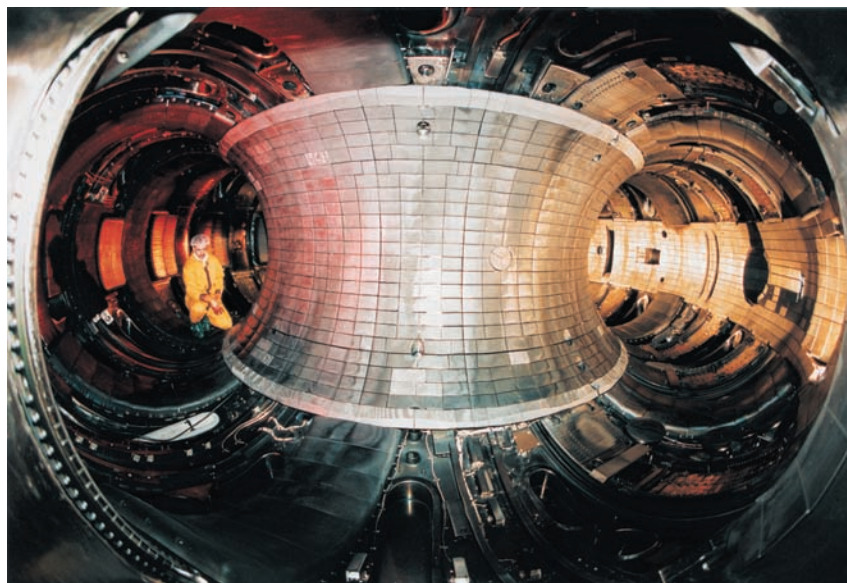
As in the fission process, a significant amount of mass is converted into energy. Fusion energy is the origin of almost all our energy, since it powers the sun. Millions of tons of matter are converted to energy in the sun every second. Because of its large mass, however, the sun contains enough hydrogen to “burn” for additional billions of years.

The principle of fusion was first demonstrated on this planet with a tremendously destructive device called the hydrogen bomb, which was first exploded in 1952. This bomb can be more than 1000 times as powerful as the atomic bomb, which uses the fission process.

Fission is controlled in nuclear power plants. What about fusion? Controlling fusion is technically extremely difficult. Temperatures on the order of 50 million degrees Celsius are needed so that the colliding nuclei have enough kinetic energy to overcome their mutual repulsions and cause fusion. The necessary temperature is hotter than the interior of the sun. No known materials can withstand these temperatures, so alternate containment procedures must be used. Producing electrici-



ty from a fusion reactor is perhaps the greatest technical challenge yet faced by the human race. However, the effort is well under way. The design and construction of a large fusion reactor (International Thermonuclear Experimental Reactor, or ITER) is being financed and staffed by an international consortium of nations including the United States, Japan, Russia, and the European Union. The cost is estimated at about \$8 billion over a 13-year period. It is hoped that eventually this reactor will exceed the *break-even point*, where the same amount of energy is produced by the fusion as is needed to bring about the fusion. In about 20 years, if things go well, the first fusion reactor designed to produce electricity could be built. With the amount of fossil fuel on the decline, there are not many other alternatives for energy later in the twenty-first century.



This small reactor is being used to study the feasibility of the generation of fusion power.

The advantages of controlled fusion power are impressive.

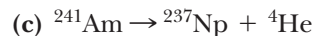
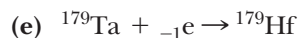
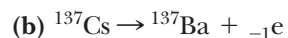
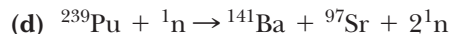
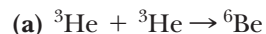
1. It should be relatively clean. Few radioactive products are formed.
2. Fuel is inexhaustible. The oceans of the world contain enough deuterium, one of the reactants, to provide the world's energy needs for a trillion years. On the other hand, there is a very limited supply of fossil fuels and uranium.
3. There is no possibility of the reaction going out of control and causing a meltdown. Fusion will occur in power plants in short bursts of energy that can be stopped easily in case of mechanical problems.

**ASSESSING THE  
OBJECTIVES FOR  
SECTION 16-7**

**EXERCISE 16-7(a) KNOWLEDGE:** Fill in the blanks.

A nuclear reaction known as fission can occur as a nuclear \_\_\_\_\_ reaction. The process whereby small nuclei combine to form a larger nucleus and a small particle is known as \_\_\_\_\_.

**EXERCISE 16-7(b) ANALYSIS:** Identify the nuclear process occurring in each of these equations.



**EXERCISE 16-7(c) SYNTHESIS:** Much of the free world opposes countries such as Iran and North Korea in their efforts to use nuclear power. How can a nuclear power plant be used to produce material for an atomic bomb?

**EXERCISE 16-7(d) SYNTHESIS:** Fusion is putting two atoms together. Fission is breaking one atom apart. In this section, we see that *both* of these processes release energy. How can opposite processes both produce energy?

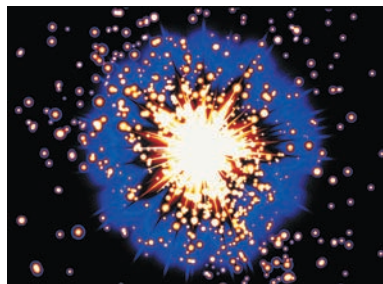
*For additional practice, work chapter problems 16-36 and 16-43.*

MAKING

IT

REAL

## Revisiting the Origin of the Elements



Elements are created in the interiors of stars.

of ancient stars or from their catastrophic explosions.

We can now revisit this topic with some of the information presented in this chapter.

The universe itself began violently about 14 billion years ago. All the matter and energy in the universe originated from a single point called the singularity. This point expanded in what is called the big bang. The fundamental particles—electrons, neutrons, and protons—were formed within minutes. Hydrogen was the primeval element from which other elements would form.

Sometime after the big bang, clouds of hydrogen gas began to clump together and contract because of the attraction of gravity. As contraction continued, the hydrogen cloud became denser and hotter (i.e., Charles's law). Eventually, the nuclei of hydrogen had enough energy to undergo fusion to produce helium. This process liberates huge amounts of energy, so the first stars began to shine brightly and the universe began to light up. After a few million

In the Prologue we described why it can be said that we are literally composed of star dust. This sounds rather melodramatic, but it is indeed true. Other than hydrogen, all other atoms in our bodies originated in the violent interiors

years, the early stars had used up their supply of hydrogen and the helium nuclei underwent fusion to form even heavier elements like carbon and oxygen, as shown here.



The fusion reactions continued in stages up to the formation of elements as heavy as iron. At this point, further fusion reactions forming heavier nuclei do not liberate energy and thus do not occur.

So how did heavier elements like lead and gold form? When a large star exhausted its supply of elements that can liberate energy by fusion, the nuclear reactions suddenly stopped. Without the energy needed to counteract gravity, the star immediately collapsed and then rebounded, ejecting its elements into outer space along with a huge cloud of neutrons. This violent event is called a supernova. The elements from the star absorbed the neutrons singly or in batches. As mentioned in this chapter, isotopes with excess neutrons decay by beta emission, forming the next higher element on the periodic table. Absorption of neutrons increased the mass number, and beta emission increased the atomic number of the isotope. An example is shown here.



These elements drifted through space as dust and gases. About 4.5 billion years ago, a cloud of hydrogen containing the dust from previous supernovas contracted and formed our sun and its planets. We are the inhabitants of the third planet out from this ordinary star.

## PART B SUMMARY

### KEY TERMS

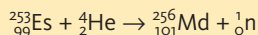
- 16-5.1 Transmutation** is the process of changing one element into another by nuclear reactions. p. 524
- 16-6.2 Neutron activation analysis** is used to change stable isotopes into radioactive isotopes for analysis. p. 527
- 16-7.1** Specific heavy nuclei undergo **fission** when bombarded with neutrons to produce lighter nuclei and release energy. p. 529
- 16-7.3 Fusion** is a nuclear process whereby light elements combine to form heavier elements and release energy. p. 532



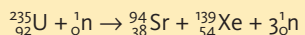
## SUMMARY CHART

## Three Types of Nuclear Reactions

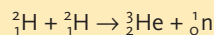
Transmutation



Fission

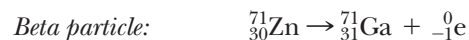


Fusion



## CHAPTER SUMMARY

The nuclei of **radioactive isotopes** are unstable and emit **radiation**. Although radioactive isotopes exist for each element, all isotopes with an atomic number greater than 83 are unstable. Originally, three types of radiation were discovered, **alpha ( $\alpha$ ) particles**, **beta ( $\beta$ ) particles**, and **gamma ( $\gamma$ ) rays**. Since then, two other types of radiation have been characterized that occur rarely in nature but more commonly in artificially produced radioactive isotopes. These are **positron ( ${}_{+1}^0\text{e}$ ) particles** and **electron capture**. These five modes of decay are illustrated by the following **nuclear equations**.



Radioactive isotopes decay at widely different rates. A measure of the rate of decay is called the **half-life ( $t_{1/2}$ )** of the isotope. Half-lives vary from billions of years to fractions of a second. A long-lived isotope is  ${}^{238}\text{U}$ , which

begins a **radioactive decay series** and ends with a stable isotope of lead after a series of alpha and beta decays.

**Ionizing Radiation** not only forms ions in surrounding matter, but causes heating and **free radical** formation. In living matter, the ions or free radicals may lead to destruction of the cells. Alpha and beta emitters are most dangerous when ingested, since they cause a high degree of ionization in close proximity to cells. Gamma rays are less ionizing but very penetrating; thus, they are also very dangerous. Radiation is detected and measured by means of film badges, **Geiger counters**, and **scintillation counters**.

The **Curie** and **Becquerel** are units that measure radiation activity while the **rem** and **sievert** are units that measure how radiation affects living tissue. A dose of 500 rem is the  $\text{LD}_{50}$  for humans. Nuclear reactions, including **neutron activation analysis**, occur when nuclei are bombarded by particles or other nuclei. This leads to the artificial **transmutation** of one element into another. **Fission** and **fusion** are also nuclear reactions. Fission is the splitting of one heavy nucleus into two more or less equal fragments and neutrons. Fusion is the joining of two light nuclei to form a heavier nucleus and a particle.

## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...   | EXAMPLES   | EXERCISES      | CHAPTER PROBLEMS              |
|---------|--|------------|----------------|-------------------------------|
| 16-1    | Write balanced nuclear equations for the five types of radiation.  | 16-1       | 1a, 1b, 1c     | 2, 3, 5, 7, 9, 12, 15, 17, 19 |
| 16-2    | Using half-lives, estimate the time needed for various amounts of radioactive decay to occur.                    | 16-2, 16-3 | 2a, 2b, 2c, 2d | 21, 22, 24, 25                |
| 16-3    | Describe how the three natural types of radiation affect matter.   |            | 3a, 3b, 3c     | 10, 13                        |
| 16-4    | Describe the common methods whereby radiation is detected and the units used to measure the amount of radiation. |            | 4a, 4b         | 26, 27, 28, 29                |
| 16-5    | Write balanced nuclear equations for the synthesis of specific isotopes by nuclear reactions.                    | 16-4       | 5a, 5b, 5c     | 30, 31, 33, 35                |
| 16-6    | List and describe the beneficial uses of radioactivity.  |            | 6a, 6b, 6c     |                               |
| 16-7    | Identify the differences between nuclear fission and natural radioactivity.                                      |            | 7a, 7c         |                               |
|         | Differentiate between nuclear fission and nuclear fusion.  |            | 7b, 7d         | 36, 37                        |

## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**16-1(a)** There are five types of radiation.

1. An alpha particle is a helium nucleus.
2. A beta particle is an electron.
3. A gamma ray is a high-energy form of light.
4. A positron is a positively charged electron.
5. Electron capture has the same effect on a nucleus as positron emission.

**16-1(b)** (a)  ${}_{37}^{87}\text{Rb}$  (b)  ${}_{89}^{227}\text{Ac}$  (c)  ${}_{27}^{54}\text{Co}$  (d)  ${}_{52}^{123}\text{Te}$   
(e)  ${}_{55}^{137m}\text{Cs}$

**16-1(c)** (a) Positron emission, since this is a proton rich isotope. (The product would be the stable isotope,  ${}^{14}\text{N}$ .) (b) Beta particle emission, since this is a neutron-rich isotope. (The product would be the stable isotope  ${}^{45}\text{Sc}$ .) (c) This is not a radioactive isotope as the neutron/proton ratio is 1:1.

**16-2(a)** The shorter the half-life, the faster an isotope decays.

**16-2(b)** After one half-life, 50% has decayed; after two half-lives, 75% has decayed; and after three half-lives, 87.5% has decayed.

**16-2(c)** After four half-lives, 4.0  $\mu\text{g}$  of the original sample is left.  $t_{1/2} = 36/4 = 9.0$  min (i.e., after 9.0 min, 32  $\mu\text{g}$  remains; after 18 min, 16  $\mu\text{g}$ ; after 27 min, 8.0  $\mu\text{g}$ ; and after 36 min, 4.0  $\mu\text{g}$ ).

**16-2(d)** We can never have a pure sample of a radioactive isotope because it is constantly decaying into different isotopes. There will always be a percentage, constantly changing, of other isotopes.

**16-3(a)** Radiation causes heating as well as the formation of ions along its path. The most ionizing type of radiation is alpha radiation, whereas the most penetrating is gamma radiation.

**16-3(b)** An ion formed is  $\text{H}_2\text{O}^+$  and a free radical is OH. The ion is a normal molecule minus an electron, and the free radical is a neutral molecule or part of a molecule with an unpaired electron.

**16-3(c)** All the particles and rays come out of a nucleus with high velocity. Collisions with the surrounding molecules or atoms in Earth's interior transmit kinetic energy to the surrounding atoms, thus increasing the heat.

**16-4(a)** Three major ways in which radiation is measured are the film badge, the Geiger counter, and the scintillation counter. The major unit used to measure the total amount of radiation is the curie. The major units that measure the amount of radiation received by a person are the rem and the sievert. The amount of radiation that is fatal to half of those that receive it is known as the LD<sub>50</sub>.

**16-4(b)** The first watch dials that glowed in the dark were coated with paint that contained zinc sulfide and radium. The steady emission of alpha particles from the radium caused the dial to glow. Unfortunately, workers

who painted the dial began to die of radiation poisoning, so this process was discontinued. Luminescent dials now glow in the dark from a small current of electricity that causes material called phosphors to glow. The clock by your bed probably has a liquid crystal display or a light emitting diode (LED).

## PART B

## EXERCISES

**16-5(a)** Balanced nuclear reactions have both a balanced mass and a balanced nuclear charge.

**16-5(b)** (a)  ${}_{23}^{52}\text{V}$  (b)  ${}_{54}^{144}\text{Xe}$  (c)  ${}_{6}^{12}\text{C}$

**16-5(c)**

(a)  ${}_{98}^{249}\text{Cf} + {}_{20}^{48}\text{Ca} \rightarrow {}_{118}^{294}\text{118} + 3{}_0^1\text{n}$   
 ${}_{118}^{294}\text{118} \rightarrow {}_{116}^{290}\text{116} + \alpha \rightarrow {}_{114}^{286}\text{114} + \alpha \rightarrow {}_{112}^{282}\text{Uub} + \alpha$

(b)  ${}^{48}\text{Ca}$  is very neutron rich and would decay by beta emission.

(c) Element 118 would be a noble gas.

**16-6(a)** Both naturally occurring and synthetic radioactive isotopes find many uses. The decay of carbon-14 can be used to date many carbon-containing fossils. Medically useful radioactive isotopes can be prepared by neutron activation. Food can be preserved by radiation with gamma radiation. PET scans make use of isotopes that emit positrons.

**16-6(b)**  ${}_{8}^{16}\text{O} + {}_1^2\text{H} \rightarrow {}_9^{18}\text{F}$      ${}_{5}^{10}\text{B} + {}_1^1\text{H} \rightarrow {}_6^{11}\text{C}$

**16-6(c)** (a) After 50,000 years (about nine half-lives), less than 0.2% of the original  ${}^{14}\text{C}$  remains. That would be very difficult to detect and measure accurately with a radiation counter. (b) The new isotope becomes "neutron rich," which means that it will likely be radioactive and decay by beta emission.

**16-7(a)** A nuclear reaction known as fission can occur as a nuclear chain reaction. The process whereby small nuclei combine to form a larger nucleus and a small particle is known as fission.

**16-7(b)** (a) fusion (b) beta emission (c) alpha emission (d) fission (e) electron capture

**16-7(c)** Some of the neutrons produced from the fission process combine with  ${}^{238}\text{U}$ , the more plentiful isotope. The  ${}^{239}\text{U}$  produced undergoes two beta decays to form  ${}^{239}\text{Pu}$ . This can be extracted (though not easily) from the control rods and made into atomic bombs.

**16-7(d)** The determining factor is the size of the nuclei. Small nuclei can undergo fusion, with the release of energy. A few large nuclei can undergo fission, with the release of energy. The break-even point on the periodic table is iron. This is why the nuclear fusion reactions in stars end with the production of iron.

## CHAPTER PROBLEMS

Throughout the text, answers to all exercises in color are given in Appendix G. The more difficult exercises are marked with an asterisk.

## Nuclear Radiation (SECTION 16-1)

**16-1.** Write isotope symbols in the form  ${}^A_ZM$  for isotopes of the following compositions.

- (a) 84 protons and 126 neutrons
- (b) 46 neutrons and a mass number of 84
- (c) 100 protons and a mass number of 257
- (d) lead-206
- (e) uranium-233

**16-2.** Write isotope symbols in the form  ${}^A_ZM$  for isotopes of the following compositions.

- (a) 86 protons and 134 neutrons
- (b) 6 protons and a mass number of 13
- (c) 22 neutrons and a mass number of 40
- (d) potassium-41
- (e) americium-243

**16-3.** Give the symbols, including mass number and charge, for the following.

- (a) an alpha particle
- (b) a beta particle
- (c) a neutron

**16-4.** A deuteron has a mass number of 2 and a positive charge of 1. Write its isotope symbol.

**16-5.** A triton has a mass number of 3 and a positive charge of 1. Write its isotope symbol.

**16-6.** Write the isotope symbol, including mass number, for the isotope that results when each of the following emits an alpha particle.

- (a)  ${}^{210}_{84}\text{Po}$
- (b)  ${}^{152}_{64}\text{Gd}$
- (c) fermium-252
- (d) Mt-266

**16-7.** Write the isotope symbol, including mass number, for the isotope that results when each of the following emits an alpha particle.

- (a)  ${}^{234}_{92}\text{U}$
- (b)  ${}^{229}_{88}\text{Ra}$
- (c)  ${}^{210}_{83}\text{Bi}$
- (d) thorium-229

**16-8.** Write the isotope symbol, including mass number, for the isotope that results when each of the following emits a beta particle.

- (a)  ${}^3_1\text{H}$
- (b)  ${}^{153}_{64}\text{Gd}$
- (c) iron-59
- (d) sodium-24

**16-9.** Write the isotope symbol, including mass number, for the isotope that results when each of the following emits a beta particle.

- (a)  ${}^{131}_{53}\text{I}$
- (b)  ${}^{234}_{91}\text{Pa}$
- (c) lead-210
- (d) nitrogen-16

**16-10.** Give the symbol of a positron. What effect does the emission of a positron have on an isotope? How are positrons detected?

**16-11.** Manganese-51 undergoes positron emission. Write the nuclear equation illustrating this reaction.

**16-12.** A certain isotope undergoes positron emission to form  ${}^{23}\text{Na}$ . Write the nuclear equation illustrating this reaction.

**16-13.** What happens to an isotope that undergoes electron capture? How is electron capture detected?

**16-14.** Germanium-68 undergoes electron capture. Write the nuclear equation illustrating this reaction.

**16-15.** A certain isotope undergoes electron capture to form  ${}^{55}\text{Mn}$ . Write the nuclear equation illustrating this reaction.

**16-16.** Complete the following nuclear equations.

- (a)  ${}^{214}_{83}\text{Bi} \rightarrow {}^{214}_{84}\text{Po} + \text{_____}$
- (b)  ${}^{90}_{37}\text{Rb} \rightarrow \text{_____} + {}^0_{-1}\text{e}$
- (c)  ${}^{26}_{14}\text{Si} \rightarrow \text{_____} + {}^0_{+1}\text{e}$
- (d)  ${}^{235}_{92}\text{U} \rightarrow \text{_____} + {}^4_2\text{He}$
- (e)  ${}^{179}_{73}\text{Ta} + {}^0_{-1}\text{e} \rightarrow \text{_____}$
- (f)  $\text{_____} \rightarrow {}^{41}_{21}\text{Sc} + {}^0_{-1}\text{e}$
- (g)  $\text{_____} \rightarrow {}^{210}_{82}\text{Pb} + {}^0_{-1}\text{e}$

**16-17.** Complete the following nuclear equations.

- (a)  ${}^{239}_{93}\text{Np} \rightarrow \text{_____} + {}^0_{-1}\text{e}$
- (b)  $\text{_____} \rightarrow {}^{93}_{44}\text{Ru} + {}^0_{+1}\text{e}$
- (c)  ${}^{226}_{86}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + \text{_____}$
- (d)  $\text{_____} \rightarrow {}^{235}_{92}\text{U} + {}^4_2\text{He}$
- (e)  ${}^{80}_{37}\text{Rb} + \text{_____} \rightarrow {}^{80}_{36}\text{Kr}$
- (f)  ${}^{32}_{15}\text{P} \rightarrow {}^{32}_{16}\text{S} + \text{_____}$

**16-18.** From the following information, write nuclear equations that include all isotopes and particles.

- (a)  ${}^{230}_{90}\text{Th}$  decays to  ${}^{226}_{88}\text{Ra}$ .
- (b)  ${}^{214}_{84}\text{Po}$  emits an alpha particle.
- (c)  ${}^{210}_{84}\text{Po}$  emits a beta particle.
- (d) An isotope emits an alpha particle and forms lead-214.
- (e)  ${}^{14}_6\text{C}$  decays to form  ${}^{14}_7\text{N}$ .
- (f) Chromium-50 is formed by positron emission.
- (g) Argon-37 captures an electron.

**\*16-19.** The decay series of  ${}^{238}_{92}\text{U}$  to  ${}^{206}_{82}\text{Pb}$  involves alpha and beta emissions in the following sequence:  $\alpha, \beta, \beta, \alpha, \alpha, \alpha, \alpha, \beta, \alpha, \beta, \beta, \beta, \alpha$ . Identify all isotopes formed in the series.

## Nuclear Decay and Half-Life (SECTION 16-2)

**16-20.** What fraction of a radioactive isotope remains after four half-lives?

**16-21.** What percent of a radioactive isotope remains after five half-lives?

**16-22.** If one starts with 20 mg of a radioactive isotope with a half-life of 2.0 days, how much remains after each interval?

- (a) four days
- (b) eight days
- (c) four half-lives

**16-23.** The half-life of a given isotope is 10 years. If we start with a 10.0-g sample of the isotope, how much is left after 20 years?

**16-24.** Start with 12.0 g of a given radioactive isotope. After 11 years, only 3.0 g is left. What is the half-life of the isotope?

**16-25.** The isotope  $^{14}_6\text{C}$  is used to date fossils of formerly living systems, such as prehistoric animal bones. If the radioactivity of the carbon in a sample of bone from a mammoth is one-fourth of the radioactivity of the current level, how old is the fossil? ( $t_{1/2} = 5760$  years)

### Effects of Radiation and Its Detection

(SECTIONS 16-3 AND 16-4)

**16-26.** Of the three types of radiation, which is the most ionizing? Which is the most penetrating? How does each type of radiation cause damage to cells?

**16-27.** How does radiation cause ionization? How does ionization cause damage to living tissues?

**16-28.** How does a film badge work? How can a film badge tell which type of radiation is being absorbed?

**16-29.** How does a Geiger counter work? How does a scintillation counter work?

### Nuclear Reactions (SECTION 16-5)

**16-30.** Complete the following nuclear equations.

- (a)  $^{35}_{17}\text{Cl} + {}^1_0\text{n} \rightarrow \text{---} + {}^1_1\text{H}$
- (b)  $^{27}_{13}\text{Al} + \text{---} \rightarrow {}^{25}_{12}\text{Mg} + {}^4_2\text{He}$
- (c)  $^{27}_{13}\text{Al} + {}^4_2\text{He} \rightarrow \text{---} + {}^1_0\text{n}$
- (d)  $^{238}_{92}\text{U} + 15{}^1_0\text{n} \rightarrow {}^{253}_{100}\text{Fm} + \text{---}$
- (e)  $^{244}_{96}\text{Cm} + {}^{12}_6\text{C} \rightarrow \text{---} + 2{}^1_0\text{n}$
- (f)  $\text{---} + {}^2_1\text{H} \rightarrow {}^{238}_{93}\text{Np} + {}^1_0\text{n}$
- (g)  $^{242}_{94}\text{Pu} + {}^{22}_{10}\text{Ne} \rightarrow {}^{260}_{104}\text{---} + \text{---}$

**16-31.** Complete the following nuclear equations.

- (a)  $^{249}_{96}\text{Cm} + \text{---} \rightarrow {}^{260}_{103}\text{Lr} + 4{}^1_0\text{n}$
- (b)  $^{15}_7\text{N} + {}^1_1\text{H} \rightarrow \text{---} + {}^4_2\text{He}$
- (c)  $^{10}_5\text{B} + {}^4_2\text{He} \rightarrow \text{---} + {}^1_1\text{H}$
- (d)  $^{249}_{98}\text{Cf} + \text{---} \rightarrow {}^{263}_{106}\text{---} + 4{}^1_0\text{n}$

**16-32.** An element on the periodic table was prepared by the following nuclear reaction.



How many neutrons were emitted in the reaction?

**16-33.** Dubnium-260 plus four neutrons is prepared by bombarding Californium-249 with what isotope?

**16-34.** Hassium-265 plus one neutron is prepared by bombarding an isotope of lead with iron-58. What is the isotope of lead?

**16-35.** Bismuth-209 can be bombarded with chromium-54, producing one neutron and what heavy element isotope?

### Fission and Fusion (SECTION 16-7)

**16-36.** When  $^{235}_{92}\text{U}$  and  $^{239}_{94}\text{Pu}$  undergo fission, a variety of reactions take place. Complete the following.

- (a)  $^{235}_{92}\text{U} + {}^1_0\text{n} \rightarrow \text{---} + {}^{146}_{58}\text{Ce} + 3{}^1_0\text{n}$
- (b)  $^{239}_{94}\text{Pu} + {}^1_0\text{n} \rightarrow {}^{141}_{56}\text{Ba} + \text{---} + 2{}^1_0\text{n}$

**16-37.** What is the difference between fission and fusion? What is the source of energy for these two processes?

**\*16-38.** In 1989, some scientists reported that they had achieved "cold fusion." This was supposedly accomplished by electrolyzing heavy water (deuterium oxide) with palladium electrodes. It was suggested that the deuterium was absorbed into the electrodes and somehow two deuterium nuclei could overcome the strong repulsions at a low temperature and fuse. Evidence was presented to indicate that more energy came out of the reaction than could be accounted for by a chemical process. There has been little support for these initial experiments, but, for a while, they generated nightly reports on the national news. The fusion of two deuterium nuclei should produce helium-4, which, according to theory, would have too much energy to be stable and so would decompose to either helium-3 or tritium. What other two particles would be produced by this decomposition? Write the appropriate nuclear equations.

### General Problems

**16-39.** Write equations illustrating each of the following nuclear processes.

- (a) Palladium-106 absorbs an alpha particle to produce an isotope and a proton.
- (b) Meitnerium-266 emits an alpha particle to form an isotope that also emits an alpha particle.
- (c) Bismuth-212 emits a beta particle.
- (d) An isotope emits a positron to form copper-60.
- (e) Plutonium-239 absorbs a neutron to produce cesium-140, another isotope, and three neutrons.
- (f) Lead-206 is bombarded by an isotope to produce seaborgium-257 and three neutrons.
- (g) An isotope captures an electron to form niobium-93.

**16-40.** Write equations illustrating each of the following nuclear processes.

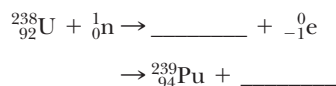
- (a) An isotope of a heavy element is bombarded with boron-11 to form lawrencium-257 and four neutrons.
- (b) An isotope emits an alpha particle to form actinium-231.
- (c) Oxygen-14 emits a particle to form nitrogen-14.
- (d) Sulfur-31 captures an electron to form an isotope.
- (e) Uranium-235 absorbs a neutron to form rubidium-90, cesium-142, and several neutrons.
- (f) Two helium nuclei fuse (in the sun) to form lithium-7 and a particle.
- (g) An isotope emits a beta particle to form lead-208.
- (h) Plutonium-239 is bombarded with an isotope to form curium-242 and a neutron.

**16-41.** The radioactive isotope  $^{90}_{38}\text{Sr}$  can accumulate in bones, where it replaces calcium. It emits a high-energy beta particle, which eventually can cause cancer.

- (a) What is the product of the decay of  $^{90}_{38}\text{Sr}$ ?  
 (b) How long would it take for a 0.10-mg sample of  $^{90}_{38}\text{Sr}$  to decay to where only  $2.5 \times 10^{-2}$  mg was left? (The half-life of  $^{90}_{38}\text{Sr}$  is 25 years.)

**16-42.** The radioactive isotope  $^{131}_{53}\text{I}$  accumulates in the thyroid gland. On the one hand, this can be useful in detecting diseases of the thyroid and even in treating cancer at that location. On the other hand, exposure to excessive amounts of this isotope, such as from a nuclear power plant, can cause cancer of the thyroid.  $^{131}_{53}\text{I}$  emits a beta particle with a half-life of 8.0 days. What is the product of the decay of  $^{131}_{53}\text{I}$ ? If one started with  $8.0 \times 10^{-6}$  g of  $^{131}_{53}\text{I}$ , how much would be left after 32 days?

**16-43.** The fissionable isotope  $^{239}_{94}\text{Pu}$  is made from the abundant isotope of uranium,  $^{238}_{92}\text{U}$ , in nuclear reactors. When  $^{238}_{92}\text{U}$  absorbs a neutron from the fission process,  $^{239}_{94}\text{Pu}$  eventually forms. This is the principle of the breeder reactor, although  $^{239}_{94}\text{Pu}$  is formed in all reactors. Complete the following reaction.



**16-44.** An isotope of hydrogen, known as tritium ( $^3\text{H}$ ), has a half-life of 12 years. If a sample of tritium was prepared 60 years ago, what was its original mass if its current mass is  $0.42 \mu\text{g}$ ?

**16-45.** A particular isotope has a half-life of 10.0 days. What percent of the original sample is left after 30.0 days?

**16-46.** A new element was created in 1994. What is the atomic number and mass number of the isotope if the nuclear reaction involved bombardment of  $^{209}\text{Bi}$  with  $^{64}\text{Ni}$  to form the new element plus one neutron?

**16-47.** The isotope  $^{269}\text{110}$  was also created in 1994. The nuclear reaction involved bombardment of an isotope with  $^{62}\text{Ni}$  and produced the new element and one neutron. What is the isotope involved in the reaction?

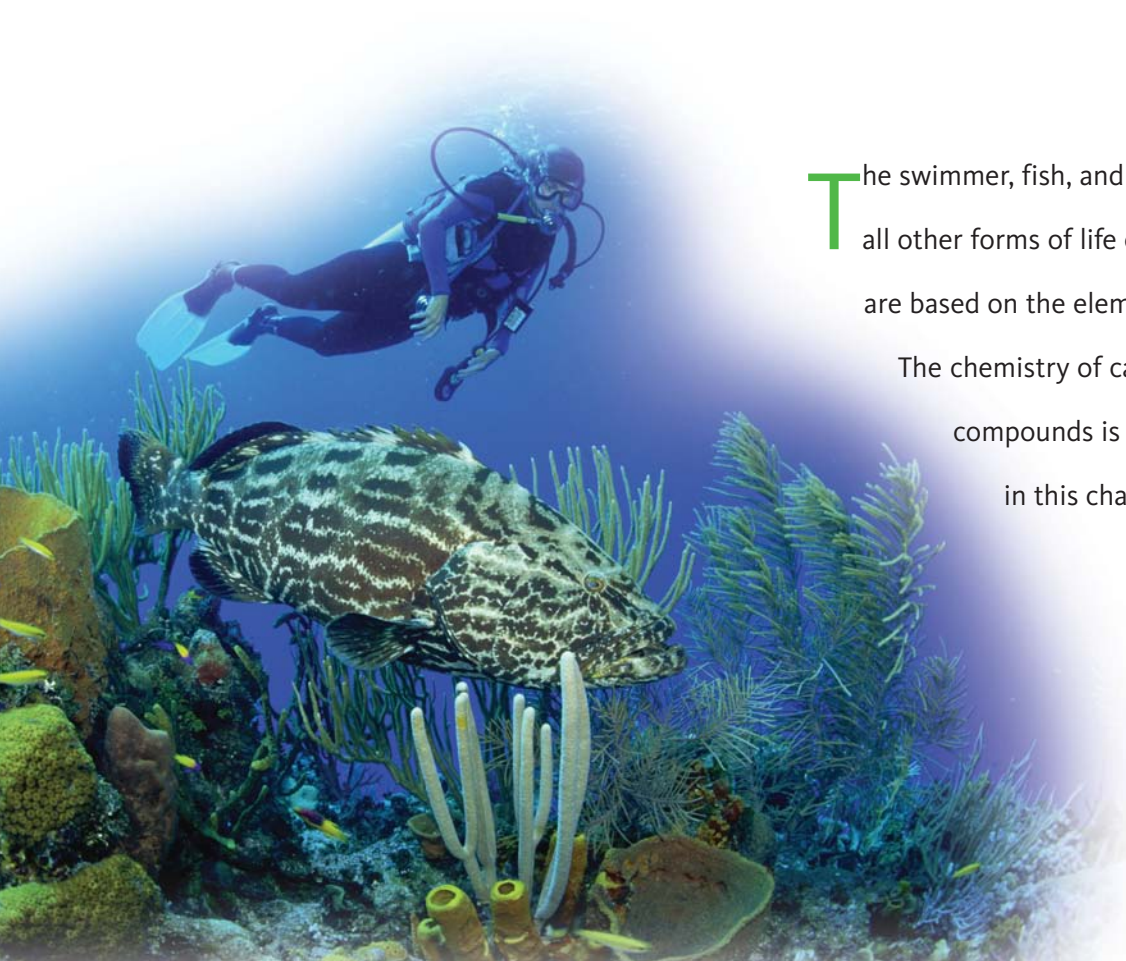
**16-48.** A team in Germany reported the formation of one atom of  $^{277}\text{112}$  in 1996 by bombarding  $^{208}\text{Pb}$  with a lighter nucleus. If one neutron is also produced, what is the isotopic notation for the lighter nucleus?

**16-49.** A team in Germany reported element  $^{282}\text{114}$ , which, according to theory, should be more stable than other superheavy elements. The reaction involves bombarding  $^{208}\text{Pb}$  with a lighter isotope. If two neutrons are also produced, what is the isotopic notation of the lighter nucleus?



CHAPTER  
17

# Organic Chemistry



The swimmer, fish, and vegetation—and all other forms of life on this planet—are based on the element carbon.

The chemistry of carbon compounds is discussed in this chapter.

**PART A**  
**HYDROCARBONS**

**17-1** Bonding in Organic Compounds

**17-2** Alkanes

**17-3** Alkenes and Alkynes



**MAKING IT REAL**

*The Age of Plastics*

**17-4** Aromatic Compounds

**PART B**  
**OTHER CLASSES OF ORGANIC COMPOUNDS**

**17-5** Alcohols and Ethers

**17-6** Aldehydes and Ketones

**17-7** Amines

**17-8** Carboxylic Acids, Esters, and Amides



**MAKING IT REAL**

*Aspirin—An Old Drug with a New Life*

**SETTING THE STAGE** Perfectly positioned about 90 million miles from a medium-sized star and protected by a strong magnetic field and a thick atmosphere, our planet glides majestically in space. Under these ideal conditions, the presence of liquid water as well as the formation and stable existence of chemical bonds that compose living systems are possible. These living systems grow and reproduce on Earth, move gracefully in the oceans, and float effortlessly in the air. All these creatures and plants are composed of compounds that include the element carbon as the central character. We, of course, consider ourselves to be the very ultimate carbon-based life-form. Could there be life-forms based on other elements? Science fiction stories would have us think so, but it is actually quite unlikely, if not impossible. In this chapter, we will see how this unique element forms the types of matter, known as organic compounds, that are part of living systems.

Organic compounds are certainly central to our lives. Hydrocarbons (compounds composed only of carbon and hydrogen) are used as fuel to power our cars and to heat our homes. Our bodies are fueled with organic compounds obtained from the food we eat in the form of sugars (carbohydrates), fats, and proteins. This food is made more palatable by organic flavorings, is wrapped in organic plastic, and is kept from spoiling with organic preservatives. Our clothes are made of organic compounds, whether these compounds come from plant and animal sources (cotton and wool) or are synthetic (nylon and Dacron). These fabrics are made colorful with organic dyes. When we are ill, we take drugs that may also be organic: aspirin relieves headaches, codeine suppresses coughs, and diazepam (Valium) calms nerves. These are only a few examples of how we use organic chemicals daily.

In Part A in this chapter, we will first review how we represent organic compounds with Lewis structures. We will then discuss various types of compounds composed only of carbon and hydrogen, their special properties, and how we name them. In Part B, we extend the discussion to organic compounds containing other atoms in addition to carbon and hydrogen.

**PART A**  
**HYDROCARBONS**
**SETTING A GOAL**

- We will learn about the structure, properties, and nomenclature of hydrocarbons.

**OBJECTIVES**

- 17-1** Write Lewis structures of simple organic compounds including isomers of a compound using, where possible, condensed and fully condensed formulas.
- 17-2 (a)** Write the formulas of straight-chain alkanes.  
**(b)** Give the IUPAC names of some simple alkanes.
- 17-3 (a)** Write the formulas of alkenes and alkynes.  
**(b)** Give the IUPAC names of some simple alkenes.  
**(c)** Describe how alkenes are used to make polymers.
- 17-4** Describe the difference between aromatic compounds and straight-chain alkenes using resonance.

**▶ OBJECTIVE FOR SECTION 17-1**

Write Lewis structures of simple organic compounds including isomers of a compound using, where possible, condensed and fully condensed formulas.

## 17-1 BONDING IN ORGANIC COMPOUNDS



**LOOKING AHEAD!** We will begin our discussions of organic compounds with a review of the bonding and properties of carbon–hydrogen compounds. Of particular interest to the discussions that follow are the Lewis structures, polarity of bonds, geometry, and polarity of molecules. ■

### 17-1.1 Organic and Inorganic Compounds

Traditionally, all chemical compounds have been relegated to two categories: organic and inorganic. **Organic compounds** include most of the compounds of carbon, especially those containing carbon–hydrogen bonds. However, much of the chemistry that we have discussed so far concerns compounds derived from minerals and other noncarbon compounds, and these are known as **inorganic compounds**. A few compounds of carbon such as  $\text{CaCO}_3$  and  $\text{LiCN}$  are considered to be inorganic compounds since they are derived from minerals and do not contain C–H bonds.

Originally, the division of compounds into the two categories was determined by whether they were derived from (or part of) a living system (organic) or from a mineral (inorganic). In fact, before 1828, it was thought that only living matter (organisms) could synthesize organic compounds and their decay products from inorganic compounds (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{NH}_3$ ). Only life had that magic ingredient of nature called the “vital force” that allowed the miracle of organic synthesis. In 1828, however, a German scientist named Friedrich Wöhler synthesized urea ( $\text{H}_2\text{NCONH}_2$ ), which had been classified as organic, from the inorganic compound ammonium cyanate ( $\text{NH}_4\text{CNO}$ ). Urea is a waste product of the metabolism of proteins and, until 1828, was thought to result only from this source. Although it was just one compound, the concept of the “vital force” was doomed. Since that time, millions of organic compounds have been synthesized from basic minerals in the laboratory.

Of all of the elements in the periodic table, only one has properties that make possible the existence of large complex molecules on which living systems are based. This, of course, is carbon. There are two reasons for carbon’s unique properties.

1. Carbon–carbon bonds are strong. This makes long chains of carbon atoms possible.
2. Carbon and hydrogen have similar electronegativities. This means that the C–H bond is essentially nonpolar. As a result, the C–H bond is not chemically reactive toward many compounds, such as water.

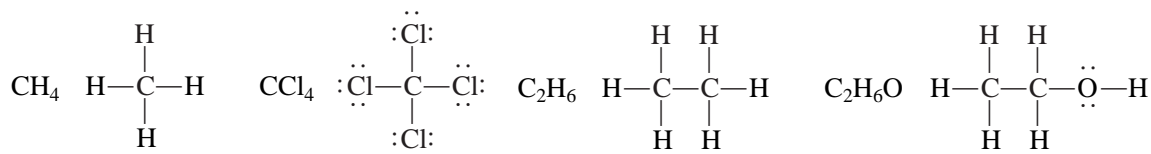
A science fiction writer may look at Group IVA in the periodic table and notice that silicon is immediately under carbon. Could the writer propose life based on silicon? In fact, such life-forms are not likely. First, silicon–silicon bonds are much weaker than carbon–carbon bonds, so long chains of silicon atoms in a molecule do not occur. Second, the Si—H bond is polar, meaning that it is chemically reactive with other polar compounds. For example, silicon–hydrogen compounds react spontaneously with water (a polar compound) at room temperature. It is hard to imagine a life-form based on small molecules that react with water. If such life existed on some distant planet, we would hope that it wouldn't get caught in the rain.

Most organic compounds are typical molecular compounds. That is, they are usually gases or liquids at room temperature or solids with low melting points. Since the C—H bond is nearly nonpolar, most organic molecules are nonpolar or, at most, have low polarity. This means that, in general, they have little solubility in water. Inorganic compounds, on the other hand, are likely to be ionic, which means that they are high-melting solids and more likely to be soluble in water.

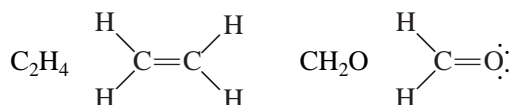
### 17-1.2 Bonding in Organic Compounds

Carbon (in Group IVA) has four valence electrons. In its compounds, carbon follows the octet rule, which means that it must form *four* bonds to have access to eight valence electrons. It may form (a) four single bonds to four different atoms, (b) a double bond to one atom and two single bonds to two others, (c) two double bonds to two different atoms, or (d) a triple bond to one atom and one single bond to one other atom. Examples of each of these four cases are shown, written as Lewis structures.

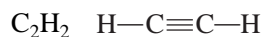
#### a. Single bonds



#### b and c. Double bonds



#### d. Triple bonds



As we will see, organic compounds are classified according to the types of bonds in their molecules. Thus, writing correct Lewis structures is an important endeavor and is reviewed in Example 17-1.

### EXAMPLE 17-1

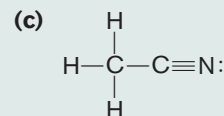
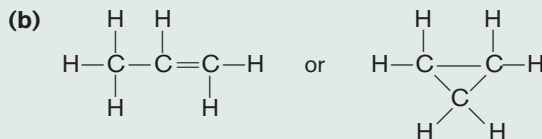
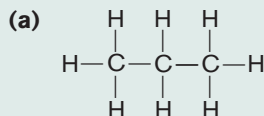
#### Writing Lewis Structures of Some Organic Compounds

Write Lewis structures for the following compounds.

- (a)  $\text{C}_3\text{H}_8$     (b)  $\text{C}_3\text{H}_6$     (c)  $\text{H}_3\text{C}_2\text{N}$  (skeletal structure is CCN with all H's on one C)

#### PROCEDURE

Review the rules for writing Lewis structures from Section 9-3. Remember that H can be bonded to only one atom, so it will always be on the periphery of the structure. Generally, H forms one bond; oxygen, two; nitrogen, three; and carbon, four.

**SOLUTIONS**

**ANALYSIS**

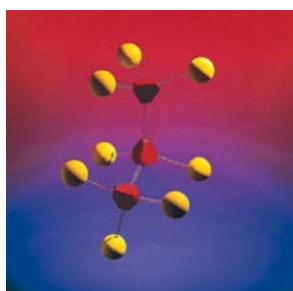
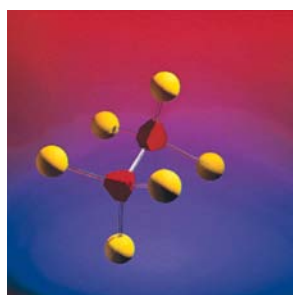
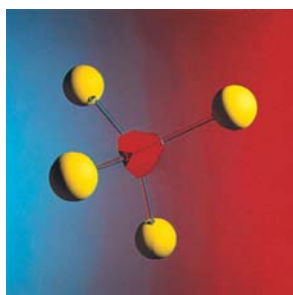
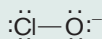
In (a) only single bonds occur. In (b), the first structure must have a double bond. If you place the double bond between the first two carbons, you have a structure identical with the one shown. It is just turned around. The second structure represents a compound that actually exists, known as cyclopropane. Obviously, more than one compound can have the same formula but different structures. These are known as isomers and are discussed next. The structure shown in (c) is the only possibility where the hydrogens are all on one carbon and has the sequence of atoms shown.

**SYNTHESIS**

Are there any common compounds where the bonding described in the Procedure is not followed? Yes. There is one major exception—carbon monoxide, which has the structure



There are also Lewis structures involving oxyanions where oxygen forms one bond. For example, the hypochlorite ion has the following representation

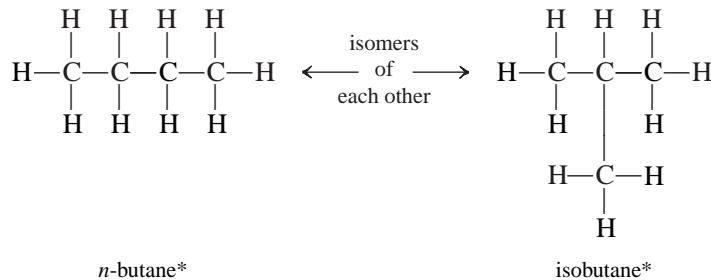


**FIGURE 17-1** Geometry of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$

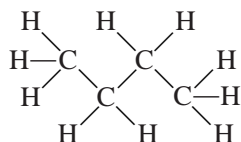
In these hydrocarbons, each carbon is at the center of a tetrahedron.

**17-1.3 Representation of Isomers**

Many times we find that there is more than one Lewis structure for a given formula. Such is the case with butane,  $\text{C}_4\text{H}_{10}$ , since two correct structures can be drawn. *Compounds with different structures but the same molecular formula are called isomers.*



These Lewis structures represent the molecules as flat or two-dimensional. In fact, when carbon is bonded to four other atoms, it lies in the center of a tetrahedron. In the actual three-dimensional structure, the  $\text{H}-\text{C}-\text{H}$  bond angle is about  $109^\circ$ . A truer representation of the structure of *n*-butane is



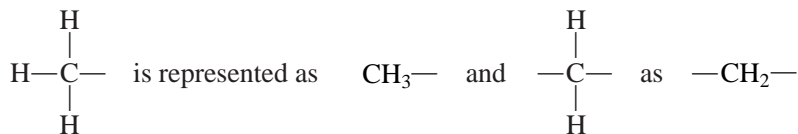
This representation is somewhat awkward, however, so long-chain structures are usually shown in a straight line even though they actually have a three-dimensional geometry. A true representation of the structure requires the use of molecular models. In Figure 17-1, the  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  molecules are represented by “ball-and-stick” models. In a three-dimensional representation, we can see that all the hydrogens in the  $\text{C}_2\text{H}_6$  molecule are identical.

\*The *n* is an abbreviation for *normal* and refers to the isomer in which all the carbons are bound consecutively in a continuous chain. The *iso*-prefix refers to the isomer in which there is a branch involving three carbons attached to a carbon chain or another atom.

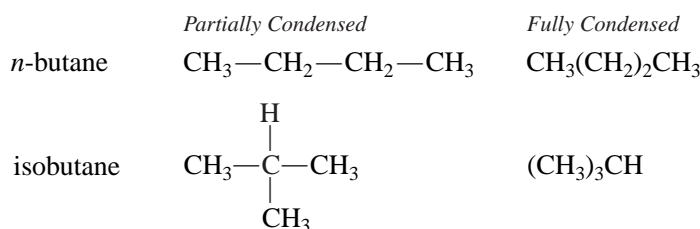


### 17-1.4 Condensed Formulas

Many of the compounds that we will mention in the following sections have several repeating units. Drawing these structures can become quite tedious if all hydrogens and carbons are written out. A **condensed** formula in which separate bonds are not written is helpful. For example,



Depending on what we are trying to show, the structure may be partially or fully condensed.



In a fully condensed structure, it is understood that the  $\text{CH}_2$ 's in parentheses are in a continuous chain and the  $\text{CH}_3$ 's in parentheses are attached to the same atom.

A few other compounds and their isomers are shown in Table 17-1. As you can see, the number of isomers increases as the number of carbons increases, and addition of a **heteroatom** (*any atom other than carbon or hydrogen*) also increases the number of isomers.

**TABLE 17-1** Isomers

|                                |   |  |  |
|--------------------------------|---|--|--|
| $\text{C}_5\text{H}_{12}$      | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$<br><i>n</i> -pentane            | $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CH}_3 \end{array}$ isopentane            | $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ neopentane |
| $\text{C}_3\text{H}_6$         | $\text{H}_2\text{C}=\text{CHCH}$<br>propene   | $\begin{array}{c} \text{H}_2\text{C} \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{CH}_2 \end{array}$ cyclopropane | (Note that the carbons can also be arranged in a ring or <i>cyclic</i> structure.)                                 |
| $\text{C}_2\text{H}_6\text{O}$ | $\text{CH}_3\text{CH}_2\text{OH}$<br>ethanol  | $\text{H}_3\text{C}-\text{O}-\text{CH}_3$<br>dimethyl ether  |  |
| $\text{C}_3\text{H}_6\text{O}$ | $\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CH}_2\text{CH} \end{array}$ propanal | $\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$ propanone                   | $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$<br>allyl alcohol and others  |

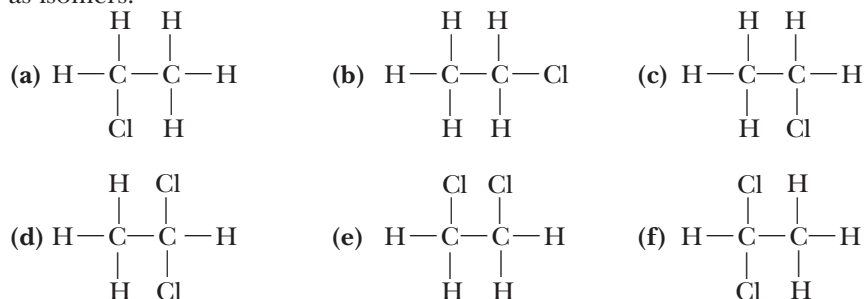
**ASSESSING THE  
OBJECTIVE FOR  
SECTION 17-1**

**EXERCISE 17-1 (a) KNOWLEDGE:** Fill in the blanks.

Lewis structures of organic compounds illustrate that carbon forms a total of \_\_\_\_\_ bonds to other atoms. Two different compounds that share the same formula are known as \_\_\_\_\_. Elements other than carbon and hydrogen that appear in an organic compound are known as \_\_\_\_\_ atoms.

**EXERCISE 17-1(b) ANALYSIS:** Write the Lewis structures of all of the isomers of pentane ( $C_5H_{12}$ ). Write them as partially condensed structures.

**EXERCISE 17-1(c) SYNTHESIS:** Which of the following can be classified as isomers?



For additional practice, work chapter problem 17-3.

### OBJECTIVES FOR SECTION 17-2

(a) Write the formulas of straight-chain alkanes. (b) Give the IUPAC names of some simple alkanes.

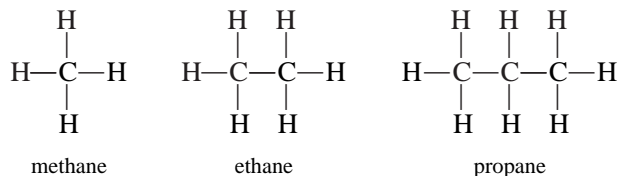
## 17-2 ALKANES



**LOOKING AHEAD!** In the next three sections, we will discuss organic compounds composed of only two elements (carbon and hydrogen). These compounds are classified into four categories based on the type of bonding in the molecules. In this section, we will investigate carbon–hydrogen compounds that contain only single covalent bonds. ■

### 17-2.1 Homologous Series

Natural gas, gasoline, and candle wax are all composed of hydrocarbons. **Hydrocarbons** are compounds that contain only carbon and hydrogen. These particular hydrocarbons are also classified as alkanes. **Alkanes** are hydrocarbons that contain only single covalent bonds. Since the carbons in these molecules bond to the maximum number of hydrogens, alkanes are known as **saturated** hydrocarbons. Alkanes can be described by the general formula  $C_nH_{2n+2}$ . This refers only to *open-chain alkanes*, meaning that the carbons do not form a ring. The simplest alkane ( $n = 1$ ) is methane ( $CH_4$ ), in which the carbon shares *four pairs of electrons* with four different hydrogen atoms. The next alkane ( $n = 2$ ) is ethane ( $C_2H_6$ ), and the third is propane ( $C_3H_8$ ). These alkanes are members of a homologous series. *In a homologous series, the next member differs from the previous one by a constant structure unit, which is one carbon and two hydrogens ( $CH_2$ ).*



The names in Table 17-2 are the basis for the names of all organic compounds. By altering them slightly, we can name other classes of organic compounds that are discussed later. Two systems of nomenclature are used in organic chemistry. The most systematic is the one devised by the International Union of Pure and Applied Chemistry (the IUPAC system). Although the rules for naming complex molecules can be extensive, we will be concerned with just the basic concepts.

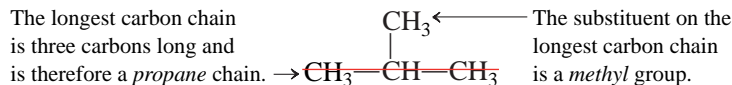
Compounds are also known by *common* or *trivial* names. Sometimes these names follow a pattern; sometimes they do not. They have been used for so many years that it is hard to break the habit of using them. When a chemical that is frequently known by its common name is encountered, that name is given in parentheses.

### 17-2.2 IUPAC Names

The name of a simple organic compound has two parts; the base of the name gives the number of carbons in the longest carbon chain, and the ending tells what kind of a compound it is. The underlined portions of the names in Table 17-2 are the basis of the names used for compounds containing 1 through 10 carbons in the longest chain; *meth-* stands for one carbon, *eth-* for two carbons, and so on. The ending used for alkanes is *-ane*. Therefore, the one-carbon alkane is methane, the two-carbon alkane is ethane, and so on.

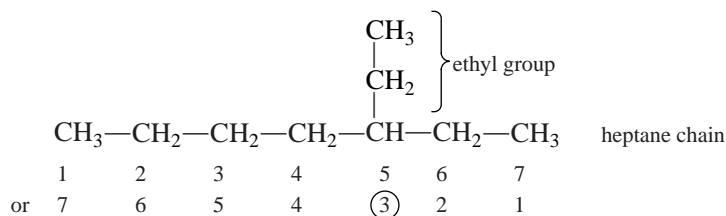
Organic compounds can exist as unbranched compounds (all carbons bound to each other in a continuous chain) or as branched compounds (where at least one carbon is joined to three or four others). Previously, we indicated that *n*-butane is an unbranched alkane and that isobutane is a branched alkane. The IUPAC system bases its names on the longest carbon chain in the molecule, whereas the common names frequently include all of the carbons in the name (e.g., isobutane). The longest carbon chain in isobutane is three carbons long and is therefore considered a propane in the IUPAC system. Note that isobutane has a CH<sub>3</sub> group attached to a propane chain. In this system of nomenclature, the branches are named separately. *Since the branches can be considered as groups of atoms substituted for a hydrogen, the branches are called substituents. Substituents that contain one less hydrogen than an alkane are called alkyl groups.* Alkyl groups are not compounds by themselves; they must always be attached to some other group or atom. They are named by taking the alkane name, dropping the *-ane* ending, and substituting *-yl*. The most common alkyl groups are given in Table 17-3.

Thus, the alkyl substituent in isobutane is a methyl group. The IUPAC name for isobutane is *methylpropane*.



If the same group is substituted on either the same carbon or another carbon, the prefix *di-* is used to indicate two groups. If the same group is substituted on three carbons, the prefix *tri-* is used to indicate three groups. For example, the IUPAC name for neopentane (see Table 17-1) is *dimethylpropane*.

When the main chain is long and the substituent could be placed on one of several different carbons, the location of the substituent is designated by a number. The carbons of the longest chain are numbered from the end that gives the substituent the lowest number. Thus, the following compound is named 3-ethylheptane rather than 5-ethylheptane.



**TABLE 17-2** Alkanes

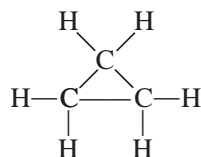
| FORMULA                         | NAME           |
|---------------------------------|----------------|
| CH <sub>4</sub>                 | <u>methane</u> |
| C <sub>2</sub> H <sub>6</sub>   | <u>ethane</u>  |
| C <sub>3</sub> H <sub>8</sub>   | <u>propane</u> |
| C <sub>4</sub> H <sub>10</sub>  | <u>butane</u>  |
| C <sub>5</sub> H <sub>12</sub>  | <u>pentane</u> |
| C <sub>6</sub> H <sub>14</sub>  | <u>hexane</u>  |
| C <sub>7</sub> H <sub>16</sub>  | <u>heptane</u> |
| C <sub>8</sub> H <sub>18</sub>  | <u>octane</u>  |
| C <sub>9</sub> H <sub>20</sub>  | <u>nonane</u>  |
| C <sub>10</sub> H <sub>22</sub> | <u>decane</u>  |

**TABLE 17-3** Alkyl Groups (One to Four Carbons)

| ALKYL GROUP <sup>a</sup>  | NAME                                    |
|---|---|
| CH <sub>3</sub> —   | methyl                                  |
| CH <sub>3</sub> CH <sub>2</sub> —                                 | ethyl                                   |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —                 | <i>n</i> -propyl                        |
| (CH <sub>3</sub> ) <sub>2</sub> CH—                               | isopropyl                               |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> — | <i>n</i> -butyl                         |
| (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> —               | isobutyl                                |
| CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )—             | <i>sec</i> -butyl                       |
| (CH <sub>3</sub> ) <sub>3</sub> C—                                | <i>tert</i> -butyl (or <i>t</i> -butyl) |

<sup>a</sup> The dash (—) shows where the alkyl group is attached to a carbon atom or a hetero atom.

When the carbons form a ring, the name is prefixed with *cyclo*-. Therefore, the three-carbon ring compound



is called cyclopropane. Cycloalkanes have the general formula  $C_nH_{2n}$ .

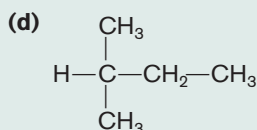
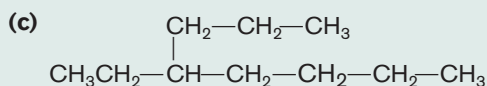
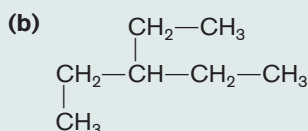
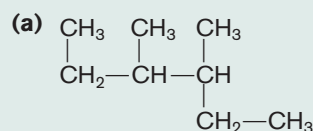
### EXAMPLE 17-2

#### Determining and Naming the Longest Chain

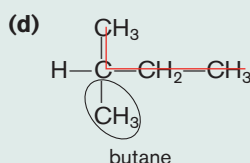
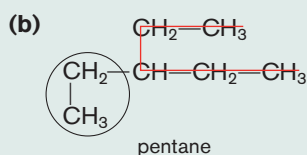
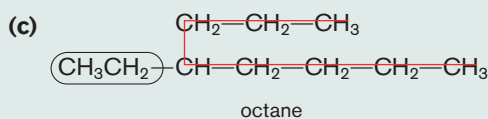
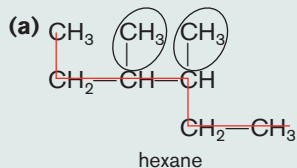
Draw a line through the longest carbon chain in the following compounds and circle the substituents. Name the longest chain.

#### PROCEDURE

First identify the longest chain of consecutive carbon atoms and name the chain using Table 17-2. The groups attached to this chain are the substituents.



#### SOLUTIONS



#### ANALYSIS

Since molecules are free to twist and turn as they please, we have the same luxury when writing them on a two-dimensional surface like a piece of paper or a computer screen. For simplicity, when we write a structure, we usually show the longest chain going straight across and use a numbering system that goes left to right. However, we are not obliged to do this. The longest chain can twist and turn through the structure as well, making it critical to be careful to check each possibility when trying to find the main chain. Furthermore, the substituents may be attached to either end, necessitating a check to see which direction along the main chain yields the smallest substituent numbers.

#### SYNTHESIS

All of these possibilities for structures are what makes organic chemistry such a vast field for study. Molecules have the potential to get complicated quite quickly. The first three alkanes have only one possible structure. Butane has two possible isomers, *n*-butane and isobutane. Pentane has three isomers. Hexane has five. Heptane has nine. By the time you get to decane, there are 75 unique ways to arrange 10 carbon atoms with a main chain and substituents. It's quite a trick to attempt to write each one without duplicating the order. Can you draw the nine unique structures of heptane?

**EXAMPLE 17-3****Naming Alkanes by the IUPAC Method**

Name the compounds in Example 17-2 by the IUPAC method.

**PROCEDURE**

Identify the longest continuous chain of carbon atoms. Use that for the base name. Identify the substituents using Table 17-3 and number their positions along the longest chain. Be sure that you use the smallest total number for the substituents.

**SOLUTIONS**

- (a) 3,4-dimethylhexane      (b) 3-ethylpentane      (c) 4-ethyloctane      (d) methylbutane

**ANALYSIS**

In (a) and (b), notice that the names are the same regardless of the direction on the carbon chain. In (c), if you started from the other end, the name would be 5-ethylpentane, which would not be correct. In (d), no number is necessary since it has only one possible structure. If one used a number it would be 2-methylbutane, but if the methyl were on the adjacent carbon, it would still be 2-methylbutane, so the number is not needed.

**SYNTHESIS**

As you become more and more familiar with the official naming system for organic molecules, consider becoming more aware of the chemicals in the foods you eat and the products you use daily. A quick scan of the contents of cosmetics, cleaners, ointments, and medicines will reveal names of compounds or fragments of names that may likely sound much more familiar. Consider phenylpropanolamine, a common decongestant. The first part of the ingredient ends in *-yl*, indicating that it is a substituent. There is the base name *-propan-* in the middle of the name, indicating a 3-carbon main chain. The *-olamine* at the end simply tells us the type of molecule it is.

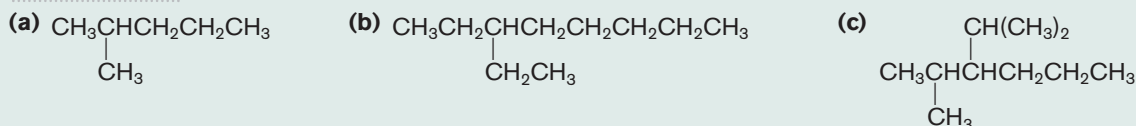
**EXAMPLE 17-4****Writing Condensed Structures from a Name**

Write the condensed structures of the following.

- (a) 2-methylpentane    (b) 3-ethyloctane    (c) 3-isopropyl-2-methylhexane (Substituent groups are listed in alphabetical order.)

**PROCEDURE**

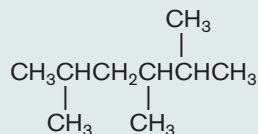
Write the carbons of the base name in a straight line, followed by the hydrogens bonded to them. Substituents go in parenthesis after the carbon to which they're attached. Alternately, they may be placed above or below the main chain, with a line drawn indicating to which carbon they are bonded.

**SOLUTION****ANALYSIS**

Recall that carbon forms four bonds in organic molecules. Therefore, when written as a condensed structure, if the carbon is attached to one other carbon, it is written as  $\text{CH}_3$ ; to two carbons,  $\text{CH}_2$ ; to three carbons,  $\text{CH}$ ; and to four carbons, simply  $\text{C}$ .

**SYNTHESIS**

Sometimes, when deciding which way to number a chain, the numbers can be very close and it may not be immediately obvious. For example, consider the following structure



The two possibilities are 2,3,5-trimethylhexane and 2,4,5-trimethylhexane. The numbers in the first example add to 10 and in the second add to 11. The first is the correct name.





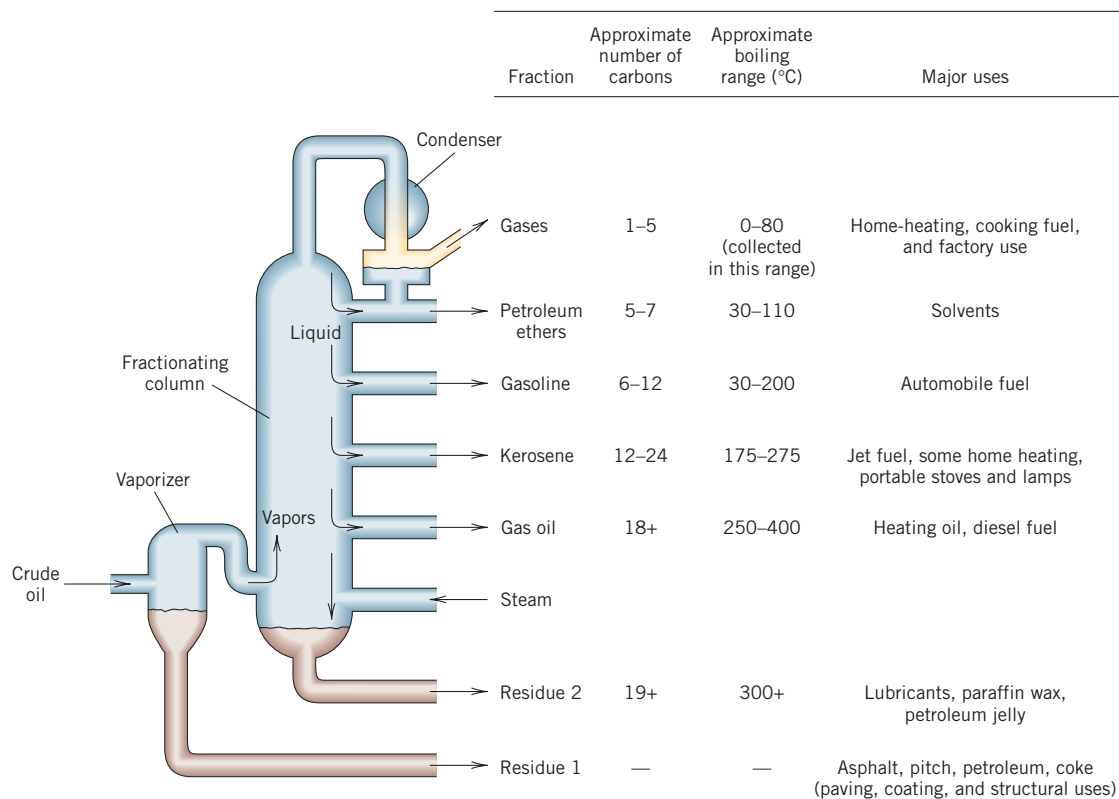
**FIGURE 17-2** An Oil Refinery The crude oil is processed in large refineries.

Since alkanes are essentially nonpolar compounds, the only intermolecular forces of attraction between molecules are London forces. These forces depend on the volume of the molecules. Since the molar mass is roughly proportional to the volume, we can state that the lighter the molecules, the weaker the London forces. (See Section 11-2.) As a result, the boiling points of alkanes are related to their molar masses. The lighter alkanes are the more volatile. *Volatility* refers to the tendency of a liquid to vaporize to the gaseous state and is related to its boiling point. Alkanes with 4 or fewer carbon atoms are all gases at room temperature and considered highly volatile. Those with 5 to 18 carbons are liquids, whereas those with more than 18 carbons are low-melting solids (resembling candle wax). All alkanes are odorless and colorless. They are also extremely flammable.

### 17-2.3 Sources of Alkanes

There are two major sources of alkanes, natural gas and crude oil (petroleum). Natural gas is mainly methane with smaller amounts of ethane, propane, and butanes. Unlike natural gas, petroleum contains hundreds of compounds, the majority of which are open-chain and cyclic alkanes. Before we can make use of petroleum, it must be separated into groups of compounds with similar properties. Further separation may or may not be carried out depending on the final use of the hydrocarbons.

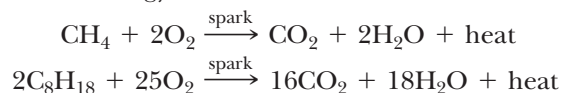
Crude oil is separated into groups of compounds according to boiling points by distillation in a refinery. (See Figure 17-2.) In such a distillation, the liquid is boiled, and the gases move up a large column that becomes cooler and cooler toward the top. Compounds condense (become liquid) at different places in the column, depending on their boiling points. As the liquids condense, they are drawn off, providing a rough separation of the crude oil. Some of the material has too high a boiling point to vaporize and remains in the bottom of the column. A drawing of this process and the various fractions obtained is shown in Figure 17-3. Note that the fewer the carbon atoms in the alkane, the lower the boiling point (the more volatile it is).



**FIGURE 17-3** Refining of Petroleum Oil is separated into fractions according to boiling points.

The composition of crude oil itself varies somewhat depending on where it is found. Certain crude oil, such as that found in Nigeria and Libya, is called light oil because it is especially rich in the hydrocarbons that are present in gasoline. Otherwise, one fraction can be converted into another by three processes: cracking, re-forming, and alkylation. **Cracking** changes large molecules into small molecules. **Re-forming** removes hydrogens from the carbons and/or changes unbranched hydrocarbons into branched hydrocarbons. (Branched hydrocarbons perform better in gasoline; that is, they have a higher octane rating.) **Alkylation** takes small molecules and puts them together to make larger molecules. In all of these processes, catalysts are used, but there is a different catalyst for each process.

About 96% of all oil and gas is burned as fuel, whereas only 4% is used to make other organic chemicals. As a fuel, hydrocarbons burn to give carbon dioxide, water, and a great deal of heat energy.



Industrially, most synthetic organic chemicals have their ultimate origin in *the alkanes obtained from crude oil*. These **petrochemicals** are put to a wide range of uses in the manufacture of fibers, plastics, coatings, adhesives, synthetic rubber, some flavorings, perfumes, and pharmaceuticals.

### ASSESSING THE OBJECTIVES FOR SECTION 17-2

**EXERCISE 17-2(a) KNOWLEDGE:** Fill in the blanks.

A hydrocarbon that has only single bonds in its molecules is classified as an \_\_\_\_\_. The principal sources of this class of compounds are \_\_\_\_\_ gas and \_\_\_\_\_. The latter liquid is separated into component compounds in a \_\_\_\_\_. The separation is accomplished because light alkanes are more \_\_\_\_\_ than the heavier compounds. One type of alkane can be converted into another in a refinery by the processes of \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.

**EXERCISE 17-2(b) KNOWLEDGE:** Give the IUPAC names for each of the isomers of pentane. (Refer to Exercise 17-1(b) in Assessing the Objective for Section 17-1.)

**EXERCISE 17-2(c) SYNTHESIS:** What is distinctive about the bonding of the carbon in alkanes? What is the geometry around each carbon in an alkane?

*For additional practice, work chapter problems 17-8, 17-18, and 17-19.*

## 17-3 ALKENES AND ALKYNES

### OBJECTIVES FOR SECTION 17-3

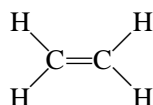
(a) Write the formulas of alkenes and alkynes. (b) Give the IUPAC names of some simple alkenes. (c) Describe how alkenes are used to make polymers.



**LOOKING AHEAD!** The second class of hydrocarbons we will discuss are those that contain a double bond somewhere in the carbon chain. These compounds are important in the production of many plastics. A third class that we will study in this section has triple bonds. ■

### 17-3.1 Alkenes

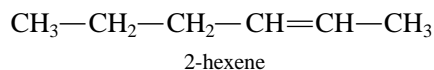
**Alkenes** are hydrocarbons that contain a double bond. Organic compounds with multiple bonds are said to be **unsaturated**. The general formula for an open-chain alkene with one double bond is  $\text{C}_n\text{H}_{2n}$ , which, you may recall, is also the formula of cyclic alkanes. The simplest alkene is ethene (common name ethylene), which has the structure



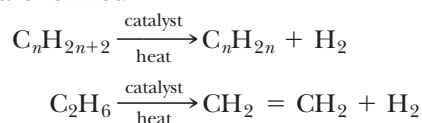


The plastic bag is made of polyethylene.

Alkenes are named by dropping the *-ane* ending of the corresponding alkane and substituting *-ene*. The location of the double bond is indicated by number in a manner similar to the naming of branched alkanes by the IUPAC method. The double bond is located by numbering the carbon-carbon bonds starting from the end closest to the double bond in the main hydrocarbon chain. The smallest number for a double bond takes precedence over the numbering of any substituents on the carbon chain.

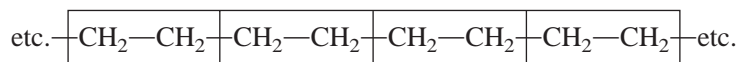
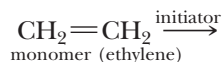


Only small amounts of alkenes are found naturally in crude oil; the majority are made from alkanes by the re-forming process during the refining of crude oil. When alkanes are heated over a catalyst, hydrogen is lost from the molecule and alkenes together with hydrogen are formed



### 17-3.2 Polymers

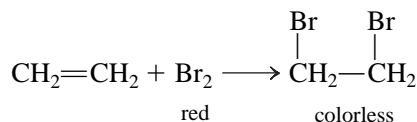
A large amount of alkenes are produced industrially to make polymers. When certain compounds called initiators are added to an alkene or a mixture of alkenes, the double bond is broken and the alkenes become joined to each other by single bonds. This produces a high-molar-mass molecule called a **polymer**, which has repeating units of the original alkene (called the monomer).



written as  $\text{CH}_2\text{—CH}_2$   
polymer (polyethylene)

These types of polymers are named by adding *poly-* to the name of the alkene used to form the polymer. In the example shown above, the polymer was made from ethylene (usually common names are used for polymers), and so the polymer is called polyethylene. If the name of the polymer contains two words, the alkene name is enclosed in parentheses [e.g., poly(methyl methacrylate)]. This rule is not always followed for some well-known polymers such as polyvinyl chloride. When writing the condensed structure of a polymer, we abbreviate the structure by giving the repeating unit in parentheses along with a subscript *n* to indicate that the monomer is repeated many times. Groups attached to the double bond affect the properties of the polymer, and by varying the group, we can vary the uses for which the polymer is suited. (See Figure 17-4.) Some commonly used polymers and their uses are given in Table 17-4.

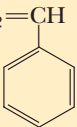
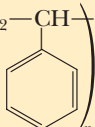
Compounds can add to the double bond to form new single bonds and therefore new compounds. A test based on such a reaction, the addition of bromine to an alkene, is used to show the presence of alkenes. It is a very simple test to perform. The disappearance of the red color of bromine when it is added to a liquid means that multiple bonds are present (the dibromide formed is colorless). We will talk more about this test when we discuss aromatic compounds.





**FIGURE 17-4** **Polymers** The frying pan is coated with Teflon, which gives it a “nonstick” surface. Polypropylene is used to make artificial turf, and polystyrene (Styrofoam) is used for insulation.

**TABLE 17-4** **Polymers**

| MONOMER  | POLYMER  | SOME COMMON TRADE NAMES                    | USES   |
|--|--|--|--|
| ethylene<br>$\text{CH}_2=\text{CH}_2$  | polyethylene<br>$(\text{CH}_2-\text{CH}_2)_n$  | Polyfilm <sup>a</sup> Marlex <sup>b</sup>  | Electrical insulation, packaging (plastic bags), floor covering, plastic bottles, pipes, tubing  |
| propylene<br>$\text{CH}_2=\text{CH}$<br> <br>$\text{CH}_3$   | polypropylene<br>$(\text{CH}_2-\text{CH})_n$<br> <br>$\text{CH}_3$   | Herculon <sup>c</sup>                      | Pipes, carpeting, artificial turf, molded auto parts, fibers   |
| vinyl chloride<br>$\text{CH}_2=\text{CH}$<br> <br>$\text{Cl}$  | polyvinyl chloride (PVC)<br>$(\text{CH}_2-\text{CH})_n$<br> <br>$\text{Cl}$  | Tygon <sup>d</sup>                         | Wire and cable coverings, pipes, rainwear, shower curtains, tennis court playing surfaces  |
| styrene<br>$\text{CH}_2=\text{CH}$<br> <br> | polystyrene<br>$(\text{CH}_2-\text{CH})_n$<br> <br> | Styrofoam <sup>a</sup> Styran <sup>a</sup> | Molded objects (combs, toys, brush and pot handles), refrigerator parts, insulating material, phonograph records, clock and radio cabinets |
| tetrafluoroethylene<br>$\text{CF}_2=\text{CF}_2$   | polytetrafluoroethylene<br>$(-\text{CF}_2-\text{CF}_2)_n$  | Teflon <sup>e</sup> Halon <sup>f</sup>     | Gaskets, valves, tubing, coatings for cookware   |
| methyl methacrylate<br>$\text{CH}_2=\text{C}$<br>  $\text{CH}_3$<br>  $\text{CO}_2\text{CH}_3$                                 | poly(methyl methacrylate)<br>$(\text{CH}_2-\text{C})_n$<br>  $\text{CH}_3$<br>  $\text{CO}_2\text{CH}_3$                               | Plexiglas <sup>g</sup> Lucite <sup>e</sup> | Glass substitute, lenses, aircraft glass, dental fillings, artificial eyes, braces   |
| acrylonitrile<br>$\text{CH}_2=\text{CH}$<br> <br>$\text{CN}$   | polyacrylonitrile<br>$(\text{CH}_2-\text{CH})_n$<br> <br>$\text{CN}$   | Orlon <sup>e</sup> Acrilan <sup>h</sup>    | Fibers for clothing, carpeting   |

<sup>a</sup>Dow Chemical Co.

<sup>b</sup>Phillips Petroleum Co.

<sup>c</sup>Hercules, Inc.

<sup>d</sup>U.S. Stoneware Co.

<sup>e</sup>E. I. Du Pont de Nemours & Co.

<sup>f</sup>Allied Chemical Corp.

<sup>g</sup>Rohm & Haas Co.

<sup>h</sup>Monsanto Industrial Chemicals, Inc.



## The Age of Plastics



Plastics are everywhere.

In the classic movie of the late 1960s, *The Graduate*, Dustin Hoffman's character was informed that the key to the future involved one word—"Plastics." It wasn't wrong then and it still isn't. More and more of our infrastructure is changing from natural substances to the polymers we know as plastics.

In this century we are on the cusp of even greater polymer discoveries that are just becoming imaginable today and will surely be followed by unimaginable discoveries tomorrow.

Actually, plastics have been known for about 200 years. The first synthetic polymer was made by Schoenbein (UK) in the early 1800s and was known as a *Colloidion*. It was a hard, transparent film used in medicine and later in photography. In 1872, John Wesley Hyatt produced *Celluloid*, which was also used in photography and in combs and portable windows. In 1888, G. W. A. Kahlbaum (Switzerland) made a methacrylate polymer that was later used to make unbreakable beer glasses. In 1897, W. Krishe and A. Spitteler (Germany) made a condensation polymer that was a substitute for ivory. In 1910, L. H. Baekeland (U.S.) manufactured *Bakelite*, the first all-synthetic plastic, from phenol and formaldehyde. It had a high-temperature resistance, so it could be used in ashtrays and eventually in cabinets for radios and televisions.

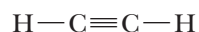
The 1930s was an important decade for plastics, which included polyacrylics and polyesters (Julian Hill at DuPont Chemical Co). Nylon (a polyamide) was first made in 1934 by Donald Cofman, also at DuPont. Individuals working for large corporations rather than working alone were now making discoveries. We still know many of them by their trade names, such as Lucite and Plexiglas.

The explosion of plastics into our everyday lives actually began with an important discovery in the 1950s. Two scientists, Giulio Natta (Italy) and Karl Ziegler (Germany), discovered ways of using heterogeneous catalysts to polymerize ethylene to polyethylene. This new method produced polymers more cheaply and easily than other methods. More importantly, the plastics produced by this procedure had much higher strengths and chemical resistance and thus many more applications.

One hundred years ago almost everything that we wore or used was made from natural substances such as wood, metal, or natural fibers. The space station, cell phones, laptop computers, eyeglasses, and many modern clothes are now synthetic. And we are not finished. Plastics that conduct electricity will soon be available and will probably replace metals in electrical wiring. Many new and exciting types of polymers are being studied. Carbon atoms arranged in tubes (called *nanotubes*) and polymers that extend outward from a central core (called *dendrimers*) give promise of applications we have yet to imagine.

### 17-3.3 Alkynes

**Alkynes** are hydrocarbons that contain a triple bond. The general formula for an open-chain alkyne with one triple bond is  $C_nH_{2n-2}$ . The simplest alkyne is ethyne (acetylene), which has the structure

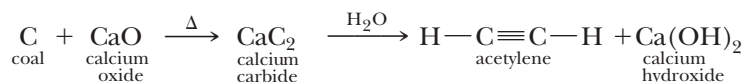


Alkynes are named just like alkenes except that *-yne* is substituted for the alkane ending instead of *-ene*. Thus,

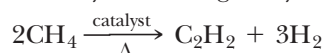


is named 3-octyne.

Alkynes are rare in nature, but they can be prepared synthetically. Acetylene can be made from coal by first reacting the coal with calcium oxide at high temperature and then treating the calcium carbide formed with water.

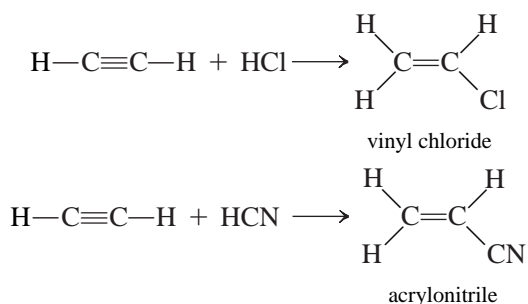


A more common method of making acetylene is the re-forming process. Methane is heated in the presence of a catalyst, forming acetylene and hydrogen.





Although acetylene is used in oxyacetylene torches, its most important application is in the synthesis of specific alkenes for polymers. For example, acetylene reacts with hydrogen chloride to form vinyl chloride or with hydrogen cyanide to form acrylonitrile. These alkenes are then used to manufacture polyvinyl chloride and polyacrylonitrile, respectively.



**ASSESSING THE OBJECTIVES FOR SECTION 17-3**

**EXERCISE 17-3(a) KNOWLEDGE:** Fill in the blanks.

Alkenes are known as \_\_\_\_\_ hydrocarbons because they contain a \_\_\_\_\_ bond. An important use of these compounds is in the manufacture of \_\_\_\_\_. Alkynes contain a \_\_\_\_\_ bond. The general formula of a straight-chain alkene is \_\_\_\_\_ and of a straight chain alkyne is \_\_\_\_\_.

**EXERCISE 17-3(b) ANALYSIS:** Show the partially condensed Lewis structures of the following.

(a) 2-methyl-2-pentene (b) 4,4, dimethyl-1-pentyne

**EXERCISE 17-3(c) ANALYSIS:** Provide the IUPAC name for the following.

(a)  $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_3$   
(b)  $\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$

**EXERCISE 17-3(d) ANALYSIS:** What is the repeating unit of polypropylene?

**EXERCISE 17-3(e) SYNTHESIS:** An important concept of alkenes is the presence of cis and trans isomers. These isomers occur because the carbons in the double bond are locked into place by the nonrotating double bond. In the cis isomer the hydrogens attached to the carbons that form the double bond lie on the same side, whereas in the trans isomer they are opposite each other. Draw the cis and trans isomer of 2-pentene. Can alkanes or alkynes form cis and trans isomers?

*For additional practice, work chapter problems 17-25, 17-31, and 17-33.*

## 17-4 AROMATIC COMPOUNDS

**OBJECTIVE FOR SECTION 17-4**

Describe the difference between aromatic compounds and straight-chain alkenes using resonance.

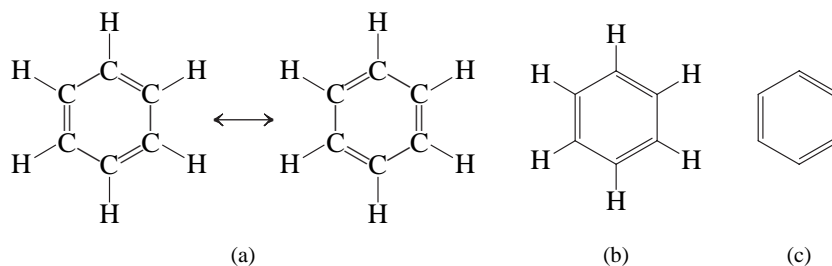


**LOOKING AHEAD!** The final category of hydrocarbons involves cyclic compounds that are particularly stable. The most important member of this group involves a six-membered ring. These compounds are discussed in this section. ■

### 17-4.1 The Structure of Benzene

Benzene ( $\text{C}_6\text{H}_6$ ) is a six-membered ring compound. Its Lewis structure can be written with alternating single and double bonds between adjacent carbons. In fact, two identical resonance structures can be written for benzene, which indicates that all six bonds are equivalent. The two resonance Lewis representations of benzene are

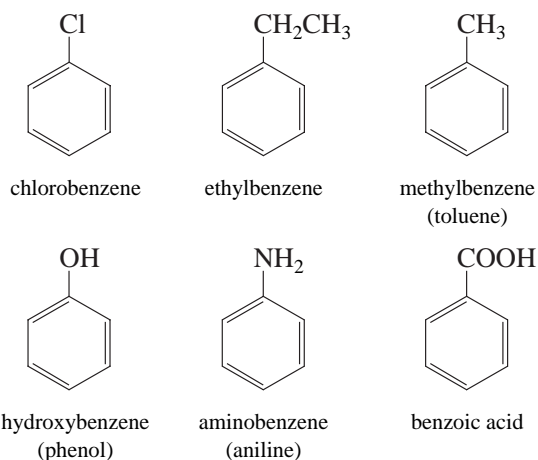
shown below in (a). The Lewis representation in (b) is simplified by omitting the carbons. In (c), the structure is simplified further by omitting the hydrogens.



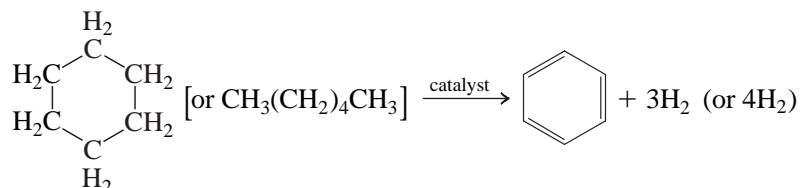
The benzene molecule is symmetrical and planar. It is also chemically unreactive compared to alkenes. For example, benzene does not “decolorize” a solution of bromine as do straight-chain alkenes (see Section 17-3.3). It is this special stability that allows us to classify benzene among a unique class of ring hydrocarbons known as **aromatic compounds**.

### 17-4.2 Derivatives of Benzene

There are other ring hydrocarbons that are also aromatic and can be written with alternating single and double bonds, but we will confine our discussion to benzene and derivatives of benzene. A **derivative of a compound** is produced by the substitution of a group or hetero atom for a hydrogen on the molecules of the original compound. Compounds that contain the benzene ring can often be recognized by name because they are named as derivatives of benzene. Others have been given their own distinctive name (shown in parentheses below). The following are the simplified structures and the names of some common derivatives of benzene.



Although some benzene and toluene are present in crude oil, additional quantities can be obtained by the re-forming process. When cyclohexane and/or hexane are heated with a catalyst, benzene is formed. Coal is another source of benzene. When coal is heated to high temperatures in the absence of air, some benzene is formed.



Benzene and toluene find application mainly as solvents and as starting materials to make other aromatic compounds. Benzene must be handled with care, however, because it has been found to be a potent carcinogen (it can cause cancer). Phenol and its derivatives are used as disinfectants and preservatives, as well as in the manufacture of dyes, explosives, drugs, and plastic.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 17-4

**EXERCISE 17-4(a) KNOWLEDGE:** Fill in the blanks.

Benzene is the most important example of an \_\_\_\_\_ hydrocarbon. It has \_\_\_\_\_ major resonance structures. Its geometry is described as \_\_\_\_\_. A \_\_\_\_\_ of benzene is formed by the replacement of a hydrogen with a hydrocarbon or a hetero atom group. For example, phenol has a \_\_\_\_\_ group on the benzene ring.

**EXERCISE 17-4(b) ANALYSIS:** Write the Lewis structure of isopropylbenzene.

**EXERCISE 17-4(c) SYNTHESIS:** When there are two groups or hetero atoms on the benzene ring, three isomers are possible. Write the Lewis structures of the three isomers of dichlorobenzene.

*For additional practice, work chapter problem 17-35.*

PART A  
SUMMARY

## KEY TERMS

- 17-1.1** The compounds on which life is based are known as **organic** compounds. **Inorganic** compounds do not usually contain C—H bonds. p. w-4
- 17-1.3** Different compounds that have the same formula are known as **isomers**. p. w-6
- 17-1.4** Writing Lewis structures for complex organic compounds is simplified by writing **condensed** formulas. p. w-7
- 17-1.4** A **hetero atom** in an organic compound is any atom other than carbon or hydrogen. p. w-7
- 17-2.1** **Alkanes** are known as **hydrocarbons** that are said to be **saturated** because they contain only single bonds. Successively larger molecules form a **homologous series**. p. w-8
- 17-2.2** Alkanes may contain **alkyl groups** which are known as **substituents**. p. w-9
- 17-2.3** **Cracking, re-forming** and **alkylation** are processes used in the refining of petroleum. They form **petrochemicals** used in industry or for fuel. p. w-13
- 17-3.1** **Alkenes** are **unsaturated** hydrocarbons that contain at least one double bond. p. w-13
- 17-3.2** Alkenes can be combined into long chains which form one type of **polymer**. p. w-14
- 17-3.3** **Alkynes** are unsaturated hydrocarbons that contain at least one triple bond. p. w-16
- 17-4.1** **Aromatic compounds** are ring hydrocarbons with alternating double and single bonds. p. w-18
- 17-4.2** A **derivative** of an aromatic compound contains attached hetero atoms or other groups in place of a hydrogen. p. w-18

## SUMMARY CHART

| Types of Hydrocarbons |                 |          |                      |   |
|-----------------------|-----------------|----------|----------------------|---|
| Name of Series        | General Formula | Example  | Name                 | Comments  |
| Alkane                | $C_nH_{2n+2}$   | $C_3H_8$ | propane              | Alkanes contain only single bonds and are saturated.  |
| Alkene                | $C_nH_{2n}$     | $C_3H_6$ | propene<br>propylene | Alkenes contain double bonds and are unsaturated.   |
| Alkyne                | $C_nH_{2n-2}$   | $C_3H_4$ | propyne              | Alkynes contain triple bonds and are unsaturated.   |
| Aromatic              | —               | $C_6H_6$ | benzene              | Aromatic compounds are cyclic, unsaturated hydrocarbons, but they are less reactive than alkenes. |

**PART B**  
OTHER CLASSES OF  
ORGANIC COMPOUNDS

**SETTING A GOAL**

- You will learn of the great diversity of organic compounds that arise from the presence of functional groups.

**OBJECTIVES**

- 17-5** List the general structures, names, properties, and uses of alcohols and ethers.
- 17-6** List the general structures, names, properties, and uses of aldehydes and ketones.
- 17-7** List the general structures, names, properties, and uses of amines.
- 17-8** List the general structures, names, properties, and uses of carboxylic acids, esters, and amides.

**▶ OBJECTIVE FOR SECTION 17-5**

List the general structures, names, properties, and uses of alcohols and ethers.

## 17-5 ALCOHOLS AND ETHERS



**LOOKING AHEAD!** In this section, we will examine two classes of compounds that contain one oxygen as a hetero atom where the oxygen forms single bonds to two other atoms. The first is a familiar class of compounds known as alcohols. The second class is known as ethers. ■

### 17-5.1 Functional Groups

Methane ( $\text{CH}_4$ ) boils at a very low  $-164^\circ\text{C}$  and thus is a gas at room temperature. If one chlorine atom is substituted for a hydrogen atom on the carbon, the resulting compound,  $\text{CH}_3\text{Cl}$  (chloromethane), has properties very different from those of methane. Chloromethane is a polar compound with a higher molar mass than methane, so it boils at a much higher  $-24^\circ\text{C}$ . The presence of the chlorine atom has a significant effect on the properties of the original compound. In most compounds, the nature and bonding of the hetero atom (or atoms) control the chemistry or the function of the molecule. *In an organic compound, the atom or group of atoms that determines the chemical nature of the molecule is known as the **functional group**.* In most cases, one or more hetero atoms are involved in the functional group. However, in the cases of alkenes and alkynes the functional groups are the double bond and triple bond, respectively, which is the location of most of their chemical reactivities. Each functional group has a strong influence on the chemistry of the compounds that contain it and thus establishes a specific class of compounds. Our first functional group with a hetero atom involves the presence of an oxygen atom with single bonds to two carbons or one carbon and one hydrogen.

### 17-5.2 Alcohols

**Alcohols** are a class of organic compounds that contain the *OH* functional group (known as a **hydroxyl group**) in place of a hydrogen atom on a carbon chain. The word *alcohol* is most familiar to us as the active ingredient in alcoholic beverages. This, however, is just one of many different chemicals classified as alcohols. Two others familiar alcohols are rubbing alcohol and wood alcohol.

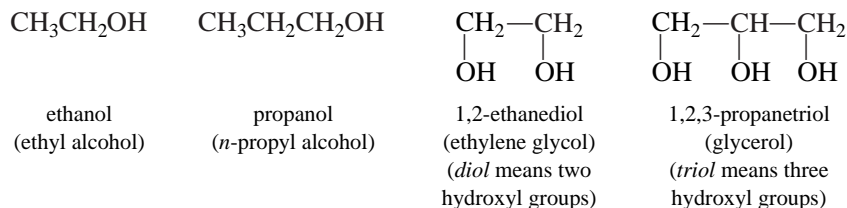
Alcohols are named by taking the alkane name, dropping the *-e*, and substituting *-ol*. Common names are obtained by just naming the alkyl group attached to the  $\text{—OH}$  followed by *alcohol*. Some familiar alcohols (see Figure 17-5) have more than one



**FIGURE 17-5 Alcohols**  
A major ingredient in each of these products is an alcohol.

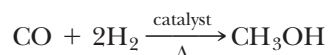
\*The R or R' represents a group such as an alkyl or an aromatic group.

hydroxyl group. (In naming alcohols with more than one hydroxyl group, the *-e* in the alkane is not dropped.) Four examples of alcohols are



Methanol and ethanol can both be obtained from natural sources. Methanol can be prepared by heating wood in the absence of oxygen to about 400°C; at such high temperatures, methanol, together with other organic compounds, is given off as a gas. Since methanol was once made exclusively by this process, it is often called wood alcohol.

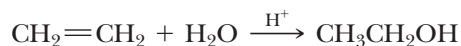
Currently, methanol is prepared from synthesis gas, a mixture of CO and H<sub>2</sub>. When CO and H<sub>2</sub> are passed over a catalyst at the right temperature and pressure, methanol is formed.



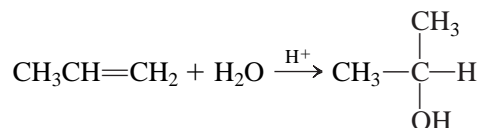
Ethanol (often known simply as alcohol) is formed in the fermentation of various grains. (Therefore, it is also known as grain alcohol.) In fermentation, the sugars and other carbohydrates in grains are converted to ethanol and carbon dioxide by the enzymes in yeast.



Industrially, ethanol is prepared by reacting ethylene with water in the presence of an acid catalyst.



2-Propanol (isopropyl alcohol) can be prepared from propene (propylene) in the same way.



Methanol has been used as a solvent for shellac, as a denaturant for ethanol (it makes ethanol undrinkable and therefore free from excise taxes), and as an antifreeze for automobile radiators. It is very toxic when ingested. In small doses it causes blindness, and in large doses it can cause death.

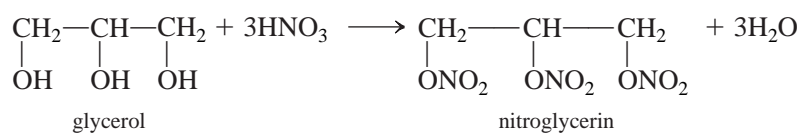
Ethanol is present in alcoholic beverages such as beer, wine, and liquor. The “proof” of an alcoholic beverage is two times the percent by volume of alcohol. If a certain brand of bourbon is 100 proof, it contains 50% ethanol. Ethanol is also mixed with gasoline to form a mixture that is used as an automobile fuel. Currently, some automobile fuel contains as much as 85% ethanol. Ethanol is an excellent solvent and has been used as such in perfumes, medicines, and flavorings. Ethanol and 2-propanol (rubbing alcohol) are used as antiseptics and as rubbing compounds to cleanse the skin and lower a feverish person’s temperature. While ethanol is not as toxic as methanol, it can cause coma or death when ingested in large quantities. 2-Propanol is also quite toxic.

Ethylene glycol is the major component of antifreeze and coolant used in automobiles. It is also used to make polymers, the most common of which is Dacron, a polyester, which is discussed later in this chapter.

Glycerol, which can be obtained from fats, is used in many applications where lubricants and/or softeners are needed. It has been used in pharmaceuticals,



cosmetics, foodstuffs, and some liqueurs. When glycerol reacts with nitric acid, it produces nitroglycerin, which is a powerful explosive.

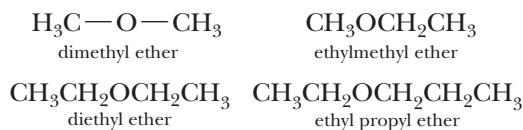


Nitroglycerin is also a strong smooth-muscle relaxant and vasodilator and has been used to lower blood pressure and to treat angina pectoris.

### 17-5.3 Ethers

An **ether** contains an oxygen bonded to two hydrocarbon groups (rather than one hydrocarbon group and one hydrogen, as in alcohols). The simplest ether, dimethyl ether, is an isomer of ethanol but has very different properties.

The common names of ethers are obtained by naming the alkyl groups on either side of the oxygen and adding *ether*.



Diethyl ether is made industrially by reacting ethanol with sulfuric acid. In this reaction, two ethanol molecules are joined together, with the loss of an H<sub>2</sub>O molecule.



The most commonly known ether, diethyl ether (or ethyl ether, or just ether), was, in the past, used extensively as an anesthetic. It has the advantage of being an excellent muscle relaxant that doesn't greatly affect blood pressure, pulse rate, or rate of respiration. On the other hand, ether has an irritating effect on the respiratory passages and often causes nausea. Its flammability is also a drawback because of the danger of fire and explosions. Diethyl ether is rarely used now as an anesthetic. Other anesthetics that do not have its disadvantages have taken its place.

#### ASSESSING THE OBJECTIVE FOR SECTION 17-5

**EXERCISE 17-5(a) KNOWLEDGE:** Fill in the blanks.

The functional group in an alcohol is known as a \_\_\_\_\_ group. In ethers, the oxygen is attached to two \_\_\_\_\_ groups. Ethyl alcohol is produced from sugars in a process known as \_\_\_\_\_. A diol is an alcohol with \_\_\_\_\_ OH groups.

**EXERCISE 17-5(b) ANALYSIS:** Two alcohols and an ether have the formula C<sub>3</sub>H<sub>8</sub>O. Write Lewis structures for the compounds that have this formula. Give the names of each.

**EXERCISE 17-5(c) SYNTHESIS:** Of the compounds shown in the previous problem, the ether is more volatile than the alcohols. Explain.

#### OBJECTIVE FOR SECTION 17-6

List the general structures, names, properties, and uses of aldehydes and ketones.

## 17-6 ALDEHYDES AND KETONES



**LOOKING AHEAD!** The next two classes of compounds also have oxygen as the lone hetero atom. In these two classes, however, the oxygen is bonded to only one carbon by a double bond. ■

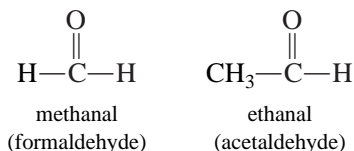
The functional group of aldehydes and ketones is a carbonyl group. A **carbonyl group** is a carbon with a double bond to an oxygen.



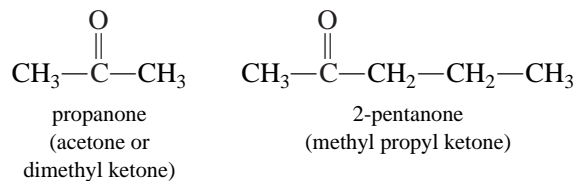
In **aldehydes** the carbonyl group is bound to at least one hydrogen, whereas in **ketones** the carbonyl group is bound to two hydrocarbon groups.

Aldehydes are named by dropping the *-e* of the corresponding alkane name and substituting *-al*. Therefore, the two-carbon aldehyde is ethanal. Ketones are named by taking the alkane name, dropping the *-e*, and substituting *-one*. The common names of ketones are obtained by naming the alkyl groups on either side of the C=O and adding *ketone*.

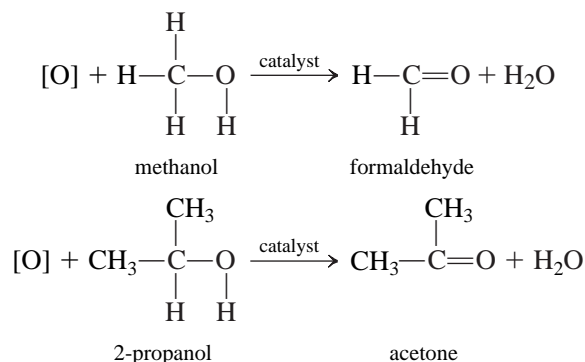
## Aldehydes



## Ketones



Many aldehydes and ketones are prepared by the oxidation of alcohols. Industrially, the alcohol is oxidized by heating it in the presence of oxygen and a catalyst. About half of the methanol produced industrially is used to make formaldehyde by oxidation. Acetone can be prepared in the same fashion by oxidation of 2-propanol. In the following reactions, the [O] represents an oxidizing agent that removes hydrogen (to form H<sub>2</sub>O) from the alcohol.



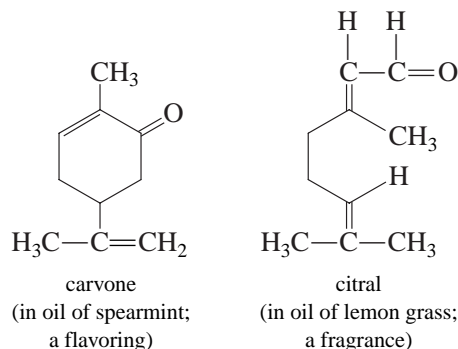
Aldehydes and ketones have uses as solvents, in the preparation of polymers, as flavorings, and in perfumes. The simplest aldehyde, formaldehyde, has been used as a disinfectant, antiseptic, germicide, fungicide, and embalming fluid (as a 37% by mass water solution). It has also been used in the preparation of polymers such as Bakelite (the first commercial plastic) and Melmac (used to make dishes). Formaldehyde polymers have also been used as coatings on fabrics to give “permanent press” characteristics.

The simplest ketone, acetone, has been used mainly as a solvent. It is soluble in water and dissolves relatively polar and nonpolar molecules. It is an excellent solvent for paints and coatings.



The specimen is preserved in a formaldehyde solution.

More complex aldehydes and ketones, such as the following two examples, are used in flavorings and perfumes.



**ASSESSING THE  
OBJECTIVE FOR  
SECTION 17-6**

**EXERCISE 17-6(a) KNOWLEDGE:** Fill in the blanks.

The functional group in aldehydes and ketones is a \_\_\_\_\_ group. In aldehydes, the functional group is attached to at least one \_\_\_\_\_ atom.

**EXERCISE 17-6(b) ANALYSIS:** Two aldehydes and one ketone have the formula  $C_4H_8O$ . Write Lewis structures for the compounds that have this formula. Give the names of each.

**EXERCISE 17-6(c) SYNTHESIS:** Is hydrogen bonding involved in pure aldehydes or ketones? Can there be hydrogen bonding between water as a solvent and aldehydes and ketones? Do you think they are water soluble?

**OBJECTIVE FOR  
SECTION 17-7**

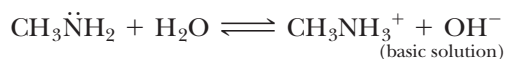
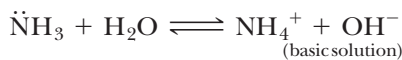
List the general structures, names, properties, and uses of amines.

## 17-7 AMINES

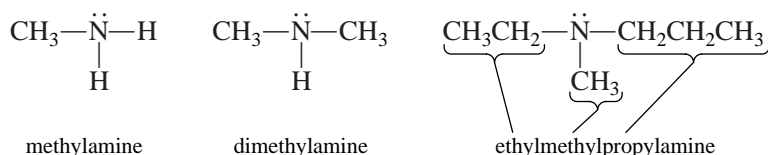


**LOOKING AHEAD!** In this section, we will introduce a class of compounds that has nitrogen as the hetero atom. This class of organic compounds is known as amines and includes many familiar medications. ■

An **amine** contains a nitrogen with single bonds to a hydrocarbon group and two other groups that may be hydrocarbons or hydrogens. The nitrogen in amines has one pair of unshared electrons similar to ammonia,  $NH_3$ . As we learned in Chapter 13,  $NH_3$  utilizes the unshared pair of electrons to form weakly basic solutions in water. In a similar manner, amines are characterized by their ability to act as bases.

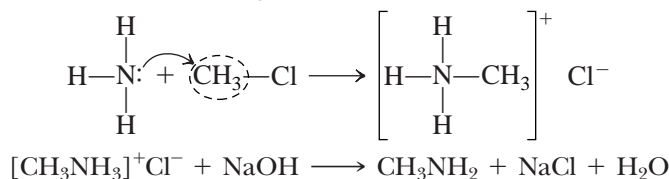


The common names of amines are obtained by listing the alkyl groups (in alphabetical order) attached to the nitrogen and adding *-amine*.



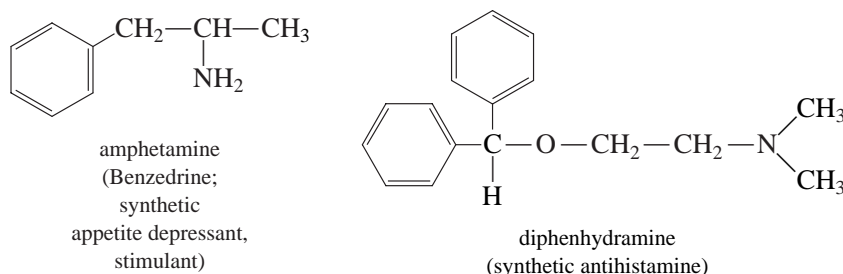
Simple amines are prepared by the reaction of ammonia with alkyl halides (e.g.,  $CH_3Cl$ ). In the reaction shown below, the electron pair on the nitrogen forms a bond

to the  $\text{CH}_3$  group, forming a methyl ammonium cation. The amine can then be prepared by the reaction with a strong base such as  $\text{NaOH}$ .



Amines are used in the manufacture of dyes, drugs, disinfectants, and insecticides. They also occur naturally in biological systems and are important in many biological processes.

Amine groups are present in many synthetic and naturally occurring drugs. (See Figure 17-6.) They may be useful as antidepressants, antihistamines, antibiotics, antiobesity preparations, antinauseants, analgesics, antitussives, diuretics, and tranquilizers, among others. Frequently, a drug may have more than one use. Codeine, for example, is both an analgesic (pain reliever) and an antitussive agent (cough suppressant). Many amine drugs are sold as the “hydrogen hydrochloride.” This is the ionic form of the amine, which contains the ammonium type cation and the chloride anion. As ionic compounds, they are solid and sold in pill form. They are then soluble in water. Often, a drug may be obtained from plants or animals. One such class of compounds is the alkaloids, which are amines found in plants. Two common drugs are



**FIGURE 17-6 Amines** The active ingredient in an antihistamine is an organic amine.

**EXERCISE 17-7(a) KNOWLEDGE:** Fill in the blanks.

In amines the hetero atom is a \_\_\_\_\_ atom that may have up to \_\_\_\_\_ hydrocarbon groups attached to it. Amines form \_\_\_\_\_ solutions in water.

**EXERCISE 17-7(b) ANALYSIS:** Four amines have the formula  $\text{C}_3\text{H}_9\text{N}$ . Write the Lewis structures of the amines and their names.

**EXERCISE 17-7(c) SYNTHESIS:** A free amine is often a liquid or volatile solid. However, many drugs made of amines are sold as “hydrochlorides,” which are the salts of amines. These are always solids, so they can be taken in pill form. Explain. Write the formula of ethylamine hydrochloride (actually, the name is ethylammonium chloride.)

**ASSESSING THE OBJECTIVE FOR SECTION 17-7**

**17-8 CARBOXYLIC ACIDS, ESTERS, AND AMIDES**



**LOOKING AHEAD!** Another class of organic compounds is known as carboxylic acids. The acids and two classes that are derivatives of the acids (esters and amides) are our final topics in this introduction to organic chemistry. ■

**OBJECTIVE FOR SECTION 17-8**

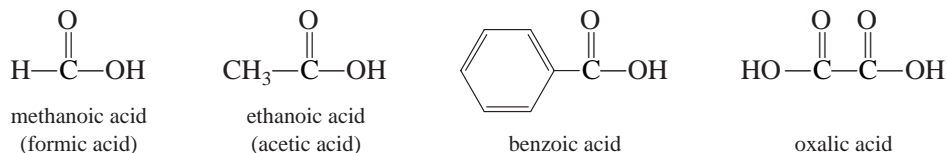
List the general structures, names, properties, and uses of carboxylic acids, esters, and amides.

### 17-8.1 Carboxylic Acids

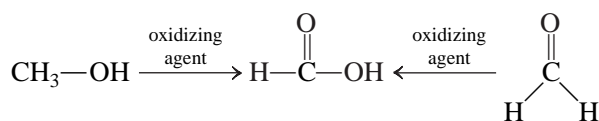
Acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ), the sour component of vinegar, is an example of a carboxylic acid. **Carboxylic acids** contain the functional group



known as a **carboxyl group**. For example, the condensed structure of acetic acid is  $\text{CH}_3\text{COOH}$ . Carboxylic acids are named by dropping the *-e* from the alkane name and substituting *-oic acid*. Examples of some common carboxylic acids are



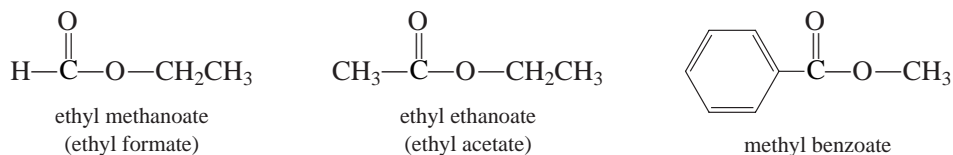
Carboxylic acids are made by the oxidation of either alcohols or aldehydes. Formic acid, which was first isolated by distilling red ants, can be made by oxidizing either methanol or formaldehyde.



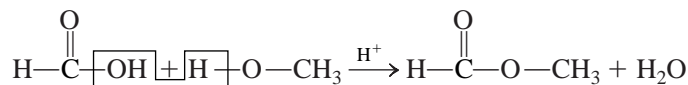
Acetic acid can be made from the oxidation of ethanol. In fact, this is what happens when wine becomes “sour.” Wine vinegar is produced by air oxidation of alcohol in ordinary wine.

### 17-8.2 Esters

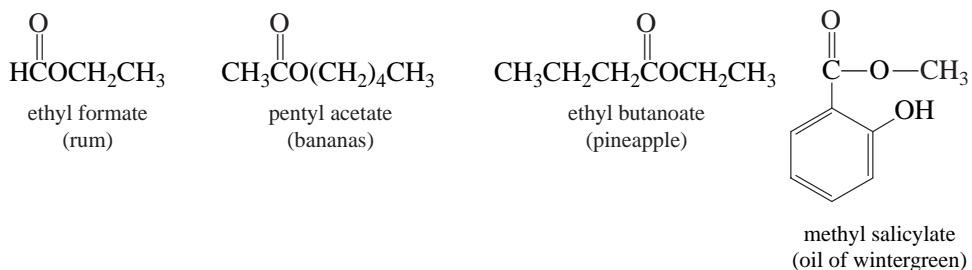
An **ester** is a derivative of a carboxylic acid, where a hydrocarbon group is substituted for the hydrogen in the carboxyl group. Esters are named by giving the name of the alkyl group attached to the oxygen, followed by the acid name with the *-ic* ending replaced by *-ate*. Some examples of esters are



Esters are made by the reaction of alcohols with carboxylic acids. In the reaction,  $\text{H}_2\text{O}$  is split off from the molecules (OH from the acid and H from the alcohol) as the remnants of the two molecules are joined.



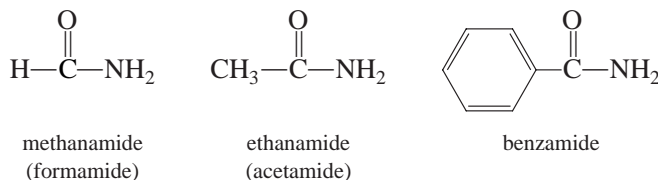
We all distinguish the various fruits by their unique odors. These pleasant odors are all caused by esters. Four of these esters are shown with their familiar odors.



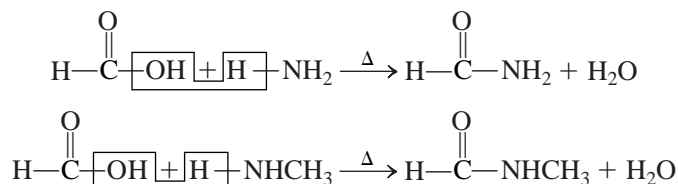


### 17-8.3 Amides

An **amide** is also a derivative of a carboxylic acid, where an amino group is substituted for the hydroxyl group of the acid. Amides are named by dropping the *-oic acid* portion of the carboxylic acid name and substituting *-amide*. Examples of amides are

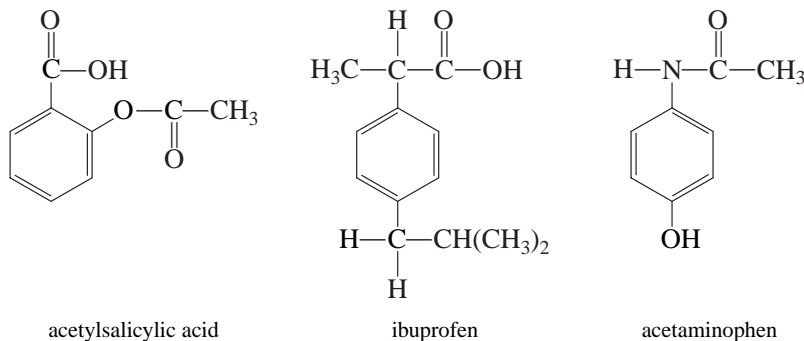


Amides are made by a reaction similar to that in the preparation of esters. In this case, however, the carboxylic acid reacts with ammonia or an amine instead of alcohol. Again, water is split off from the two reacting molecules, and the two remnants unite.

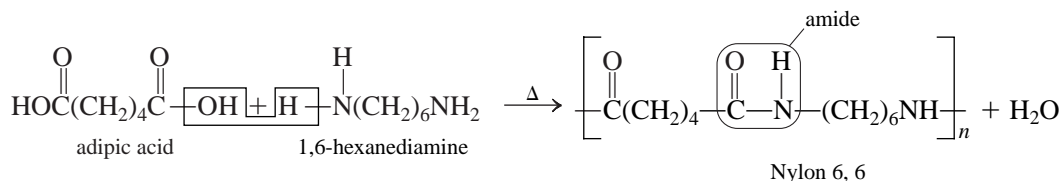


### 17-8.4 Uses in Painkillers and Polymers

Carboxylic acids, esters, and amides are frequently present in compounds that have medicinal uses. Salicylic acid has both antipyretic (fever-reducing) and analgesic (pain-relieving) properties. It has the disadvantage, however, of causing severe irritation of the stomach lining. Acetylsalicylic acid (aspirin), which is both an acid and an ester, doesn't irritate the stomach as much. Aspirin is broken up in the small intestine to form salicylic acid, which is then absorbed. Some people are allergic to aspirin and must take aspirin substitutes. The common aspirin substitutes are acetaminophen and ibuprofen. Acetaminophen is the active ingredient in Tylenol and Datril. Ibuprofen is the active ingredient in Advil and Nuprin.



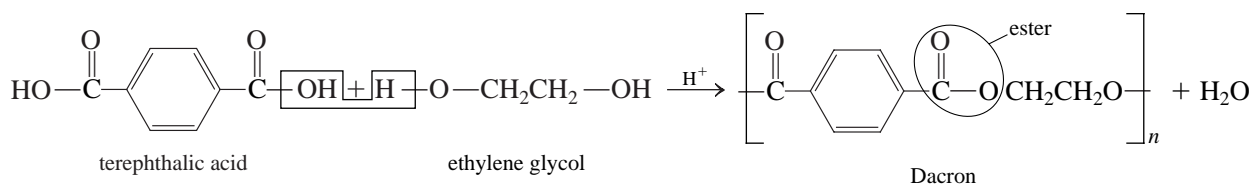
One of the biggest uses for carboxylic acids, esters, and amides is in the formation of condensation polymers. In **condensation polymers**, a small molecule (usually  $\text{H}_2\text{O}$ ) is given off during formation of the polymers. These are different from the polymers discussed earlier that resulted from the joining of alkenes (called *addition polymers*). Two of the most widely known condensation polymers are Nylon 6,6 (see Figure 17-7) and Dacron. The first is a **polyamide**, made from a **diacid** and a **diamine**; the second is a **polyester**, made from a **diacid** and a **dialcohol** (diol). Both of these polymers are used to make fibers.



**FIGURE 17-7 Nylon**  
Nylon was first synthesized by DuPont chemists. It was one of the first synthetic fibers.



Dacron is used in these sails. It is strong, light, and does not "wet."



MAKING

REAL

IT

## Aspirin—An Old Drug with a New Life



It's more than a headache remedy.

Hippocrates was a physician who lived in the fifth century B.C. He is considered the father of medicine. In fact, brand-new physicians still recite the Hippocratic Oath. Hippocrates was said to have administered to his patients a powder that was extracted from the willow tree. The powder apparently relieved the ravages of fever and moderated pain. If that actually happened, Hippocrates would have been an early user of a compound much like aspirin.

The bark of willow trees contains salicylic acid. It is the precursor to acetylsalicylic acid, which we know as aspirin.

In the 1800s, salicylic acid and its salt, sodium salicylate, were used as an antipyretic (a substance that reduces fever). It did have some bad side effects, though. It was very hard on the stomach and in many cases caused ulcers. In 1897, a scientist named Felix Hoffman worked for a company known as Bayer & Co. in Germany that manufactured dyes. Hoffman was searching for a drug that would relieve his father's severe arthritis. He wanted a compound that was like salicylic acid but that was less harsh on the stomach. By combining salicylic acid with acetic anhydride, he produced acetylsalicylic acid, a derivative of salicylic acid. He had

produced aspirin, which did indeed help his father. In 1899 Bayer began to manufacture aspirin, which, at first, was used mainly as an antipyretic. In 1903 it began to be used more as an analgesic (pain reliever) and to reduce inflammation.

Aspirin is now one of a large class of drugs known as NSAIDs (nonsteroid antiinflammatory drugs), which also includes ibuprofen (Advil) and naproxen (Aleve). Although aspirin was a big improvement over salicylic acid, it can still cause stomach trouble, so other newer (and more expensive) drugs that have fewer side effects are now being used.

In the 1970s, scientists finally began to understand how aspirin works. It was found that it inhibits the release of hormone-like substances in the body called *prostaglandins*. These substances affect the elasticity of blood vessels and the function of blood platelets. Platelets are responsible for clotting, and aspirin inhibits this function. It has been found that small, daily doses of aspirin can prevent heart attacks. It is now taken regularly by millions for just this purpose. Even more recently, studies have shown that patients who have taken aspirin for at least two years have developed Alzheimer's disease (a form of dementia) at half the rate of a control group. Small doses of aspirin have also been found to relieve high blood pressure in pregnant women.

Billions of dollars have been spent searching for new drugs to combat heart disease and Alzheimer's disease. It is ironic that one of the most effective drugs to prevent these conditions has been in medicine cabinets for over a century.

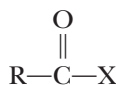
### ASSESSING THE OBJECTIVE FOR SECTION 17-8

**EXERCISE 17-8(a) KNOWLEDGE:** Fill in the blanks.

The functional group of a carboxylic acid is a \_\_\_\_\_ group. In esters, a \_\_\_\_\_ group replaces the hydrogen in the acid, whereas in amides an \_\_\_\_\_ group replaces the hydroxyl group of the acid. In both cases, a \_\_\_\_\_ molecule is produced. An ester is made by the reaction of an \_\_\_\_\_ with a carboxylic acid, and an amide is made by the reaction of an \_\_\_\_\_ with a carboxylic acid. Polyesters and polyamides are known as \_\_\_\_\_ polymers.

**EXERCISE 17-8(b) ANALYSIS:** A carboxylic acid and an ester both have the formula  $\text{C}_3\text{H}_6\text{O}_2$ . Write the Lewis structure of the two compounds and give their names.

**EXERCISE 17-8(c) ANALYSIS:** Given the general structure



X can be  $-\text{H}$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$ ,  $-\text{CH}_3$ , or  $-\text{NH}_2$ .

Fill in the blanks.

X = \_\_\_\_\_ for an aldehyde, X = \_\_\_\_\_ for a carboxylic acid, X = \_\_\_\_\_ for a ketone, X = \_\_\_\_\_ for an amide, and X = \_\_\_\_\_ for an ester.

**EXERCISE 17-8(d) SYNTHESIS:** Biological molecules known as proteins also contain an amide linkage, which in the case of proteins is known as a peptide bond. Proteins are polymers of amino acids. Two simple examples are glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) and alanine [ $\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$ ]. Write the structure of two simple proteins made from a glycine and an alanine molecule.

For additional practice, work chapter problems 17-38, 17-40, 17-42, and 17-44.

**PART B**  
**SUMMARY**

**KEY TERMS**

- 17-5.1 Functional groups** contain hetero atoms or multiple bonds in a carbon chain. p. w-20  
**17-5.2** An **alcohol** contains a **hydroxyl** (OH) functional group. p. w-20  
**17-5.3** An **ether** contains an oxygen bonded to two alkyl groups. p. w-22  
**17-6** An **aldehyde** contains a **carbonyl group** ( $\text{C}=\text{O}$ ) bonded to one hydrogen. A **ketone** contains a carbonyl group bonded to two alkyl groups. p. w-23  
**17-7** An **amine** contains a nitrogen hetero atom bonded to three hydrogens or alkyl groups. p. w-24  
**17-8.1** A **carboxylic acid** contains a **carboxyl group** (COO) bonded to one hydrogen. p. w-26  
**17-8.2** An **ester** contains a carboxyl group bonded to two alkyl groups. p. w-26  
**17-8.3** An **amide** contains a carbonyl group bonded to an amine group. p. w-27  
**17-8.4** Amides and esters can be used to make **condensation polymers**. p. w-27

**SUMMARY CHART**

| Functional Groups |   |  |  |                                   |
|-------------------|---|--|--|-----------------------------------|
| Name of Class     | Functional Group  | General Formula <sup>a</sup>                                   | Example  | IUPAC Name (Common Name)          |
| alcohols          | $\begin{array}{c}   \\ -\text{C}-\ddot{\text{O}}-\text{H} \\   \end{array}$                               | $\text{R}-\text{OH}$   | $\text{CH}_3\text{CH}_2\text{OH}$              | ethanol (ethyl alcohol)           |
| ethers            | $\begin{array}{c}   \quad \quad   \\ -\text{C}-\ddot{\text{O}}-\text{C}- \\   \quad \quad   \end{array}$  | $\text{R}-\text{O}-\text{R}'$                                  | $\text{CH}_3\text{OCH}_2\text{CH}_3$           | (ethyl methyl ether)              |
| aldehydes         | $\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\text{H} \end{array}$                                     | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$    | $\text{CH}_3\text{CH}_2\text{CHO}$             | propanal (propionaldehyde)        |
| ketones           | $\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\text{C}-\text{C}- \\   \quad \quad   \end{array}$        | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$   | $\text{CH}_3\text{COCH}_2\text{CH}_3$          | butanone (ethyl methyl ketone)    |
| amines            | $\begin{array}{c}   \\ -\text{C}-\ddot{\text{N}}- \\   \end{array}$                                       | $\text{R}-\text{NH}_2$   | $\text{CH}_3\text{CH}_2\text{NH}_2$            | (ethylamine)                      |
| carboxylic acids  | $\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\ddot{\text{O}}-\text{H} \end{array}$                     | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$   | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ | butanoic acid (butyric acid)      |
| esters            | $\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\ddot{\text{O}}-\text{C}- \\   \quad \quad   \end{array}$ | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$  | $\text{CH}_3\text{COOCH}_3$                    | methyl ethanoate (methyl acetate) |
| amides            | $\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\ddot{\text{N}}- \\   \end{array}$                        | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}_2$ | $\text{CH}_3\text{CONH}_2$                     | ethanamide (acetamide)            |

<sup>a</sup> R and R' stand for hydrocarbon groups (e.g, alkyl). They may be different groups or the same group. R may also represent a hydrogen atom in aldehydes, carboxylic acids, esters, and amides.

## CHAPTER SUMMARY

Chemical compounds have traditionally been divided into two general groups—**organic** and **inorganic**. To introduce the more than 10 million registered organic compounds, we need to find common properties or molecular structures so as to classify them into more specific groups. The first classification is the **hydrocarbons**, which can be further subdivided according to the type of bonds in the molecules of the various compounds. Each of these groups forms a **homologous series** designated by a general formula. The four hydrocarbon groups include **alkanes** (which are all said to be **saturated**), **alkenes**, **alkynes**, and **aromatic compounds**.

**Isomers**, which are more conveniently illustrated with **condensed** formulas, exist for all but the simplest members of these groups. The major sources of alkanes are natural gas and petroleum. Because of the difference in *volatility* of the alkane components of petroleum, they can be separated by distillation in a refinery. By processes of **cracking**, **re-forming**, and **alkylation**, these **petrochemicals** that are found in natural sources can be used to make many other useful hydrocarbons.

The nomenclature of hydrocarbons is somewhat complicated because of the use of both formal IUPAC names and popular common names. In the IUPAC method,

**alkyl groups** are named as **substituents** on the longest hydrocarbon chain.

Hydrocarbons all have important uses: alkanes for fuel, alkenes to make **polymers**, and alkynes to make alkenes for various polymers. Aromatics and **derivatives** of aromatics find application as solvents, drugs, and flavors.

The focal point of chemical reactivity in an organic compound is the **functional group**. This may be a double or triple bond in a hydrocarbon or **hetero atoms** that are incorporated into the molecule. Functional groups include the **hydroxyl**, **carbonyl**, and **carboxyl groups**. Derivatives of the carboxyl group include esters and amides.

The bonding environment of the hetero atom in a functional group imposes certain common properties on compounds containing that group. Thus, the functional group defines a class of compounds. The eight classes of organic compounds containing hetero atoms include **alcohols**, **ethers**, **aldehydes**, **ketones**, **amines**, **carboxylic acids**, **esters**, and **amides**. If an ester or amide linkage is made on both sides of a molecule, **condensation polymers**, which are known as polyesters and polyamides, respectively, are formed.

## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...  | EXAMPLES   | EXERCISES      | CHAPTER PROBLEMS                   |
|---------|---|------------|----------------|------------------------------------|
| 17-1    | Write Lewis structures of simple organic compounds including isomers of a compound using, where possible, condensed and fully condensed formulas. | 17-1       | 1a, 1b, 1c     | 1, 2, 4, 6, 14, 15                 |
| 17-2    | Write the formulas of straight-chain alkanes.   |            | 2a, 2c         | 7, 9, 10, 13                       |
|         | Give the IUPAC names of some simple alkanes.  | 17-2, 17-3 | 2b             | 16, 17, 20, 21, 22                 |
| 17-3    | Write the formulas of alkenes and alkynes.  |            | 3a, 3b, 3e     | 23, 24, 26, 28                     |
|         | Give the IUPAC names of some simple alkenes.  |            | 3c             | 29, 30, 31, 32                     |
|         | Describe how alkenes are used to make polymers.   |            | 3d             | 33, 34                             |
| 17-4    | Describe the difference between aromatic compounds and straight-chain alkenes using resonance.  |            | 4a, 4b, 4c     | 35, 36                             |
| 17-5    | List the general structures, names, properties, and uses of alcohols and ethers.  |            | 5a, 5b, 5c     | 37, 38, 39, 40, 51, 42, 43, 44, 46 |
| 17-6    | List the general structures, names, properties, and uses of aldehydes and ketones.  |            | 6a, 6b, 6c     |                                    |
| 17-7    | List the general structures, names, properties, and uses of amines.   |            | 7a, 7b, 7c     |                                    |
| 17-8    | List the general structures, names, properties, and uses of carboxylic acids, esters, and amides.   |            | 8a, 8b, 8c, 8d |                                    |

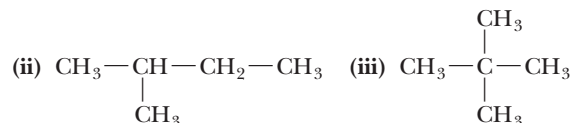
## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**17-1(a)** Lewis structures of organic compounds illustrate that carbon forms a total of four bonds to other atoms. Two different compounds that share the same formula are known as isomers. Elements other than carbon and hydrogen that appear in an organic compound are known as hetero atoms.

**17-1(b)** (i)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$



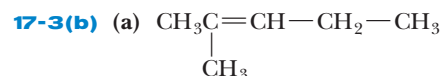
**17-1(c)** (a), (b), and (c) are all identical and are thus not isomers. (d) and (e) are isomers, but (f) is identical to (d).

**17-2(a)** A hydrocarbon that has only single bonds in its molecules is classified as an alkane. The principal sources of this class of compounds are natural gas and petroleum. The latter liquid is separated into component compounds in a refinery. The separation is accomplished because light alkanes are more volatile than the heavier compounds. One type of alkane can be converted into another by the processes of cracking, re-forming, and alkylation.

**17-2(b)** (i) *n*-pentane (ii) methylbutane (iii) dimethylpropane

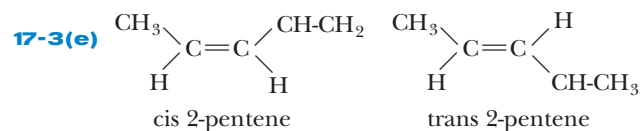
**17-2(c)** In alkanes the carbon forms only single bonds to other carbon or hydrogen atoms. Since there are four bonded pairs around each carbon, both the electronic and molecular geometry are tetrahedral.

**17-3(a)** Alkenes are known as unsaturated hydrocarbons because they contain a double bond. An important use of these compounds is in the manufacture of plastics. Alkynes contain a triple bond. The general formula of a straight-chain alkene is  $\text{C}_n\text{H}_{2n}$  and of a straight-chain alkyne is  $\text{C}_n\text{H}_{2n-2}$ .



**17-3(c)** (a) 2-pentyne (b) 3,4-dimethyl-1-hexene

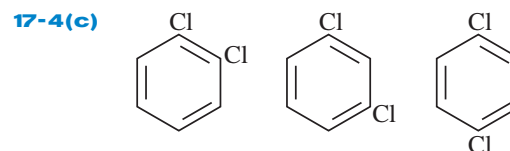
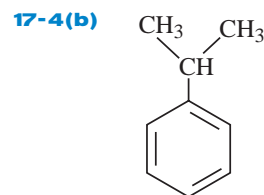
**17-3(d)**  $(-\text{CH}_2-\text{CH}(\text{CH}_3)-)$



Alkanes do not form cis-trans isomers because there is free rotation about the single bond (i.e., the carbons are not "locked" in place). Alkynes also do not form these isomers because the geometry around the triple bond is linear.

**17-4(a)** Benzene is the most important example of an aromatic hydrocarbon. It has two major resonance structures. Its geometry is described as planar. A derivative of benzene

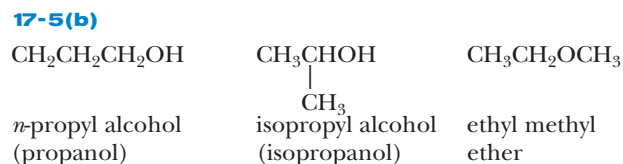
is formed by the replacement of a hydrogen with a hydrocarbon of a hetero atom group. For example, phenol has a hydroxyl group on the benzene ring.



## PART B

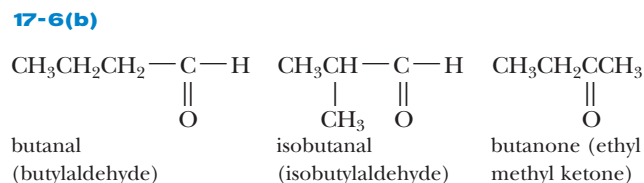
## EXERCISES

**17-5(a)** The functional group in an alcohol is known as a hydroxyl group. In ethers, the oxygen is attached to two hydrocarbon groups. Ethyl alcohol is produced from sugars in a process known as fermentation. A diol is an alcohol with two OH groups.



**17-5(c)** Since all three compounds have the same molar mass, they have approximately the same London forces. The geometry around the oxygen in all three compounds is described as V-shaped because there are two bonded pairs and two lone pairs of electrons. Therefore, all three compounds are polar. The two alcohols can form hydrogen bonds between other alcohol molecules, whereas the ether has normal dipole-dipole forces. Therefore, the alcohols have greater intermolecular attractions and thus higher boiling points (are less volatile) than the ether.

**17-6(a)** The functional group in aldehydes and ketones is a carbonyl group. In aldehydes, the functional group is attached to at least one hydrogen atom.

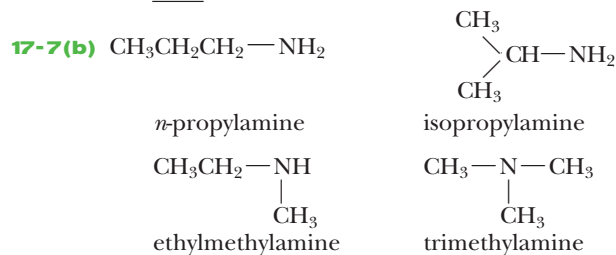


**17-6(c)** Aldehyde and ketone molecules are all polar because the geometry around the carbon in the carbonyl group is trigonal planar. Since all three groups surrounding the carbon are not the same, however, the molecules are polar. Hydrogen bonding is not involved because the hydrogens are



attached to carbon atoms rather than to an oxygen or nitrogen atom. Hydrogen bonding is involved between water and the carbonyl group, however, so the lighter-weight aldehydes and ketones are water soluble.

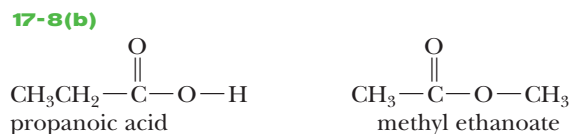
**17-7(a)** In amines the hetero atom is a nitrogen atom that may have up to three hydrocarbon groups attached to it. Amines form basic solutions in water.



**17-7(c)** An amine is a molecular compound. Molecular compounds are often gases, liquids, or volatile solids. Drugs that are molecular compounds are often found in solution. Ionic compounds are always solids and are found in pill form. The formula written as ethylaminehydrochloride is actually ethylammonium chloride; these are both illustrated below.



**17-8(a)** The functional group of a carboxylic acid is a carboxyl group. In esters, a hydrocarbon group replaces the hydrogen in the acid, whereas in amides an amino group replaces the hydroxyl group of the acid. In both cases, a water molecule is produced. An ester is made by the reaction of an alcohol with a carboxylic acid, and an amide is made by the reaction of an amine with a carboxylic acid. Polyesters and polyamides are known as condensation polymers.



**17-8(c)** X = —H for an aldehyde, X = —OH for a carboxylic acid, X = —CH<sub>3</sub> for a ketone, X = —NH<sub>2</sub> for an amide, and X = —OCH<sub>3</sub> for an ester.

**17-8(d)**  $\text{H}_2\text{NCH}_2\text{CONHCH}(\text{CH}_3)\text{COOH}$  and  $\text{H}_2\text{NCH}(\text{CH}_3)\text{NHCOCH}_2\text{COOH}$ .

Notice that these are two distinct compounds. In the first, the glycine contains the  $\text{NH}_2$  end and alanine, the  $\text{COOH}$  end. In the second compound it is just the opposite.

## CHAPTER PROBLEMS

Answers to all of the following problems are found at the end of the Chapter.

### Lewis Structures and Isomers (SECTION 17-1)

**17-1.** Draw Lewis structures for each of the following compounds. (More than one structure may be possible.)

- (a)  $\text{CH}_3\text{Br}$       (c)  $\text{C}_4\text{H}_8$       (e)  $\text{C}_2\text{H}_7\text{N}$   
 (b)  $\text{C}_3\text{H}_4$       (d)  $\text{CH}_5\text{N}$       (f)  $\text{C}_3\text{H}_8\text{O}$

**17-2.** Draw Lewis structures for each of the following compounds. (More than one structure may be possible.)

- (a)  $\text{C}_5\text{H}_{10}$       (c)  $\text{C}_4\text{H}_9\text{Cl}$   
 (b)  $\text{C}_2\text{H}_4\text{O}$       (d)  $\text{C}_3\text{H}_9\text{N}$

**17-3.** Write all the isomers for  $\text{C}_6\text{H}_{14}$ .

**17-4.** Write all the isomers for  $\text{C}_6\text{H}_{12}$ .

**17-5.** Which of the following pairs of compounds are isomers of each other? Why or why not?

- (a)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$   
 (c)  $\text{CH}_3\text{CH}_2\text{NH}_2$  and  $\text{CH}_3\text{NHCH}_3$   
 (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_3$   
 (e)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

**17-6.** Which of the following pairs of compounds are isomers of each other? Why or why not?

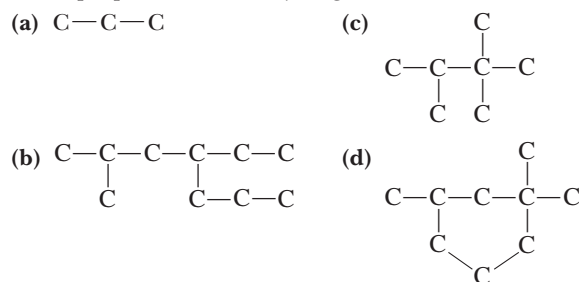
- (a)  $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$   
 (b)  $\text{CH}_3\text{CHClCH}_3$  and  $\text{CH}_3\text{CH}_2\text{CHClCH}_3$   
 (c)  $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_3$  and  $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$   
 (d)  $(\text{CH}_3)_3\text{N}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

### Alkanes (SECTION 17-2)

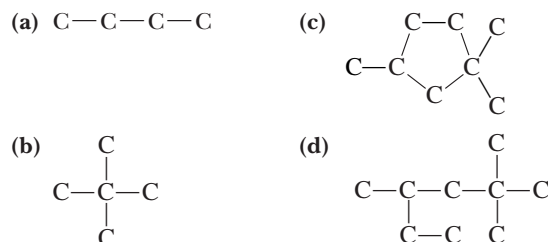
**17-7.** Which of the following are formulas of open-chain alkanes?

- (a)  $\text{C}_4\text{H}_{10}$       (c)  $\text{C}_8\text{H}_{14}$       (e)  $\text{C}_7\text{H}_{15}$       (g)  $\text{C}_{18}\text{H}_{38}$   
 (b)  $\text{C}_3\text{H}_7$       (d)  $\text{C}_{10}\text{H}_{22}$       (f)  $\text{C}_7\text{H}_{14}$       (h)  $\text{C}_9\text{H}_{15}$

**17-8.** The following skeletal structures represent alkanes. Fill in the proper number of hydrogens on each carbon atom.



**17-9.** The following skeletal structures represent alkanes. Fill in the proper number of hydrogens on each carbon atom.



**17-10.** Which of the following are formulas of alkyl groups?

- (a)  $\text{C}_4\text{H}_8$       (c)  $\text{C}_6\text{H}_{10}$       (e)  $\text{C}_6\text{H}_{13}$   
 (b)  $\text{C}_4\text{H}_9$       (d)  $\text{C}_6\text{H}_6$       (f)  $\text{C}_6\text{H}_{11}$

**17-11.** Write the formulas of any compounds listed in problem 17-7 that could be a cyclic alkane.

**17-12.** Write the formulas of any alkyl groups listed in problem 17-7.

**17-13.** Which of the following could be the formula of a cyclic alkane?

- (a)  $C_8H_{18}$  (c)  $C_6H_6$   
 (b)  $C_5H_8$  (d)  $C_5H_{10}$

**17-14.** Write the condensed structure for each of the following compounds.

- (a) 3-methylpentane (d) 4-ethyl-2-methylheptane  
 (b) *n*-hexane (e) 3-isopropylhexane  
 (c) 2,4,5-trimethyloctane (f) 2,2-dimethyl-4-*t*-butylnonane

**17-15.** Write the condensed structure for each of the following compounds.

- (a) cyclopentane  
 (b) *n*-pentane  
 (c) 3,3-dimethylpentane  
 (d) 3-ethyl-3-methylhexane  
 (e) 3,5-dimethyl-4-isopropyloctane

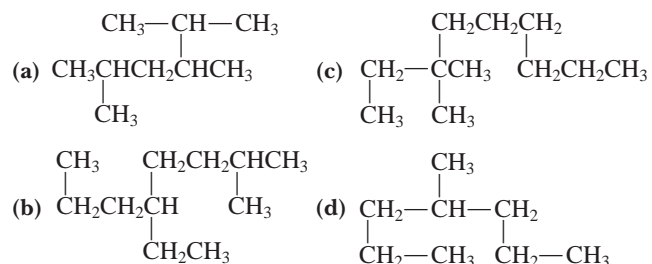
**17-16.** Write the structure and the correct IUPAC name for the following.

- (a) 2-ethyl-3-methylpentane  
 (b) 5-*n*-propyl-5-isopropylhexane

**17-17.** Write the structure and the correct IUPAC name for the following.

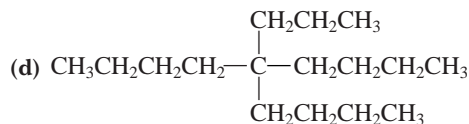
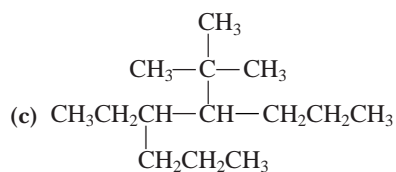
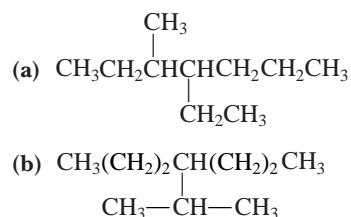
- (a) 2,3-diethylpentane  
 (b) 4-methyl-5-isopropylhexane

**17-18.** How many carbons are in the longest chain of each of the following compounds? Write the name of the longest alkane chain for each.



**17-19.** Name the substituents attached to the longest chains in the previous problem and give the IUPAC names for the compounds.

**17-20.** Give the longest chain, the substituents, and the proper IUPAC name for the following compounds.



**17-21.** Give the proper IUPAC names for (a), (b), and (c) in problem 17-8.

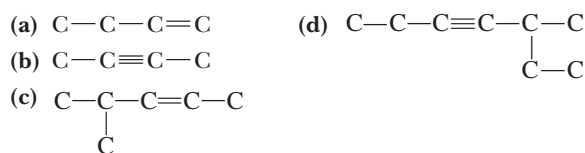
**17-22.** Give the proper IUPAC names for (a), (b), and (d) in problem 17-9.

### Alkenes and Alkynes (SECTION 17-3)

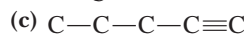
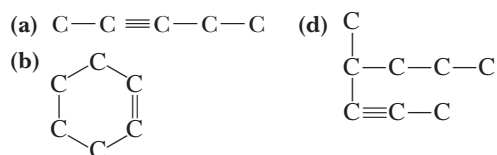
**17-23.**  $C_nH_{2n}$  can represent an alkane or an alkene. Explain.

**17-24.** What is the general formula of a cyclic alkene that contains one double bond?

**17-25.** The following skeletal structures represent alkenes or alkynes. Fill in the proper number of hydrogens on each carbon.



**17-26.** The following skeletal structures represent alkenes or alkynes. Fill in the proper number of hydrogens on each carbon.



**17-27.** Write the condensed structure for each of the following compounds.

- (a) 2-butyne  
 (b) 3-methyl-1-butene  
 (c) 3-propyl-2-hexene  
 (d) 5-methyl-3-octyne

**17-28.** Write the condensed structure for each of the following compounds.

- (a) propyne  
 (b) 3-ethyl-2-pentene  
 (c) 4,4-dimethyl-2-pentyne

**17-29.** What are the condensed structure and the correct name for 2-ethyl-3-butyne?

**17-30.** What are the condensed structure and the correct name for 2-isopropyl-2-methyl-3-hexene?

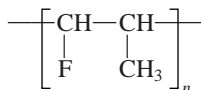
**17-31.** Give the proper IUPAC names for the compounds in problem 17-25.

**17-32.** Give the proper IUPAC names for the compounds in problem 17-26.

**17-33.** Give the abbreviated structure of the polymer that would be formed from each of the following alkenes. Name the polymer.

- (a) propylene  $\text{CH}_2=\text{CHCH}_3$   
 (b) vinyl fluoride  $\text{CH}_2=\text{CHF}$   
 (c) methyl acrylate  $\text{CH}_2=\text{CHCO}_2\text{CH}_3$

**17-34.** A certain polymer has repeating units represented by the formula.



Write the formula of the monomer.

### Aromatics (SECTION 17-4)

**\*17-35.** Naphthalene has the formula  $\text{C}_{10}\text{H}_8$  and is composed of two benzene rings that share two carbons. Write equivalent Lewis resonance structures, including hydrogens, for naphthalene.

**\*17-36.** Anthracene and phenanthrene are isomers with the formula  $\text{C}_{14}\text{H}_{10}$ . They are both composed of one benzene ring that shares four of its carbons with two other benzene rings. Write Lewis structures for the two isomers including hydrogens.

### Derivatives of Hydrocarbons (SECTIONS 17-4–17-8)

**17-37.** Which of the eight classes of compounds containing hetero atoms contains a carboxyl group? Which contains a hydroxyl group?

**17-38.** Tell how the following differ in structure.

- (a) alcohols and ethers (c) amines and amides  
 (b) aldehydes and ketones (d) carboxylic acids and esters

**17-39.** Which two classes of compounds combine to form esters? Which two classes combine to form amides?

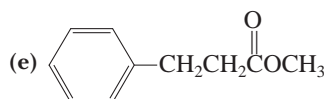
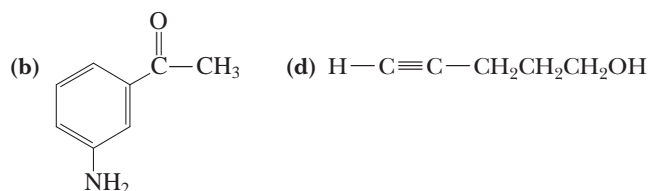
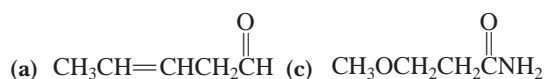
**17-40.** To which class does each of the following compounds belong?

- (a) 3-heptanone (d) 2-ethylhexanal  
 (b) 3-nonene (e) ethylbenzene  
 (c) 2-methylpentane (f) propanol

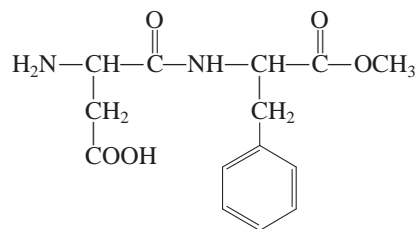
**17-41.** To which class does each of the following compounds belong?

- (a) 2-octanol (d) 3-ethyl-2-hexene  
 (b) 2-butyne (e) dimethyl ether  
 (c) ethyl pentanoate (f) aminobenzene

**17-42.** Circle and name the functional groups in each of the following compounds.



**17-43.** Aspartame is an effective sweetener that is used as a low-calorie substitute for sugar. Identify the functional groups present in an aspartame molecule.



**17-44.** Write condensed structures for the following compounds.

- (a) *n*-butyl alcohol (e) 3-pentanone  
 (b) di-*n*-propyl ether (f) propanoic acid  
 (c) trimethylamine (g) methyl acetate  
 (d) propanal (h) propanamide

**\*17-45.** Name the following compounds.

- (a)  $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_3$  (d)  $(\text{CH}_3)_3\text{C}-\text{OH}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  (e)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$   
 (c)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$

**\*17-46.** Name the following compounds.

- (a)  $\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$  (e)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$   
 (b)  $(\text{C}_2\text{H}_5)_2\text{NH}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 (d)  $\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_3$

### General Problems

**17-47.** Identify the following as an alkane, alkene, or alkyne. Assume that the compounds are not cyclic.

- (a)  $\text{C}_8\text{H}_{16}$  (e)  $\text{CH}_4$   
 (b)  $\text{C}_5\text{H}_{12}$  (f)  $\text{C}_{10}\text{H}_{20}$   
 (c)  $\text{C}_4\text{H}_8$  (g)  $\text{C}_{18}\text{H}_{38}$   
 (d)  $\text{C}_{20}\text{H}_{38}$

**17-48.** The following are possible names for one specific alkane. Write the structure and choose the correct name.

- (a) 2-ethylpentane (d) 4-methylhexane  
 (b) 1-ethyl-1-methylbutane (e) 3-methylhexane  
 (c) 2-*n*-propylbutane

**17-49.** There are three isomers for dichlorobenzene. In these molecules, two chlorines are substituted for two hydrogens on the benzene rings. Write the Lewis structures for the three isomers.

**17-50.** Write the condensed structures of a compound with seven carbon atoms in each of the four hydrocarbon classes.

**17-51.** Write the condensed structure of a compound with five carbon atoms containing each of the eight hetero atom functional groups discussed.

**17-52.** Complete the following equations.

- (a)  $C_3H_8 + \text{excess } O_2 \rightarrow$   
 (b)  $CH_2=CHCH_3 + H_2O \xrightarrow{H^+}$   
 (c)  $C_2H_5Cl + 2NH_3 \rightarrow$   
 (d)  $NH(CH_3)_2(aq) + HCl(aq) \rightarrow$   
 (e)  $CH_3CH_2COOH + NH(CH_3)_2 \rightarrow$   
 (f)  $HC\equiv CH + HBr \rightarrow$   
 (g)  $CH_3CH_2COOH + H_2O \rightarrow$

**17-53.** Complete the following equations.

- (a)  $C_3H_7OH + \text{excess } O_2 \rightarrow$   
 (b)  $CH_2=CHCH_3 + Br_2 \rightarrow$   
 (c)  $NH(CH_3)_2 + H_2O \rightarrow$   
 (d)  $CH_3CH_2CH_2OH + [O] \xrightarrow{\text{catalyst}}$   
 (e)  $CH_3CH_2COOH + CH_3OH \rightarrow$   
 (f)  $CH_3CH_2COOH(aq) + NaOH \rightarrow$

**17-54.** Give a general method for making each of the following classes of compounds.

- (a) alcohols                      (e) amides  
 (b) ketones                        (f) aldehydes  
 (c) carboxylic acids            (g) amines  
 (d) esters

**17-55.** Tell how the following can be obtained from natural sources.

- (a) ethanol                        (d) methane  
 (b) acetic acid                    (e) gasoline  
 (c) methanol

**17-56.** Give one possible use for each of the following compounds or class of compounds.

- (a) formaldehyde                (e) amines  
 (b) acetic acid                    (f) esters  
 (c) ethylene glycol              (g) alkenes  
 (d) acetylsalicylic acid        (h) alkanes

**\*17-57.** There are three isomers with the formula  $C_3H_8O$  and three isomers with the formula  $C_3H_6O_2$ . Show the Lewis structures of these six compounds and the common names of each. All contain one of the functional groups discussed.

**\*17-58.** There are two isomers with the formula  $C_3H_6O$  and four isomers with the formula  $C_3H_9N$ . Show the Lewis structures of these six compounds and the common names of each. All contain one of the functional groups discussed except hydroxyl.

**\*17-59.** Glycine has the formula  $C_2H_5NO_2$ . It is a member of a class of compounds called amino acids that combine in long chains to form proteins. Glycine contains both an amine and a carboxylic acid group. Write the structure for glycine. Write an equation illustrating the reaction of glycine as an acid in water and an equation illustrating its reaction as a base in water. Illustrate how two glycine molecules can combine to form an amide linkage (also called a peptide linkage).

## STUDENT WORKSHOP

### Organic Isomers

**Purpose:** To draw representations of several isomers with varying functional groups for a specific chemical formula. (Work in groups of three or four. Estimated time: 20 min.)

The purpose of this activity is to combine the basic principles and facts of organic chemistry with the structural information learned in previous chapters.

Consider the chemical formulas



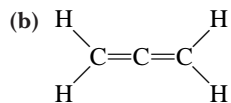
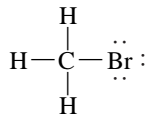
Draw as many possible isomers of these two formulas as your group can. Make sure that each carbon has four bonds and each oxygen has two bonds; the hydrogens, of course, have only single bonds.

For each isomer:

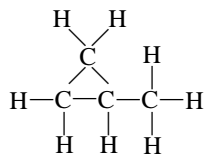
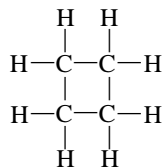
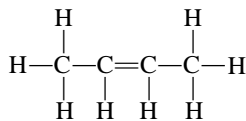
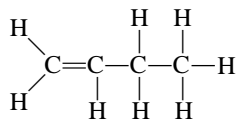
1. Draw both the full structural formula and a condensed formula.
2. Identify the type of functional group(s) present. Can you make a molecule that contains the following:
  - two esters
  - a carboxylic acid
  - a ketone and alcohol together
  - an aldehyde and an ether together
3. Identify the molecular geometry around each carbon and oxygen (if attached to two atoms).
4. Identify the bond angles found in your molecule.
5. Determine which will exhibit hydrogen bonding.

## Answers to Chapter 17 Problems

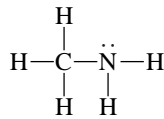
17-1. (a)



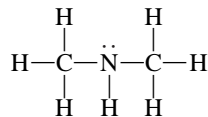
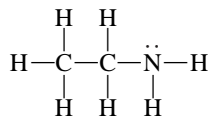
(c)



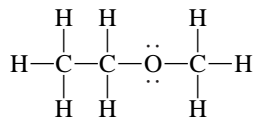
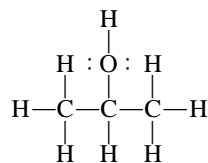
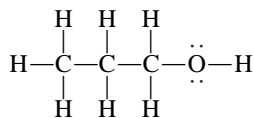
(d)



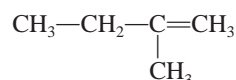
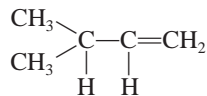
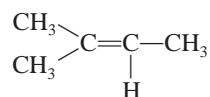
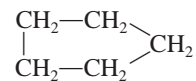
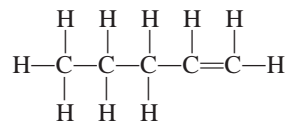
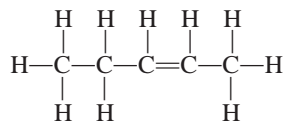
(e)



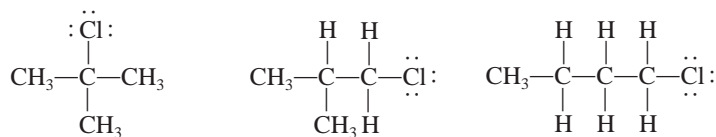
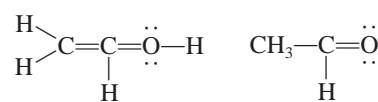
(f)



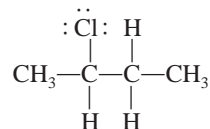
17-2. (a)



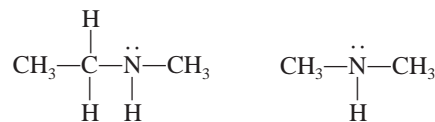
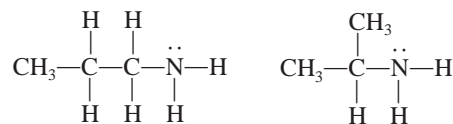
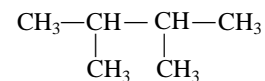
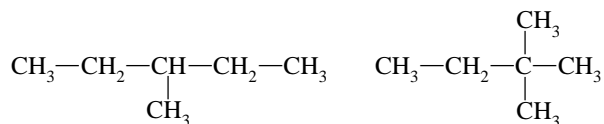
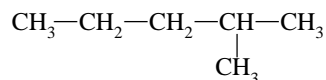
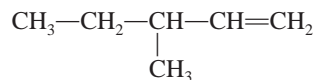
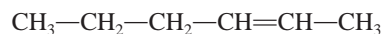
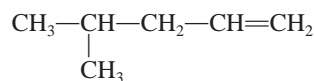
(b)



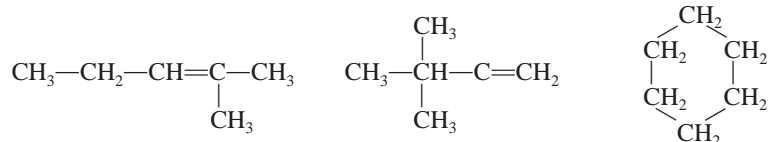
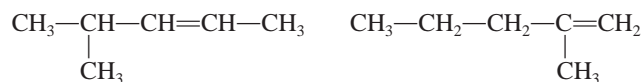
(c)



(d)

17-3.  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ 17-4.  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ 





17-5. (a) No. The second compound does not have oxygen.

(b) No. The compounds have unequal numbers of carbon atoms.

(c) Yes. Both compounds have the formula  $\text{C}_2\text{H}_7\text{N}$ .

(d) No. The compounds have unequal numbers of carbon atoms.

(e) Yes. The compounds are identical.

17-6. (a) Yes. Both compounds have the formula,  $\text{C}_5\text{H}_{12}$ .

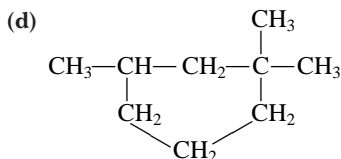
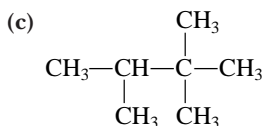
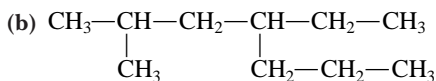
(b) No. The second compound has an additional  $\text{CH}_2$  group.

(c) Yes. The compounds are identical.

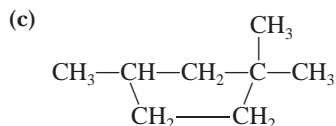
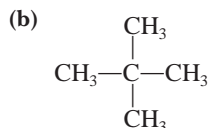
(d) Yes. Both compounds have the formula,  $\text{C}_3\text{H}_9\text{N}$ .

17-7. (a)  $\text{C}_4\text{H}_{10}$ , (d)  $\text{C}_{10}\text{H}_{22}$ , and (g)  $\text{C}_{18}\text{H}_{38}$ .

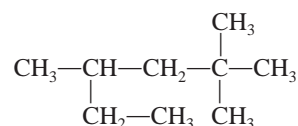
17-8. (a)  $\text{CH}_3-\text{CH}_2-\text{CH}_3$



17-9. (a)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$



(d)



17-10. (b)  $\text{C}_4\text{H}_9$  - butyl (e)  $\text{C}_6\text{H}_{13}$  - hexyl

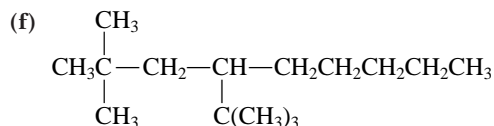
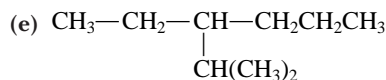
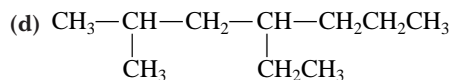
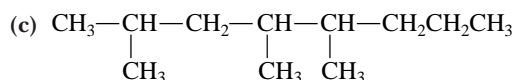
17-11. (f)  $\text{C}_7\text{H}_{14}$

17-12. (b)  $\text{C}_3\text{H}_7$  and (e)  $\text{C}_7\text{H}_{15}$

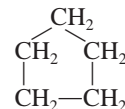
17-13. (d)  $\text{C}_5\text{H}_{10}$  could be a cyclic alkane.

17-14. (a)  $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_3$

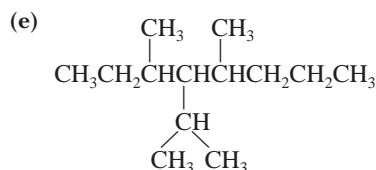
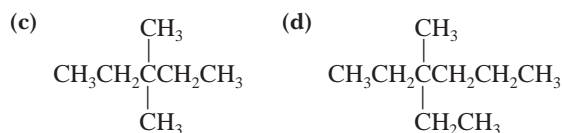
(b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

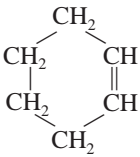
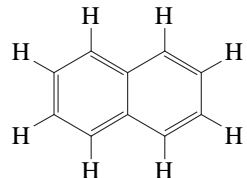


17-15. (a)

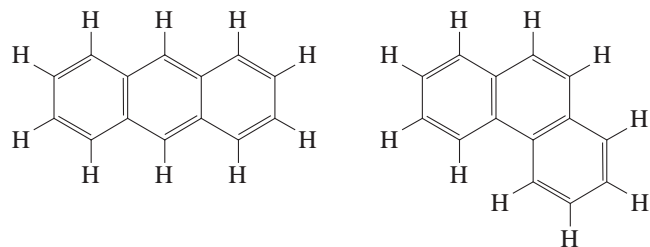


(b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



- 17-16. (a)  $\begin{array}{c} \text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CHCHCH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  3,4-dimethylhexane
- (b)  $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}(\text{CH}_3)_2 \end{array}$  4-isopropyl-4-methyloctane
- (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$  (d)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{C}\equiv\text{CCH}_3 \end{array}$
- 17-17. (a)  $\begin{array}{c} \text{CH}_3\text{CH}-\text{CHCH}_2\text{CH}_3 \\ | \quad | \\ \text{CH}_2 \quad \text{CH}_2 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$  3-ethyl-4methylhexane
- (b)  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{CH} \\ | \\ \text{CH}_3-\text{CH}-\text{CHCH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  2,3,4-trimethylheptane
- 17-18. (a) six (hexane) (b) eight (octane)  
(c) nine (nonane) (d) seven (heptane)
- 17-19. (a) three methyl 2,3,5-trimethylhexane  
(b) methyl and ethyl 5-ethyl-2-methyloctane  
(c) two methyl 3,3-dimethylnonane  
(d) one methyl 4-methylheptane
- 17-20. (a) Substituent groups are methyl and ethyl.  
Name: 4-ethyl-3-methyleptane  
(b) Substituent group is isopropyl.  
Name: 4-isopropylheptane  
(c) Substituent groups are t-butyl and ethyl.  
Name: 4-ethyl-5-t-butyloctane  
(d) Substituent groups are n-propyl and n-butyl.  
Name: 5-n-butyl-5-n-propylnonane
- 17-21. (a) propane (b) 4-ethyl-2-methylheptane  
(c) trimethylbutane
- 17-22. (a) butane (b) dimethylpropane  
(d) 2,2,4-trimethylhexane
- 17-23. This general formula is that of a straight-chain alkene with one double bond or of a cyclic alkane.
- 17-24. A cyclic alkene with one double bond is  $\text{C}_n\text{H}_{2n-2}$ .
- 17-25. (a)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$  (b)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$   
(c)  $\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}=\text{CHCH}_3 \\ | \\ \text{CH}_3 \end{array}$   
(d)  $\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}\equiv\text{CCHCH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$
- 17-26. (a)  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$  (b) 
- 17-27. (a)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$  (b)  $\begin{array}{c} \text{CH}_2=\text{CHCHCH}_3 \\ | \\ \text{CH}_3 \end{array}$   
(c)  $\text{CH}_3\text{CH}=\text{CCH}_2\text{CH}_2\text{CH}_3$   
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{CH}_2\text{CH}_2\text{CH}_3$   
(d)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCHCH}_2\text{CH}_2\text{CH}_3$   
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{CH}_3$
- 17-28. (a)  $\text{CH}_3\text{C}\equiv\text{CH}$   
(b)  $\begin{array}{c} \text{CH}_3\text{CH}_2\text{C}=\text{CHCH}_3 \\ | \\ \text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$   
(c)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{C}\equiv\text{C}-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- 17-29.  $\text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}\equiv\text{CH}$  3-methyl-1-pentyne
- 17-30.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CCH}=\text{CHCH}_2\text{CH}_3 \\ | \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$  5,5,6-trimethyl-3-heptene
- 17-31. (a) 1-butene (b) 2-butyne  
(c) 3-methyl-2-pentene (d) 5-methyl-3-heptyne
- 17-32. (a) 2-pentene (b) cyclohexane  
(c) 1-pentyne (d) 4-methyl-2-heptyne
- 17-33. (a)  $\text{-(CH}_2-\text{CH)}_n$  polypropylene  
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{CH}_3$   
(b)  $\text{-(CH}_2-\text{CH)}_n$  polyvinylfluoride  
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{F}$   
(c)  $\text{-(CH}_2-\text{CH)}_n$  polymethacrylate  
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{CO}_2\text{CH}_3$
- 17-34.  $\text{CHF}=\text{CHCH}_3$
- 17-35. 

17-36.



17-37. Carboxylic acids contain a carboxyl group, and alcohols contain only a hydroxyl group.

17-38. (a) In an ether, the oxygen is between two carbons; in an alcohol the oxygen is between a carbon and a hydrogen.

(b) In an aldehyde, a carbonyl (i.e., C=O) is between a carbon and a hydrogen; in a ketone the carbonyl is between two carbons.

 (c) In an amine, the NH<sub>2</sub> group is attached to a hydrocarbon group; in an amide, the NH<sub>2</sub> group is attached to a carbonyl group.

(d) Carboxylic acids have a hydrogen attached to an oxygen; in esters the hydrogen is replaced by a hydrocarbon group.

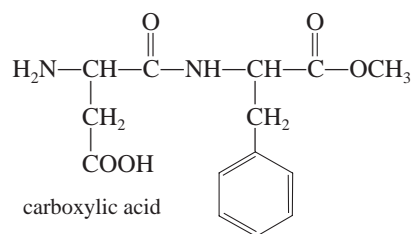
17-39. Alcohols and carboxylic acids combine to form esters. Amines and carboxylic acids combine to form amides.

 17-40. (a) ketone (b) alkene (c) alkane  
 (d) aldehyde (e) aromatic (f) alcohol

 17-41. (a) alcohol (b) alkyne (c) ester  
 (d) alkene (e) ether (f) amine

 17-42. (a) alkene and aldehyde (b) ketone and amine  
 (c) ether and amide (d) alkyne and alcohol  
 (e) ester (f) carboxylic acid

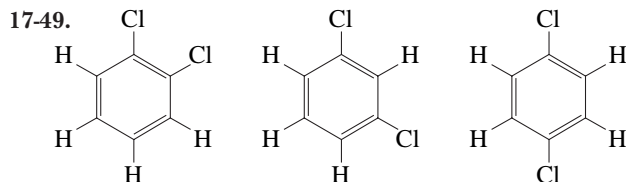
17-43. amine amide ester


 17-44. (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH  
 (b) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (c) (CH<sub>3</sub>)<sub>3</sub>N  
 (d) CH<sub>3</sub>CH<sub>2</sub>CHO (f) CH<sub>3</sub>CH<sub>2</sub>COOH  
 (e) CH<sub>3</sub>CH<sub>2</sub>C(=O)CH<sub>2</sub>CH<sub>3</sub> (g) CH<sub>3</sub>C(=O)CH<sub>3</sub>  
 (h) CH<sub>3</sub>CH<sub>2</sub>C(=O)NH<sub>2</sub>

 17-45. (a) 2-pentanone (b) butanoic acid  
 (c) acetamide (d) *t*-butyl alcohol (e) pentanal

 17-46. (a) ethyl propionate (b) diethyl amine  
 (c) *n*-butyl alcohol (d) 3-hexanone or *n*-propyl ethyl ketone  
 (e) ethanal or acetaldehyde

 17-47. (a) alkene (b) alkane (c) alkene  
 (d) alkyne (e) alkane (f) alkene  
 (g) alkane

 17-48. CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (e) 3-methylhexane

 17-50. (a)
 
$$\text{alkane } \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

 (b)
 
$$\text{alkene } \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$$

 (c)
 
$$\text{alkyne } \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}\equiv\text{CH} \\ | \\ \text{CH}_3 \end{array}$$

(d) aromatic

 17-51. (1) CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OH alcohol  
 (2) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> ether  
 (3) CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CHO aldehyde  
 (4) CH<sub>3</sub>CH<sub>2</sub>C(=O)CH<sub>2</sub>CH<sub>3</sub> ketone  
 (5) CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> amine  
 (6) CH<sub>3</sub>CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub> ester  
 (7) CH<sub>3</sub>CH<sub>2</sub>C(=O)N(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> amide  
 (8) (CH<sub>3</sub>)<sub>3</sub>CCOOH acid

 17-52. (a) C<sub>3</sub>H<sub>8</sub> + 5O<sub>2</sub> → 3CO<sub>2</sub> + 4H<sub>2</sub>O  
 (b) CH<sub>2</sub>=CHCH<sub>3</sub> + H<sub>2</sub>O → CH<sub>3</sub>CH(OH)CH<sub>3</sub>  
 (c) C<sub>2</sub>H<sub>5</sub>Cl + 2NH<sub>3</sub> → C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> + NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup>  
 (d) (CH<sub>3</sub>)<sub>2</sub>NH(aq) + HCl(aq) → (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>(aq) + Cl<sup>-</sup>(aq)  
 (e) CH<sub>3</sub>CH<sub>2</sub>COOH + (CH<sub>3</sub>)<sub>2</sub>NH → CH<sub>3</sub>CH<sub>2</sub>CON(CH<sub>3</sub>)<sub>2</sub> + H<sub>2</sub>O  
 (f) HC≡CH + HBr → CH<sub>2</sub>=CHBr  
 (g) CH<sub>3</sub>CH<sub>2</sub>COOH + H<sub>2</sub>O ⇌ CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup> + H<sub>3</sub>O<sup>+</sup>

## 17-53.

- (a)  $2\text{C}_3\text{H}_7\text{OH} + 9\text{O}_2 \rightarrow 6\text{CO}_2 + 8\text{H}_2\text{O}$
- (b)  $\text{CH}_2=\text{CHCH}_3 + \text{Br}_2 \rightarrow \text{CH}_2\text{Br}-\text{CHBrCH}_3$
- (c)  $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$
- (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO}$
- (e)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{H}_2\text{O}$
- (f)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{NaOH} \rightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}_2\text{O}$

- 17-54. (a) By addition of water to an alkene in the presence of an acid.
- (b) By the oxidation of an alcohol in the presence of a catalyst.
- (c) By oxidation of an alcohol or an aldehyde.
- (d) From the reaction of an alcohol and a carboxylic acid.
- (e) From the reaction of ammonia or an amine with a carboxylic acid.
- (f) By oxidation of an alcohol in the presence of a catalyst.
- (g) From the reaction of ammonia with an alkyl halide.

- 17-55. (a) Ethanol - Obtained from the fermentation of grains.
- (b) Acetic acid - From the air oxidation of ethanol.
- (c) Methanol - By heating wood to high temperatures in the absence of oxygen.
- (d) Methane - From natural gas. The other components can be condensed out at low temperatures.
- (e) Gasoline - From the distillation of crude oil.

- 17-56. (a) Formaldehyde is used as a disinfectant, antiseptic, germicide, fungicide, embalming fluid and in the preparation of certain polymers.
- (b) Acetic acid is the sour component of vinegar.
- (c) Ethylene glycol is used as antifreeze in automobiles and to make polymers.
- (d) Acetylsalicylic acid is used as the active ingredient in pain relievers and fever reducers.
- (e) Amines are used in the preparation of dyes, drugs, disinfectants and insecticides. They are also used to make certain polymers.
- (f) Esters are used as flavorings and in the preparation of certain polymers (polyesters).
- (g) Alkenes are used to make many polymers.
- (h) Alkanes are used as fuels and to make most other organic compounds.

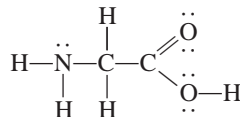
## 17-57.

- (a)  $\text{C}_3\text{H}_8\text{O}$ :  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$  *n*-propyl alcohol
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$  isopropyl alcohol
- $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_3$  ethyl methyl ether
- (b)  $\text{C}_3\text{H}_6\text{O}_2$ :  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3-\text{C}-\text{O}-\text{CH}_3 \end{array}$  methyl acetate (ester)
- $\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{C}-\text{O}-\text{CH}_2-\text{CH}_3 \end{array}$  ethyl formate (ester)
- $\text{CH}_3-\text{CH}_2-\text{COOH}$  propionic acid

## 17-58.

- $\text{C}_3\text{H}_6\text{O}$ :  $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  propionaldehyde
- $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_3$  methyl ethyl ketone
- $\text{C}_3\text{H}_9\text{N}$ :  $\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  trimethylamine
- $\text{CH}_3-\text{CH}_2-\overset{\text{H}}{\underset{|}{\text{N}}}-\text{CH}_3$  ethyl methyl amine
- $\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{H}}{\underset{|}{\text{N}}}-\text{H}$  *n*-propyl amine
- $(\text{CH}_3)_2\text{CH}-\overset{\text{H}}{\underset{|}{\text{N}}}-\text{H}$  *iso*-propyl amine

## 17-59.



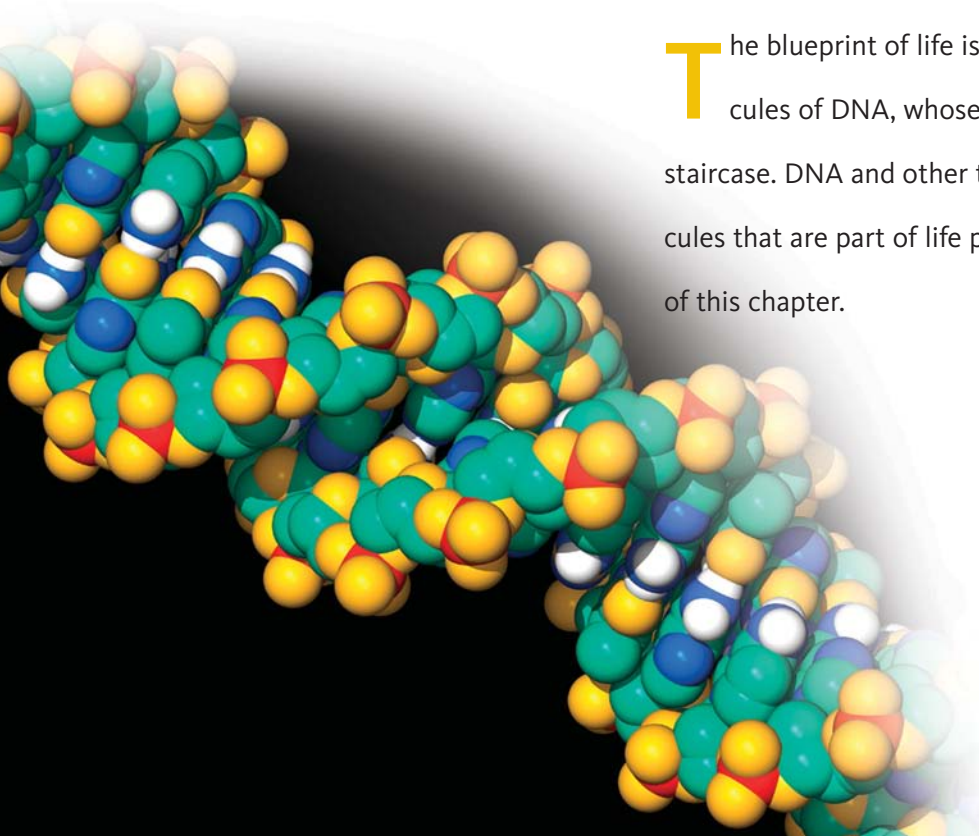
Glycine can function both as an acid (because of the carboxyl group) and as a base (because of the amine group).





CHAPTER  
18

# Biochemistry



**T**he blueprint of life is contained in the molecules of DNA, whose structure is like a spiral staircase. DNA and other types of organic molecules that are part of life processes are the subjects of this chapter.

**PART A**  
**THREE BASIC TYPES OF**  
**BIOCHEMICAL COMPOUNDS**

**18-1** Lipids



*Soap—Dissolves Away Fat*

**18-2** Carbohydrates

**18-3** Amino Acids and Proteins

**PART B**  
**BIOCHEMICAL COMPOUNDS**  
**AND LIFE FUNCTIONS**

**18-4** Enzymes

**18-5** Nucleic Acids and Genetics



*The Origin of Life*

**SETTING THE STAGE** For the past decade, the news has included results of studies indicating the importance of regular exercise and a balanced diet with plenty of fiber. We are told that a diet consisting of fats, carbohydrates, and proteins will give us energy and keep us healthy. But there should be a proper balance. Have you ever heard expressions like, “If you eat too much fat in your diet, your arteries will clog and you will die” or “If you drink a glass of red wine a day, you can help prevent heart disease”? Do you ever wonder what to believe and what is just speculation? In this day and age, we should understand at a molecular level how the human body functions in order to live happier, healthier lives.

This chapter will provide an overview of the biological molecules that collectively are the fundamental components of *biochemistry, which is the study of the molecules and reactions that occur in living organisms*. An overview of biochemistry would not be complete without a discussion of fats, carbohydrates, proteins, enzymes, and nucleic acids. Most of the molecules presented in this chapter are biological polymers. Recall from Chapter 17 that a *polymer* is a complex molecule made of many simpler repeating units known as monomers.

In Part A in this chapter, we will examine the three principal biological substances—fats, carbohydrates, and amino acids. The latter two substances also form important polymers. In Part B we will look at biological catalysts known as enzymes and the construction and replication of the molecular blueprint of life, which is a polymer known as DNA.

**PART A**  
**THREE BASIC TYPES OF**  
**BIOCHEMICAL COMPOUNDS**

**SETTING A GOAL**

- You will become familiar with the three principal biological compounds—lipids, carbohydrates, and proteins.

**OBJECTIVES**

- 18-1** Describe the different types of lipids, their common properties, and their major uses or functions.
- 18-2** Describe the different types of carbohydrates, their common properties, and their major uses or functions.
- 18-3 (a)** Describe the different types of amino acids.
- (b)** List and describe the four structures of proteins.

► **OBJECTIVE FOR SECTION 18-1**

Describe the different types of lipids, their common properties, and their major uses or functions.

## 18-1 LIPIDS



**LOOKING AHEAD!** The first types of compounds that we will examine are popularly known as fats, but we will refer to them as lipids. Lipids, which include fats, oils, and waxes, serve many functions in the body, such as protective coatings for nerve cells, as steroids and steroid hormones (cholesterol), as regulatory membranes for cells, and a means of storing energy. ■

### 18-1.1 Saponifiable Lipids

**Lipids** are nonpolar biological molecules that are insoluble in polar solvents, like water, and soluble in solvents with little or no polarity, like diethyl ether. At first glance lipids seem out of place in our bodies, since we are composed of a polar aqueous environment and lipids are nonpolar molecules. But they are important.

Lipids can be broken down into two major classes of compounds, saponifiable and nonsaponifiable lipids. **Saponifiable lipids** contain the ester bond. Examples of simple saponifiable lipids are waxes, oils, and fats. Complex saponifiable lipids contain more components, like alcohols, carbohydrates, and phosphates. Nonsaponifiable lipids do not contain an ester group. They will be discussed later in this section.

*Oils and fats are lipids that are made from glycerol and three fatty acids; they are referred to as **triglycerides**. **Fatty acids** are long-chain hydrocarbons containing a carboxylic acid functional group.* A typical lipid found in solid fats and a typical lipid found in oils are shown in Figure 18-1.

There are four key points to note regarding fatty acids.

- The hydrocarbon chain is linear, not branched.
- The number of carbon atoms in the chain is always even in size and ranges from 10 to 20.
- The only functional group besides the carboxylic acid group ( $\text{—COOH}$ ) is the double bond present in unsaturated fatty acids.
- An individual triglyceride usually contains three different fatty acids. For example, animal fat contains myristic acid [ $\text{CH}_3(\text{CH}_2)_{12}\text{COO—}$ ], palmitic acid [ $\text{CH}_3(\text{CH}_2)_{14}\text{COO—}$ ], and steric acid [ $\text{CH}_3(\text{CH}_2)_{16}\text{COO—}$ ].

One of the convenient features of lipids is that a fundamental understanding of chemistry explains everything about them. If you think of a saturated fat like those found in animals and typically referred to as lard, you think of a solid. A jar of vegetable oil is obviously a liquid. An oil is a fat in the liquid phase. The difference between a solid and liquid fat lies in the number of double bonds present in the fatty acids that make up the fat or oil and the number of carbon atoms in the fatty acid chain.

Saturated fatty acids (no carbon–carbon double bonds) are relatively compact and are thus able to pack closely together. This results in significant London forces between the separate fat molecules that hold the molecules together. Recall that the stronger the forces between molecules, the more likely the substance will be a solid. Oils have high percentages of unsaturated fatty acids (i.e., polyunsaturated fats). These double bonds disrupt the ability of the hydrocarbon chains to interact. The end result is weaker intra- and intermolecular forces of attraction that lead to lower melting points, producing liquids rather than solids at room temperature.

Solid fats can be made from oils by a process called *hydrogenation* whereby hydrogen molecules are added to the double bond, changing it to a saturated hydrocarbon and thus a solid. In most vegetable oils, the carbon atoms are on the same side of the double bond and are called *cis* isomers. Since there is no rotation about a double bond when oils are partially hydrogenated, some of the double bonds change to the *trans* isomer, which means the carbons (collectively represented as R) are on opposite sides of the double bonds. The *cis* and *trans* isomers are illustrated below.



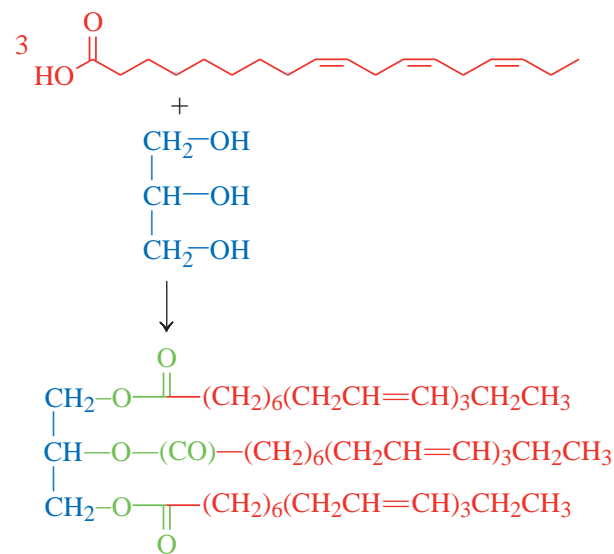
Partial hydrogenation increases the shelf life of oils, making them commercially attractive in the baking and fast-food industries. Unfortunately, *trans* fatty acids have been shown to raise blood cholesterol levels more than other types of fats and are thus linked to an increased risk of heart disease. Some communities have made the use of *trans* fatty acids in cooking illegal.

### 18-1.2 Complex Lipids

The complex lipids are presented in Figure 18-2. They are the **sphingolipids**, the **glycolipids**, and the **phospholipids**. A common sphingolipid is *sphingomyelin*. Sphingomyelin contains the alcohol sphingosine, a fatty acid, a phosphate group, and the alcohol choline. Sphingomyelins are significant in that they provide the protective coating around nerve cells that acts to prevent loss of nerve transmission. Nerve cells transmit signals as electrical impulses. The better the insulation around the impulse, the less current will be lost to the surroundings. Degradation of the *myelin sheath* (*sphingomyelins* surrounding nerve cells) occurs in individuals who suffer from multiple sclerosis. The symptoms of this disease include diminished coordination, impaired vision, and muscle fatigue. Glycolipids are very similar to sphingolipids except that a carbohydrate in the glycolipid replaces the phosphate and choline of the sphingolipid. In Section 18-2 of this chapter, we will learn of the various carbohydrates. A common glycolipid is a cerebroside. **Cerebrosides** are glycolipids that contain the alcohol sphingosine, a fatty acid, and a carbohydrate. They are principally found in the brain and at nerve synapses. Phospholipids contain either the alcohol sphingosine or glycerol, a fatty acid, a phosphate group, and another alcohol. A common example of a phospholipid is phosphatidylcholine, which contains the alcohol glycerol, two fatty acids, a phosphate group, and the alcohol choline. **Phosphatidylcholine** is a phospholipid that serves as a membrane component in cell walls.

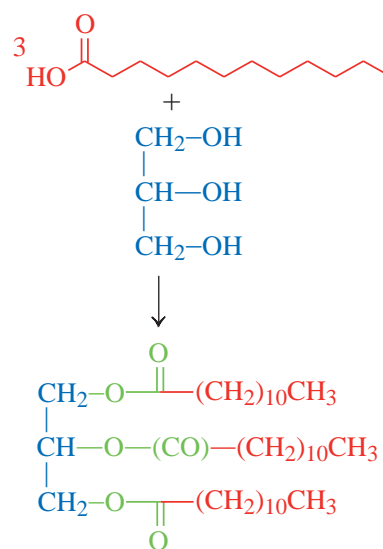
Oil

3 Fatty acids + Glycerol (alcohol)



Fat

3 Fatty acids + Glycerol (alcohol)



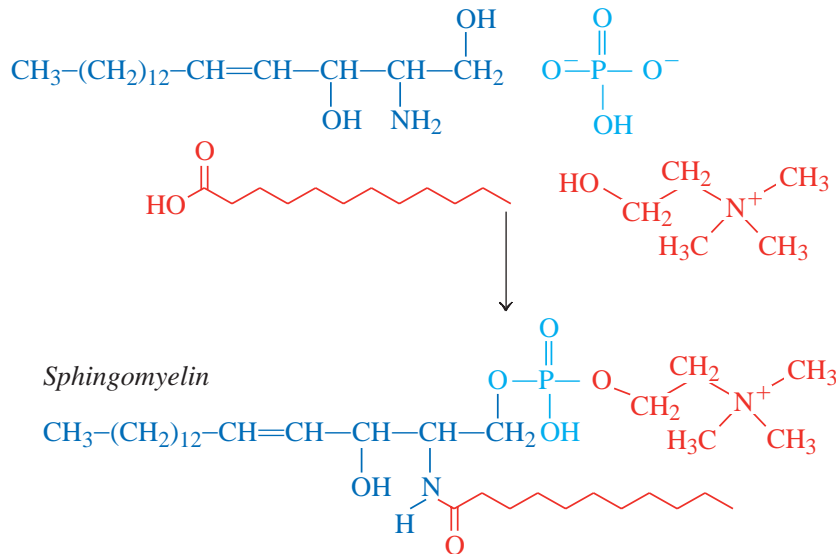
**FIGURE 18-1 Saturated and Unsaturated Lipids**  
Fatty acids that have no double bonds form saturated lipids, while fatty acids with double bonds form unsaturated lipids.

**Saponification** is the base-catalyzed decomposition of a lipid to an alcohol and a carboxylate salt. This reaction is specific for the ester group in the molecule. This reaction is the opposite of the formation of an ester from an alcohol and carboxylic acid, discussed in Section 17-8. (See Figure 18-3.)

The fatty acid salt that is produced in the reaction is known as soap. Soaps can be used to dissolve fats and oils by forming micelles. A **micelle** is a cluster of fatty acid

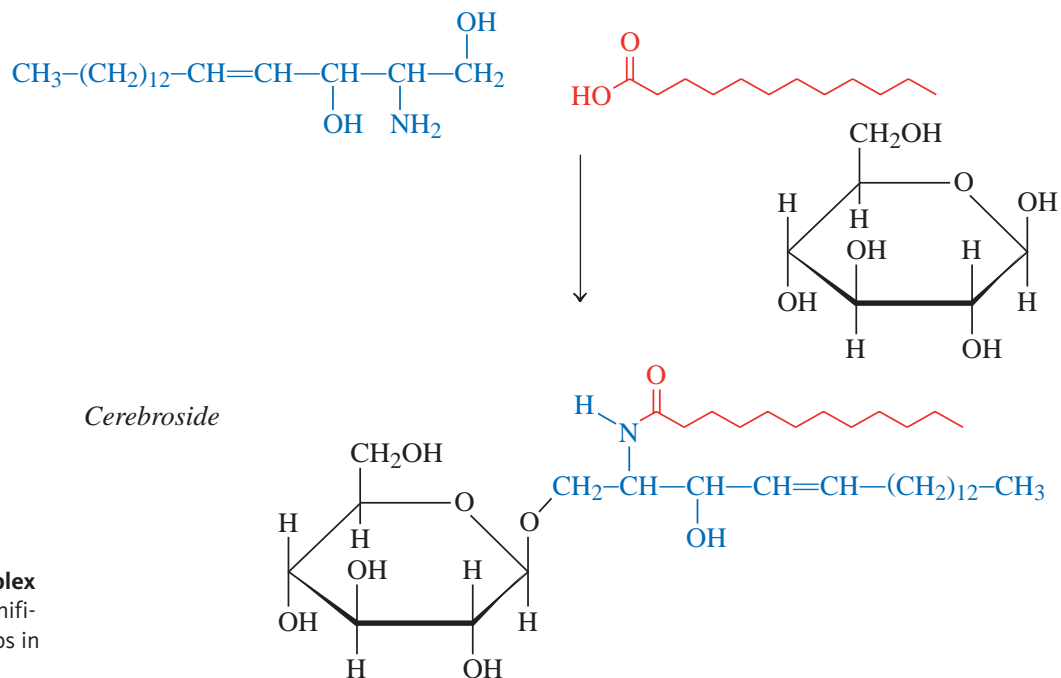
### Sphingolipid

Sphingosine + Fatty acid + Phosphate + Choline (alcohol)



### Glycolipid

Sphingosine + Fatty acid +  $\beta$ -D-glucose (a carbohydrate)



**FIGURE 18-2 Complex Lipids** These lipids are saponifiable lipids that contain groups in addition to fatty acids.



*Phospholipid*

Glycerol + 2 Fatty acids + Phosphate + Choline (alcohol)

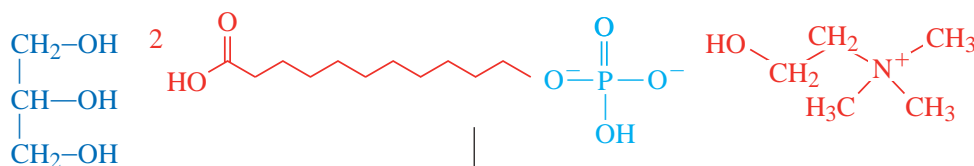
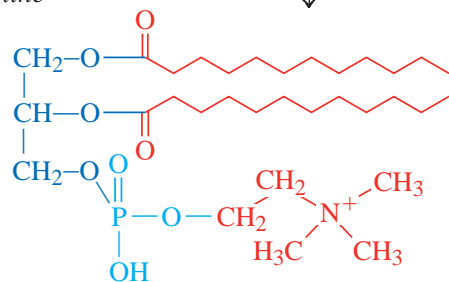
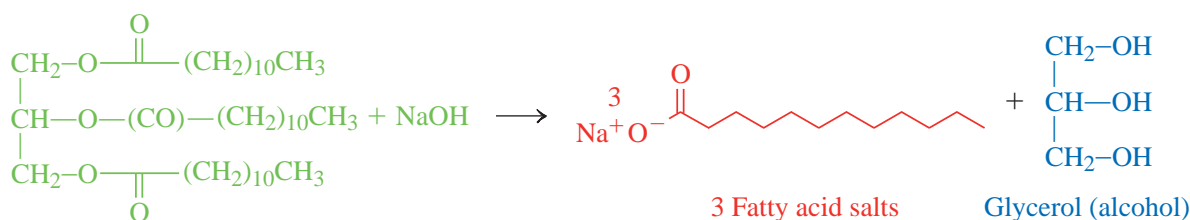
*Phosphatidylcholine*

FIGURE 18-2 Continued.

**Fat**

Ester bonds shown in green

Fatty acids shown in red

Glycerol shown in blue

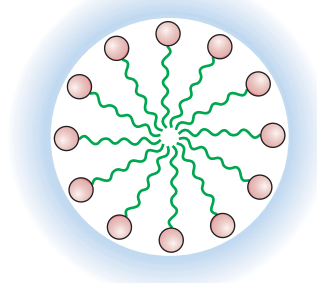
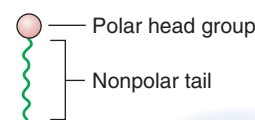
**FIGURE 18-3 Saponification of a Triglyceride** This reaction produces soaps and glycerol.

salts that surround a drop of oil and allow it to be soluble in water. (See Figure 18-4.) The action of soap is described in more detail in the “Making It Real” that follows.

**18-1.3 Steroids**

The largest class of **nonsaponifiable lipids** is the steroids. **Steroids** are lipids that contain a characteristic nucleus consisting of four fused cyclic carbon rings. The four-ring nucleus contains 17 carbon atoms, with each ring labeled A to D. The nucleus common to all steroids is present in cholesterol, testosterone, estrogen, and progesterone. Cholesterol is the most common steroid in the human body. Your body uses cholesterol to synthesize progesterone, which in turn is converted to testosterone. In women, testosterone is modified to produce estrogen. Figure 18-5 shows the similarities between the steroid nucleus, cholesterol, and the steroid hormones progesterone, testosterone, and estrogen, respectively.

From a dietary perspective, most people still consider fat to be a basic evil. In reality, your body needs, stores, and uses fat. Some unsaturated fatty acids are essential for health and must be ingested. However, fat contains the highest caloric value per gram of any biological molecule. The unfortunate repercussion of this high-energy content is that once your body stores fat, it is very difficult to burn it off. A more abundant and easier to utilize class of biological molecules is the carbohydrates.



**FIGURE 18-4 Formation of Micelles** The tail of a stearate ion is composed of a hydrocarbon that is nonpolar. The polar head group is ionic (polar). The micelle is a drop of oil with the nonpolar ends of the stearate ion inside the oil; the polar ends on the outside are attracted to polar water molecules.

**MAKING**  
**IT**  
**REAL**

### Soap—Dissolves Away Fat



The foam from soap is a result of micelles.

For how long have the parents of the world been trying to get their children to wash their hands and face with soap and water? Actually, we don't know. The history of soap is somewhat obscure. It was apparently used in ancient Babylon around 2800 B.C. to clean garments. However, the use of soap to cleanse the body was not mentioned until

about A.D. 200. Now soap and its synthetic cousins, detergents, are a necessary part of daily hygiene.

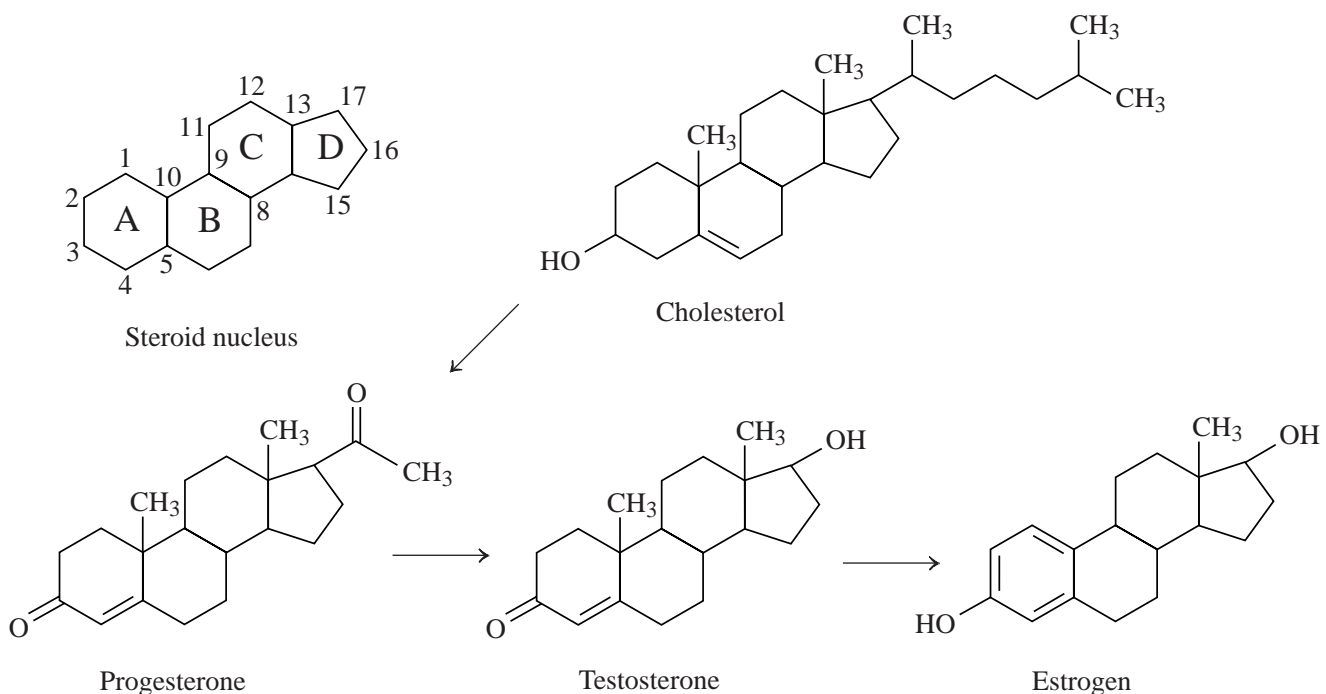
Soap was traditionally made by mixing animal fat with ashes of plants, which were a source of lye (sodium hydroxide). The chemical reaction produces soap (sodium stearate) and glycerin, a smooth, oily compound. Most soap originally made this way probably didn't smell very good and was quite harsh, as it still contained some lye. The use of perfumes, other additives, and controlled conditions now produce a gentler product.

A close look at the sodium stearate formula unit tells us how soap works. One end of the stearate anion is a long

chain of a hydrocarbon group (carbon and hydrogen). This end is essentially nonpolar. On the other end of the molecule is an ionic group that is highly polar.

Recall that nonpolar molecules dissolve in nonpolar liquids (e.g., oils) and ionic compounds dissolve in polar liquids (e.g.,  $H_2O$ ). Thus, the nonpolar end of this compound dislikes water (*hydrophobic*, or "water-fearing") but the other end is attracted to water (*hydrophilic*, or "water-loving"). When soapy water is in contact with an oil stain, the hydrophobic end dissolves in the oil and the hydrophilic end stays in contact with the water. Small drops of oil (called *micelles*) then break away and are suspended in the water because of their ionic charge. Since the micelles all have the same charge on the surface, they do not clump together. They stay suspended and can be rinsed away. (See Figure 18-4.)

One of the problems with ordinary soap is that it forms an insoluble compound with both  $Ca^{2+}$  and  $Mg^{2+}$ . These ions are present in "hard water," so a precipitate forms when soap is used in this water. This precipitate forms a soap scum, which is sometimes referred to as "bathtub ring." In 1946, Proctor and Gamble introduced Tide, the first synthetic detergent. Because the polar end of the fatty acid is enhanced, the solubility in water is increased, meaning that insoluble salts do not form.



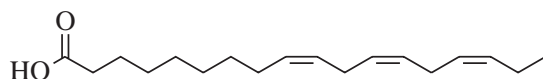
**FIGURE 18-5 Steroids** Steroids are nonsaponifiable lipids.

ASSESSING THE  
OBJECTIVE FOR  
SECTION 18-1

**EXERCISE 18-1(a) KNOWLEDGE:** Fill in the blanks.

When an alcohol and a carboxylic acid come together and water is lost, an \_\_\_\_\_ bond will form. The difference between a fat and an oil is that a fat is \_\_\_\_\_ at room temperature while an oil is \_\_\_\_\_. A saponifiable lipid contains an \_\_\_\_\_ linkage. A \_\_\_\_\_ is a cluster of fatty acid salts that surround a drop of oil and allow it to be soluble in water. Cholesterol is different from sphingolipids, glycolipids, and phospholipids because it is a \_\_\_\_\_ lipid.

**EXERCISE 18-1(b) ANALYSIS:** Identify the significant components of the following fatty acid.



**EXERCISE 18-1(c) ANALYSIS:** What are the products of the saponification of the fatty acid  $\text{CH}_3(\text{CH}_2)_{14}\text{COOC}_2\text{H}_5$ ?

**EXERCISE 18-1(d) SYNTHESIS:** The labels on many products say that they contain partially hydrogenated fatty acids yet also indicate that they have zero grams of trans fat. Do you think these products actually contain trans fat? Some products report the presence of mono- and diglycerides. What are those? Why can't a steroid be saponified?

*For additional practice, work chapter problems 18-1 and 18-3.*

## 18-2 CARBOHYDRATES

▶ OBJECTIVE FOR  
SECTION 18-2

Describe the different types of carbohydrates, their common properties, and their major uses or functions.



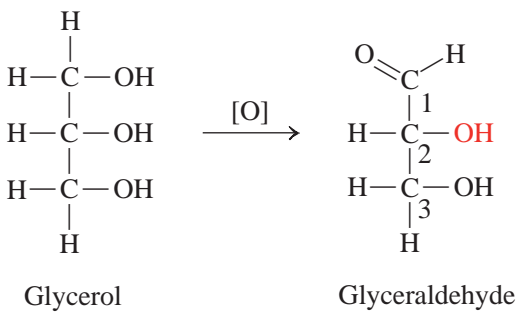
**LOOKING AHEAD!** An understanding of carbohydrates assumes a basic knowledge of the properties and chemistry of aldehydes ( $\text{R}-\text{CHO}$ ), ketones ( $\text{R}-\text{CO}-\text{R}'$ ), and alcohols ( $\text{R}-\text{OH}$ ). All of these functional groups contain oxygen, thus making simple carbohydrates polar molecules. Unlike lipids, carbohydrates are soluble in polar solvents like water. ■

## 18-2.1 Monosaccharides

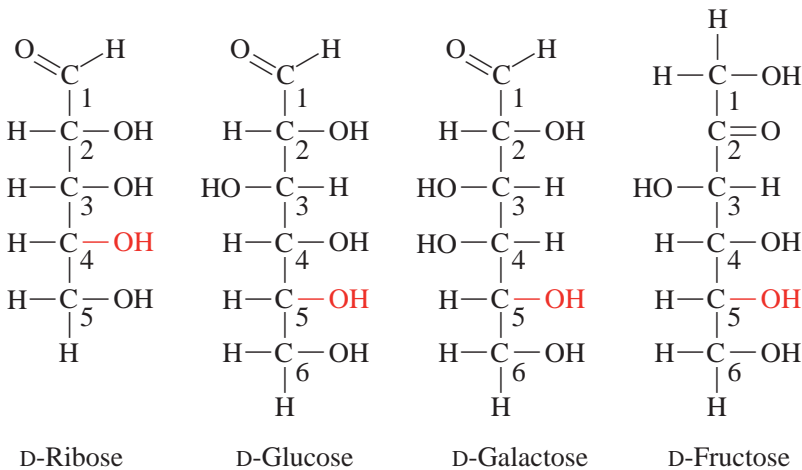
Carbohydrates are the most abundant biological molecules. They make up approximately 75% of all plant matter. **Carbohydrate** literally means “carbon and water.” In fact, many of them do have the empirical formula  $\text{C}_n(\text{H}_2\text{O})_n$ . Carbohydrates can be simple molecules or polymers containing multiple molecular units. Although they do not contain as much energy per gram as fats, carbohydrates are the most common source of energy for humans.

This section first discusses the monosaccharides, then the disaccharides, and finally the polysaccharides. An understanding of monosaccharides will help us understand carbohydrates in general. A **monosaccharide** is a polyhydroxy aldehyde or polyhydroxy ketone. If a monosaccharide contains an aldehyde group, it is referred to as an **aldose**. If it contains a ketone group, it is referred to as a **ketose**. The number of carbon atoms is also included in the name. A **pentose** sugar contains five carbon atoms and a **hexose** contains six.

The most important monosaccharides are glyceraldehyde, ribose, deoxyribose, glucose, galactose, and fructose. Glyceraldehyde is significant because it is the simplest of the sugars. If you refer to the previous section on fats, you will notice that a simple fat contains the alcohol glycerol. Oxidation of one of the alcohol groups



**FIGURE 18-6 Glyceraldehyde**  
Glyceraldehyde is an aldopentose.



**FIGURE 18-7 Common Monosaccharides** Common monosaccharides have special functions in the body.

of glycerol will yield glyceraldehyde.\* Your body is a magnificent machine in the simplicity by which it can convert a fat precursor into a simple sugar. Let's look further at glyceraldehyde. (See Figure 18-6.) The carbons are numbered from the top, which contains the aldehyde group, down to the bottom, which contains a  $\text{CH}_2\text{OH}$  group.

Ribose contains an aldehyde, four hydroxyl groups, and five total carbon atoms. Thus, it is referred to in a general sense as an aldopentose. The aldehyde group is written on the top, three hydroxyl groups on the right side of the chain, and a  $-\text{CH}_2\text{OH}$  group on the bottom. It does make a difference whether the OH group is written to the right or the left. When carbon has four different groups attached, two different orientations (isomers) in space are possible. These two isomers are called

*optical isomers* and differ from each other as your left hand differs from your right hand. In fact, the two isomers are labeled as D (for *dextro*, or "right-handed") and L (for *levo*, or "left-handed"). If we change the direction of an OH group from right to left or vice versa, we are actually indicating a separate optical isomer. Glucose is an aldohexose and fructose is a ketohexose. Figure 18-7 shows four other important monosaccharides. The D before each name refers to a specific optical isomer. There is also an L form of the isomer, but that form is not important in biochemical processes.

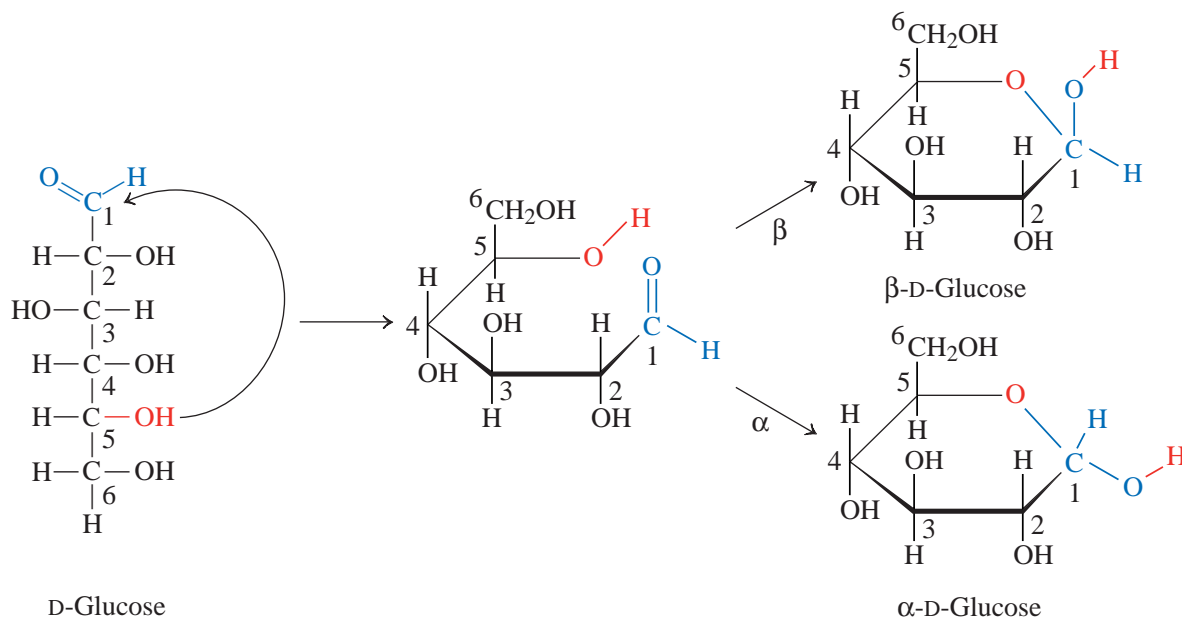
## 18-2.2 Ribose and Deoxyribose

Each of the monosaccharides in Figure 18-7 plays a significant role in biochemistry. Ribose is one of the essential building blocks for ribonucleic acid (RNA). If you replace the  $-\text{OH}$  on carbon 2 of ribose with an  $-\text{H}$ , you will get deoxyribose, which is an essential building block for deoxyribonucleic acid (DNA). These two nucleic acids, RNA and DNA, will be discussed later in this chapter. Glucose is an essential carbohydrate in humans. It is commonly referred to as either *dextrose*, *grape sugar*, or *blood sugar*. Much of the short-term energy available to humans is in the way of glucose. A proper glucose level in our bloodstream is essential to our health. Improper regulation of glucose by insulin is associated with diabetes. Fructose is an extraordinarily sweet sugar that gives many types of fruit their characteristic sweet taste.

Monosaccharides actually exist in aqueous solution mostly as cyclic compounds. For glucose, only about 2% exists in the straight-chain form like that shown in Figure 18-7. The remaining 98% is in the cyclic form. The straight-chain sugar converts to the cyclic form when the hydroxyl group in red (see Figure 18-8) forms a bond to the carbonyl carbon ( $\text{C}=\text{O}$ ) of the aldehyde or ketone. For ribose and fructose, the ring will contain five sides, including the oxygen of the hydroxyl; for glucose and galactose, the ring will contain six sides, including the oxygen of the hydroxyl. The formation of cyclic glucose is illustrated in Figure 18-8.

When a monosaccharide converts to the cyclic form, two different orientations are possible, but both are in equilibrium with the straight-chain form in aqueous solution. The two orientations are designated alpha ( $\alpha$ ) and beta ( $\beta$ ). Hydroxyl groups in the straight-chain depiction of a carbohydrate that are on the right side of the chain will appear down in the cyclic form of the carbohydrate. In the opposite manner, hydroxyl groups in the straight-chain depiction that are on the left side of the chain will appear up in the cyclic form of the carbohydrate.

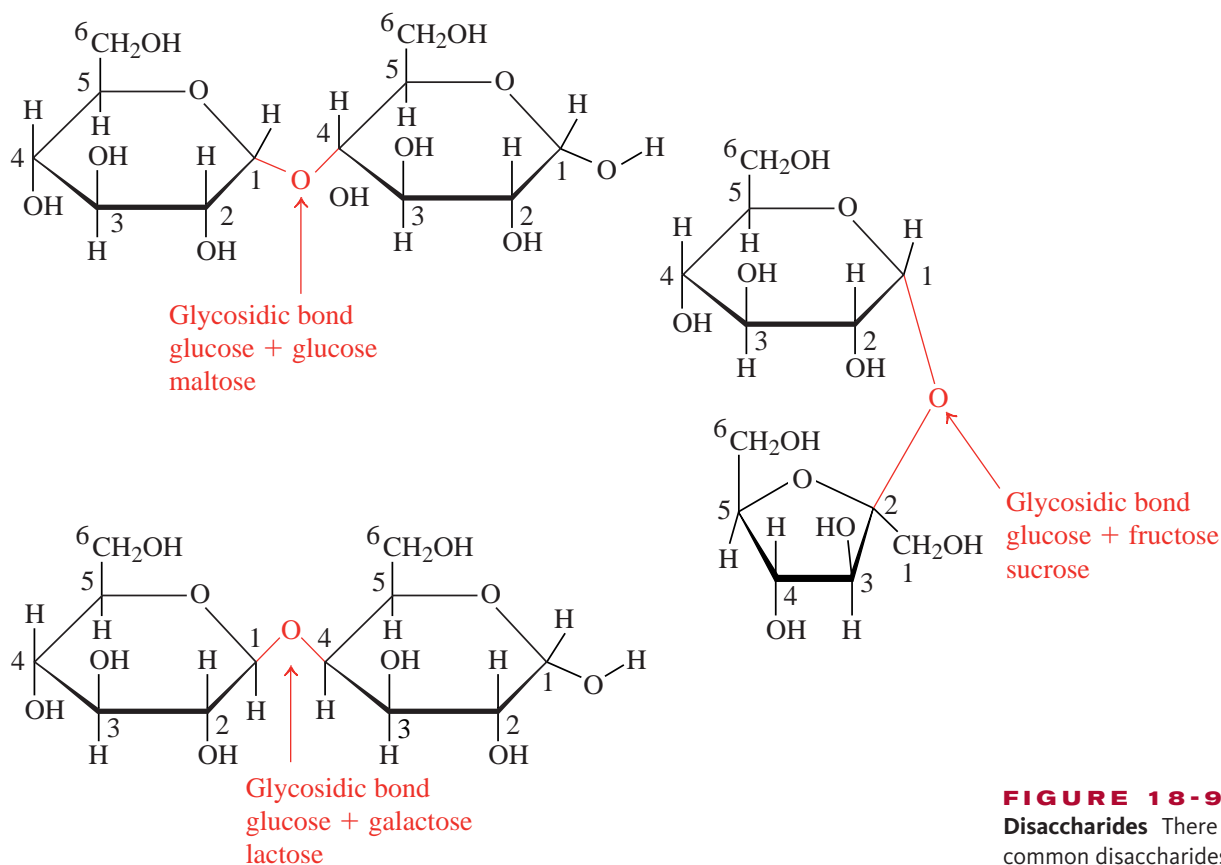
\* Oxidation is gain of oxygen or loss of hydrogen. In this case, it is the loss of hydrogen ( $\text{H}_2$ ) to make an aldehyde from an alcohol.



**FIGURE 18-8 Cyclic Glucose** The cyclic form of glucose is the more predominant.

### 18-2.3 Disaccharides

**Disaccharides** are made up of two cyclic monosaccharides connected with what is called a *glycoside bond*. A **glycoside bond** is an ether ( $C-O-C$ ) bond between two sugar molecules. The two monosaccharides condense together to form the glycoside bond and a water molecule. The three major disaccharides are sucrose (ordinary table sugar), which is composed of glucose and fructose; lactose (milk sugar), which is composed of glucose and galactose; and maltose, which contains two glucose units. Figure 18-9 shows the structures of the three disaccharides.



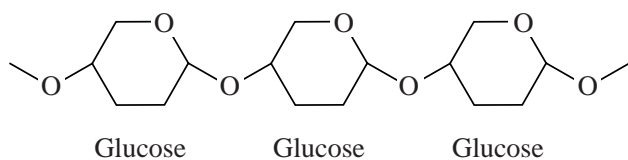
**FIGURE 18-9 Three Disaccharides** There are three common disaccharides.



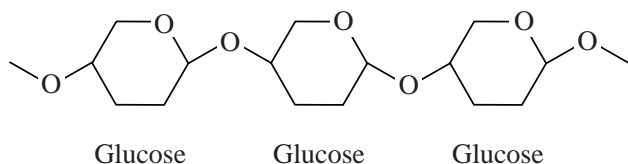
Disaccharides are not directly utilized by the body but must first be broken down to monosaccharides. Digestion of all three requires specific enzymes and an acidic environment (like in the stomach) to catalyze these reactions. Some infants have a rare disease known as galactosemia in which they lack the ability to metabolize galactose. It is a very serious disease and must be quickly identified so milk products can be avoided. Most babies are tested for this problem at birth. As we age, we sometimes lose the ability to metabolize lactose because of a shortage of lactase, the enzyme that breaks down lactose. This causes severe stomach distress. The good news is that pills and liquids containing lactase can be taken and one can enjoy a dish of ice cream.

### 18-2.4 Polysaccharides

**Polysaccharides** by definition are carbohydrates consisting of many monosaccharide-repeating units joined together by glycoside bonds. The three most commonly encountered polysaccharides are starch, glycogen, and cellulose. Starch is the primary energy-storage component in plants. It is made up of glucose molecules joined together by glycoside bonds in straight chains but also contains many polysaccharide branches. (See Figure 18-10.) Starch is typically much larger than glycogen—the energy-storage polysaccharide in animals. Glycogen is stored by humans in liver and muscle tissue. It has the same chemical composition as starch, but it is branched at more regular intervals. When your body requires more energy, glycogen is broken down to glucose, which can then be utilized in metabolism.



**FIGURE 18-10 Starch** Starch is a polymer of glucose.



**FIGURE 18-11 Cellulose** Cellulose is another polymer of glucose.

Cellulose is a structural component of many plants and is also made up exclusively of glucose units. The orientation of glycoside bonds is subtly different. (See Figure 18-11.) This difference is important, however. The enzyme that breaks down starch and glycogen does not work on cellulose, so animals are unable to digest cellulose. Certain types of animals called ruminants (e.g., cows) contain a bacteria in one of their stomachs that can break down cellulose into glucose so that they indirectly digest the cellulose in grass. For us, it forms what we call the bulk or fiber in our diet as it passes through undigested. In fact, most commercially available laxatives contain cellulose and cellulose derivatives. There is currently a great deal of research directed at synthetically breaking down cellulose into glucose units. Glucose could then be used to produce ethanol for fuel (called cellulosic ethanol). Instead of just using the starch in a kernel of corn, we could use the whole corn stalk, husk and all, to make ethanol. This would make the process much more economical and reduce dependence on fossil fuels.

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#### ASSESSING THE OBJECTIVE FOR SECTION 18-2

**EXERCISE 18-2(a) KNOWLEDGE:** Fill in the blanks.

Ribose would be considered an \_\_\_\_\_ because it has an aldehyde functional group, has five carbon atoms, and is a simple sugar. Maltose, lactose, and sucrose contain two monosaccharides held together by a \_\_\_\_\_ linkage. Starch and cellulose are both polymers of the monosaccharide \_\_\_\_\_.

**EXERCISE 18-2(b) ANALYSIS:** Glucose, fructose, and galactose are three monosaccharides that form three common disaccharides. Name the three disaccharides and the monosaccharides of which they are composed.

**EXERCISE 18-2(c) SYNTHESIS:** What is the difference between cellulose and starch? Why can't we digest cellulose and use its components for energy? Are starchy foods such as potatoes and pasta different from ordinary table sugar?

*For additional practice, work chapter problems 18-8, 18-13, and 18-14.*

## 18-3 AMINO ACIDS AND PROTEINS

## ▶ OBJECTIVES FOR SECTION 18-3

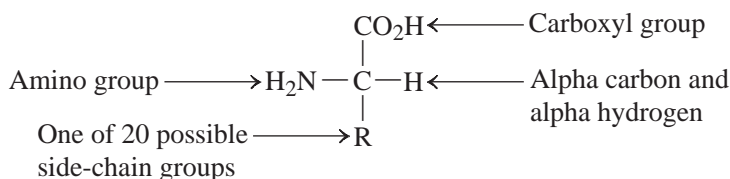
(a) Describe the different types of amino acids. (b) List and describe the four structures of proteins.



**LOOKING AHEAD!** A third type of important biological compound is known as an amino acid. In this section, we will examine the nature of amino acids, which form the building blocks of the polymers known as proteins. ■

## 18-3.1 Amino Acids

**Amino acids** are organic molecules that contain both an amino group ( $\text{—NH}_2$ ) and a carboxylic acid group ( $\text{—COOH}$ ). Although there are hundreds of known amino acids, proteins in humans are combinations of only 20 common amino acids. They are called alpha amino acids from the ancient Greek system of nomenclature that used the Greek letter alpha ( $\alpha$ ) to indicate the position *one removed* from the functional group. Thus, for amino acids, the amino group and the carboxyl group are removed from each other by one carbon atom, called the alpha carbon. In all 20 amino acids, the alpha carbon atom also has a hydrogen atom attached that is referred to as the alpha hydrogen atom. The difference between the 20 common amino acids is therefore the fourth group attached to the alpha carbon atom. This fourth group can be classified as either nonpolar, polar neutral, acidic, or basic. The generic structure of an amino acid is shown below.



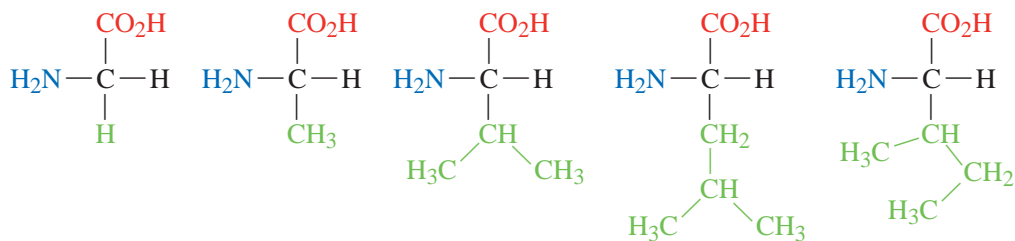
It is the  $\text{—R}$  group or side chain that designates whether the amino acid will be nonpolar, polar neutral, acidic, or basic. Figure 18-12 separates the 20 common amino acids into one of four main categories. There are eight amino acids that are known as *essential amino acids*. Our bodies cannot synthesize these amino acids from other amino acids, so they must be ingested. That is why protein is an essential part of our diet. In addition to the name, a three-letter and a one-letter symbol are included for each amino acid.

Since the alpha carbon has four different groups attached (except for glycine), these molecules form D and L optical isomers. Interestingly, life on this planet produces and metabolizes only the L-form of amino acids. There are a few rare examples of naturally occurring D-amino acids, but in general, plants and animals produce exclusively L-amino acids. The two isomers are represented in Figure 18-13a.

## 18-3.2 Dipeptides

As we learned in Chapter 17, alcohols and carboxylic acids react to form an ester linkage which was utilized in the formation of triglycerides. We also found that amines and carboxylic acids react to form the amide linkage and split off water. Thus one amino acid can link with another by means of an amide linkage. *In the case of the polymerization of amino acids, the amide linkage is referred to as a **peptide bond**.* In fact, proteins are made of repeating amino acid units linked by peptide bonds. *Two amino acids can link to form a **dipeptide**.* Actually, any two amino acids can link in two different ways depending on which amino acid has the  $\text{NH}_2$  (called the N-terminus) and which has the  $\text{COOH}$  (called the C-terminus). Therefore, if you write the amino group to the left and the carboxyl group to the right for two amino acids, the carboxyl group of one amino acid and the amino group of the next amino acid can form an amide bond (see Figure 18-13b). If the two were reversed, we would obtain a different dipeptide. In the case of glycine and valine forming a dipeptide, the two possibilities are

a. Nonpolar amino acids



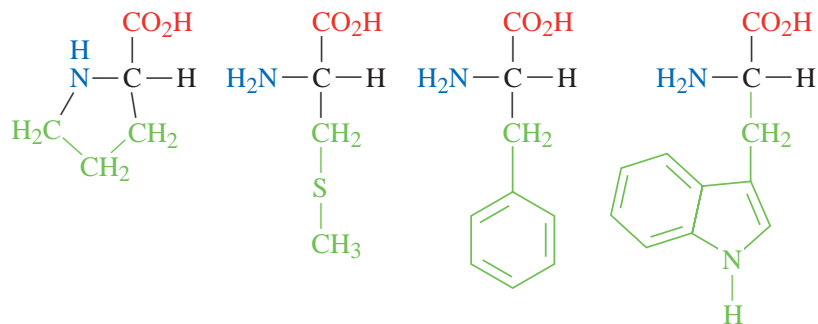
Glycine  
(Gly, G)

Alanine  
(Ala, A)

Valine  
(Val, V)

Leucine  
(Leu, L)

Isoleucine  
(Ile, I)



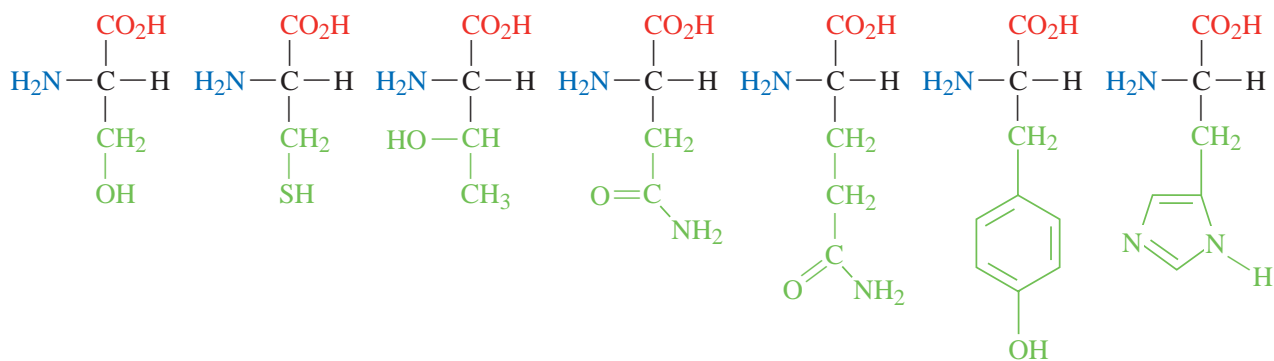
Proline  
(Pro, P)

Methionine  
(Met, M)

Phenylalanine  
(Phe, F)

Tryptophan  
(Trp, W)

b. Polar neutral amino acids



Serine  
(Ser, S)

Cysteine  
(Cys, C)

Threonine  
(Thr, T)

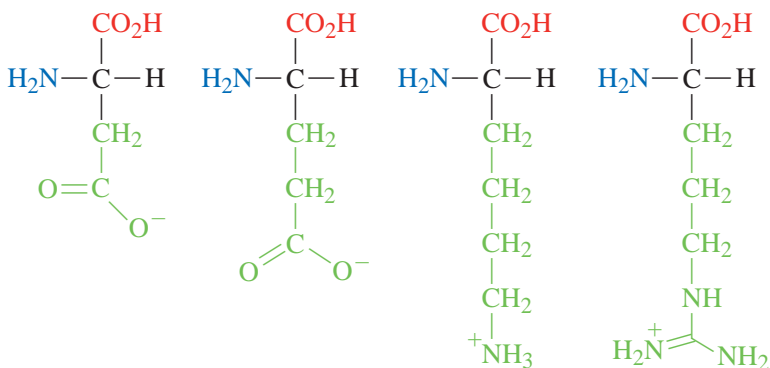
Asparagine  
(Asn, N)

Glutamine  
(Gln, Q)

Tyrosine  
(Tyr, Y)

Histidine  
(His, H)

c. Acidic and basic amino acids



Aspartic acid  
(Asp, D)

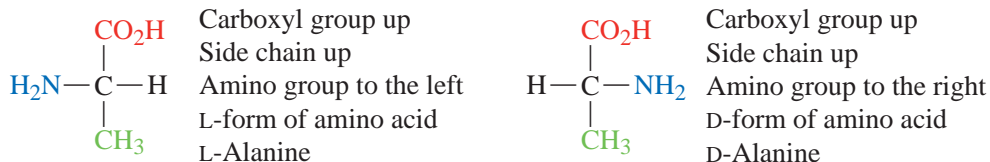
Glutamic acid  
(Glu, E)

Lysine  
(Lys, K)

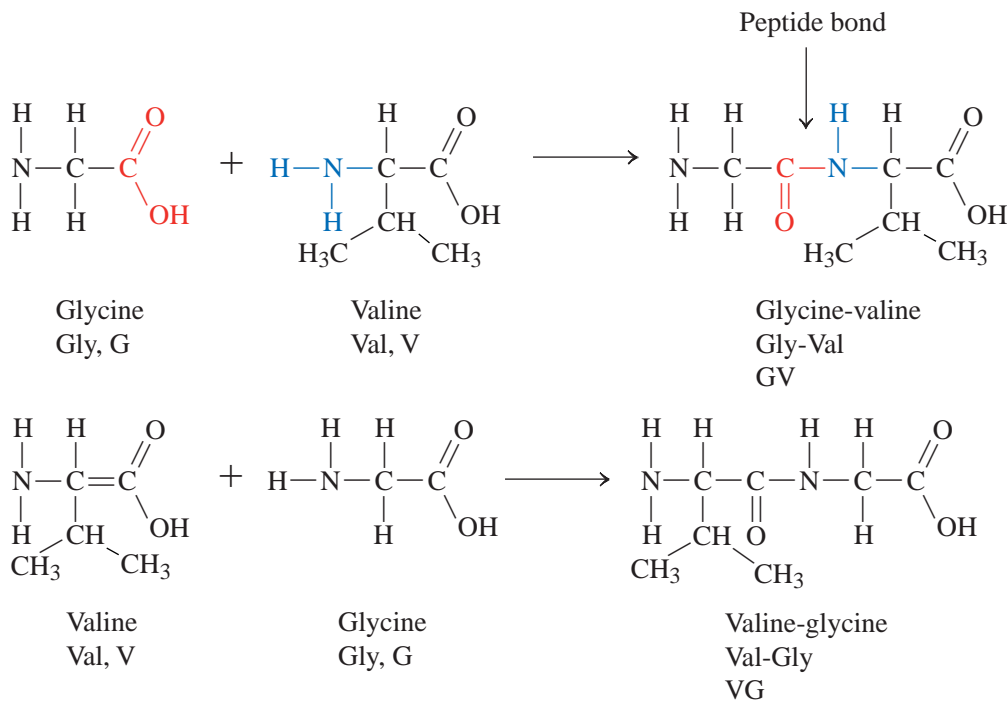
Arginine  
(Arg, R)

**FIGURE 18-12 Amino Acids** The 20 common amino acids.

## a. The D- and L-forms of alanine



## b. Glycine and valine joining to form a peptide bond



**FIGURE 18-13**  
**Optical Isomers and**  
**Dipeptides** (a) Two optical isomers of an amino acid. (b) Two dipeptides formed from two amino acids.

written as Gly-Val, or simply GV. It is inferred from the name GV that the glycine is the N-terminus and the Valine is the C-terminus. The other possible dipeptide would be labeled VG.

### 18-3.3 Proteins

A **protein** is a biological polymer made of repeating amino acid monomer units linked together by peptide bonds. The functions of proteins include structure, catalysis, movement, transport, hormones, protection, storage, and regulation.

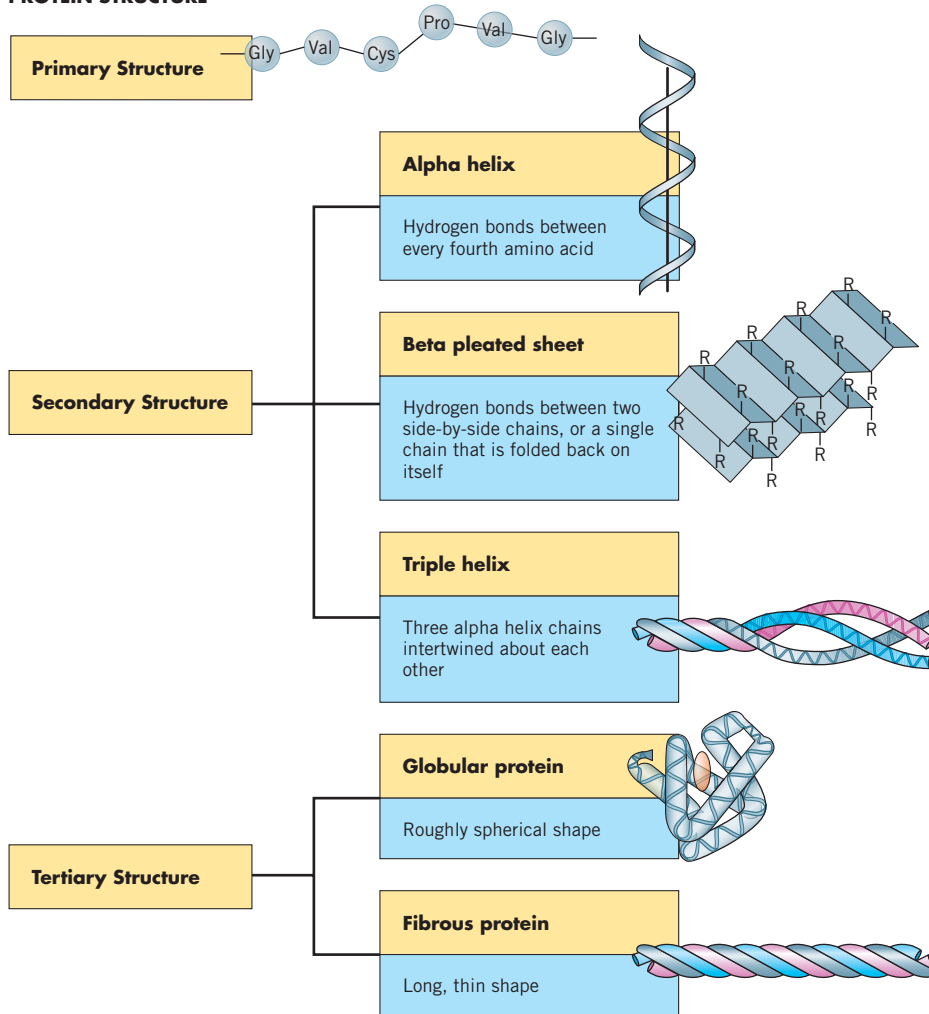
From Figure 18-13b, you can see that the dipeptide begins with the amino group. As the length of the peptide grows, one end is the N-terminus. The growing polymer chain always ends with the C-terminus. This carboxyl group can then bind to additional amino acids to eventually form a complete protein containing thousands of amino acid units.

There are three levels of protein structure that we will discuss. These structures are referred to as primary ( $1^\circ$ ), secondary ( $2^\circ$ ), and tertiary ( $3^\circ$ ) structures.

A protein is just an extension of the simpler case of the dipeptide. The primary structure of a protein ( $1^\circ$ ) refers to the order of amino acids in the polymer. It always begins with the N-terminus and concludes with the C-terminus. The order of amino acids is as specific to the protein as are the letters to a word. For example, a sequence of four amino acids could be GVAG.

The secondary structure of a protein ( $2^\circ$ ) refers to the backbone interactions. If you think of a series of amino acids linked together, the one thing that is consistent is the repeating peptide bonds. These peptide bonds in combination with the alpha carbon

## PROTEIN STRUCTURE



**FIGURE 18-14** Levels of Protein Structure Proteins have secondary and tertiary structures.

another segment of the protein. The hydrogen bonds form between the layers of the sheet, and the side chains alternate between inside the two chains to outside the chains. The triple helix is a combination of three  $\alpha$ -helices that are wound around each other to create an elastic cordlike formation comparable to a length of twine. The elasticity and strength of the triple-helix structure explains why it is a major component of skin in the form of collagen and connective tissue like that of ligaments.

The tertiary structure of a protein ( $3^\circ$ ) is the overall structure. Proteins typically have a tertiary structure that is either globular or fibrous. **Globular proteins** are roughly spherical in shape, comparable to unmolded, uncooked pizza dough. **Fibrous proteins** have a long, thin, rodlike shape. The factors that establish tertiary structure are the side-chain interactions of the amino acids. Recall from Figure 18-12 that the four classes of amino acid side chains are nonpolar, polar neutral, acidic, and basic. The nonpolar amino acid side chains will be attracted to one another by London forces. In biochemistry, this interaction is referred to as a hydrophobic interaction. In the same manner that like dissolves like, amino acid side chains that are hydrophobic will be attracted to other hydrophobic amino acids. The polar-neutral amino acids are polar because they contain either a hydrogen bond acceptor (O or N) or a hydrogen bond donor (H). Thus, the interactions that exist between the polar-neutral amino acids are hydrogen bonds. Acidic and basic amino acids at neutral pH will have a negative and positive charge, respectively. The saying that “opposite charges attract” is especially true in this type of interaction, known as electrostatic attraction. The fourth and strongest of the interactions that stabilize the tertiary structure of a protein is known as a disulfide bond. Disulfide bonds are covalent bonds that form between two cysteine amino

atom make up the backbone of the protein. The components of the peptide bonds are the elements HONC. The C=O portion of the peptide bond can serve as a hydrogen bond acceptor and the N—H portion of the peptide bond can serve as a hydrogen bond donor. Thus, the hydrogen-bonding interactions between the peptide bonds of a protein are responsible for what is called the secondary structure of the protein. This can occur in three different ways. The  $\alpha$ -helix has the N—H of one peptide bond hydrogen bonding to the C=O of a peptide bond that is four amino acids farther down the chain. A repeating pattern of this nature results in a helical formation that looks like a phone cord. All the side chains are oriented out from the core of the helix, and all the hydrogen-bonding interactions are parallel to the center of the coil. (See Figure 18-14.) The  $\beta$ -pleated sheet is an arrangement that is like the top sheet on your bed. The peptide chain folds back upon itself, allowing the peptide bonds of one stretch of the protein to be within hydrogen-bonding distance of the peptide bonds of



acids. Reduction of the thiol group of the cysteine results in a sulfur-to-sulfur covalent bond between the two side chains of two different cysteines. Ways to think of the many levels of protein structure can be seen in Figure 18-14.

**ASSESSING THE  
OBJECTIVES FOR  
SECTION 18-3**

**EXERCISE 18-3(a) KNOWLEDGE:** Fill in the blanks.

The four classes of amino acids are \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_. The three types of protein secondary structure are \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_. Hydrophobic interactions, electrostatic attraction, hydrogen bonding, and disulfide bonds are involved in stabilizing the \_\_\_\_\_ structure of a protein.

**EXERCISE 18-3(b) ANALYSIS:** Classify the following side chains on amino acids as nonpolar, polar neutral, acidic, or basic.

- (a)  $-\text{CH}_2\text{CH}_2\text{NH}_2$                       (c)  $-\text{CH}_2\text{CH}_2\text{OH}$   
(b)  $-\text{CH}_2\text{CH}_2\text{CH}_3$                       (d)  $-\text{CH}_2\text{CH}_2\text{COOH}$

**EXERCISE 18-3(c) SYNTHESIS:** Show the structure of a protein that has the sequence GAT. How many other possible proteins could be made from these three amino acids?

*For additional practice, work chapter problems 18-18 and 18-23.*

**PART A  
SUMMARY**

**KEY TERMS**

- 18-1.1** Fats are also known as **lipids**. **Saponifiable lipids** contain the ester group and include **triglycerides**, which are composed of glycerol and three **fatty acid** groups. p. w-44
- 18-1.2** Complex lipids include **sphingolipids**, **glycolipids**, and **phospholipids**. **Cerebroside** is an important glycolipid, and **phosphatidylcholine** is an important phospholipid. p. w-45
- 18-1.2** The process of **saponification** involves breaking the ester bond to form an alcohol and the salt of a fatty acid known as a soap. **Micelles** solubilize fats in water. p. w-46
- 18-1.3** **Steroids** are **nonsaponifiable lipids**. p. w-47
- 18-2.1** A **monosaccharide** is one **carbohydrate** molecule. It may be either an **aldose** or a **ketose** as well as a **pentose** or a **hexose** carbohydrate. p. w-49
- 18-2.3** A **disaccharide** contains two carbohydrate units joined by a **glycoside bond**. p. w-51
- 18-2.4** A **polysaccharide** is a polymer containing multiple carbohydrate units. p. w-52
- 18-3.1** An **amino acid** contains both a carboxylic acid and an amine group. p. w-53
- 18-3.2** A **dipeptide** contains two amino acid molecules joined by a **peptide bond**. p. w-53
- 18-3.3** A **protein** is a polymer containing multiple amino acid groups. p. w-55
- 18-3.3** The tertiary structure of a protein may be either a **globular** or a **fibrous protein**. p. w-56

**SUMMARY CHARTS**

*Three Basic Biological Substances*

|               |                 |   |
|---------------|-----------------|---|
| Fats (lipids) | Saponifiable    | Triglycerides                               |
|               | Nonsaponifiable | Complex lipids                              |
|               | Monosaccharides | Steroids                                    |
| Carbohydrates | Monosaccharides | Aldose and ketose sugars                    |
|               | Disaccharides   | Pentose and hexose sugars                   |
|               | Polysaccharides | Sucrose, maltose, fructose                  |
| Amino acids   | Monomers        | Glycogen, starch, cellulose                 |
|               | Dipeptides      | Nonpolar, polar neutral, acidic, basic      |
|               | Proteins        | Two sequences                               |
|               |                 | Primary, secondary, and tertiary structures |

*Three Levels of Protein Structure*

- 1° structure: amino acid sequence
- 2° structure:  $\alpha$ -helix,  $\beta$ -pleated sheet, triple helix
- 3° structure: four major interactions—hydrophobic, hydrogen bonding, electrostatic, disulfide bond

**PART B**  
**BIOCHEMICAL COMPOUNDS**  
**AND LIFE FUNCTIONS**
**SETTING A GOAL**

- You will learn how the three basic types of biological molecules contribute to the complex molecules of life itself.

**OBJECTIVES**

- 18-4** Describe the effects of conditions on enzymes and how they function.
- 18-5 (a)** Describe the structure of DNA and RNA and the attractions between base pairs. **(b)** Describe the process of replication and transcription.

**▶ OBJECTIVE FOR SECTION 18-4**

Describe the effects of conditions on enzymes and how they function.

## 18-4 ENZYMES



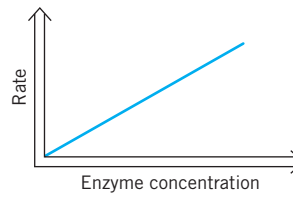
**LOOKING AHEAD!** Every process in your body is regulated and made possible by the activity of enzymes. Enzymes can be thought of as the worker bees that keep the hive alive. The enzymes that we will discuss are all proteins with primary, secondary, and tertiary structures, as discussed in the previous section. ■

An **enzyme** is a protein that is used to catalyze biological reactions. It is a protein with a purpose. Recall that a catalyst is a substance that lowers the activation energy of a reaction, allowing it to occur more easily, but does not get used up in the reaction. If you think of your body as a huge factory, the enzymes would be the workers that make the factory operational. Your body is in the business of taking in raw materials in the way of food and beverages; breaking down the complex fats, carbohydrates, and proteins into simpler units; and then making necessary immediate energy while converting any excess into appropriate storage molecules. Consider for a moment working conditions for your factory employees. Under ideal conditions you will get the most from your workers. In the case of the enzymes in your body, the ideal work environment is dependent on pH, the concentration of the enzyme, the concentration of the reacting compound, and temperature.

### 18-4.1 The Effects of Conditions on Enzymes

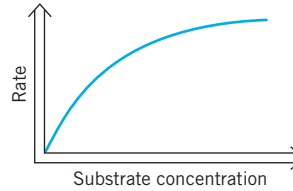
To understand the significance of these dependencies, recall that enzymes are proteins and that hydrophobic interactions, hydrogen bonding, electrostatic attraction, and disulfide bonds stabilize the tertiary structure of the protein. Thus, a significant change in pH will cause dramatic impacts on the ability of amino acid side chains to hydrogen bond and may even alter the electrostatic attraction between basic and acidic side chains. There will be a point at which an enzyme will function at its maximum capacity to catalyze a biological reaction. This point is referred to as the optimal pH. Through evolution, your body has adapted to provide enzymes an optimal environment for activity. Your mouth has a pH of around 5; blood, 7.4; urine, 6.2; stomach, 2; and intestines, 8. It is not by chance that these various parts of the body are so drastically different in pH.

With regard to enzyme concentration, there is a linear relationship between reaction rate and the amount of enzyme present. (See Figure 18-15a.) More products will be produced over the same amount of time as the amount of enzyme in a system is increased. It is not that the reaction occurs faster in a single isolated case but rather that there are more enzymes causing the reaction to be catalyzed at the same time. If there is a limited amount of enzyme, then it is the amount of substrate (the biological molecule being acted on by the enzyme) that determines the rate of the reaction. As the level of substrate is increased, the rate of the reaction will increase until the enzyme cannot go any faster. At this point, the reaction rate levels off. The saturation point is reached when the concentration of substrate is in excess and the enzyme cannot catalyze the reaction any faster. (See Figure 18-15b.) The final factor that affects enzyme activity is temperature. If you consider that atoms move faster as temperature increases, it is reasonable to conclude that every layer of secondary and tertiary structure will be destroyed by excessive heat. *The process by which excessive heat destroys the secondary and tertiary structure of a protein or enzyme is known as denaturation.* As with pH, enzymes function best at a certain temperature known as the optimal temperature. (See Figure 18-15c.) The optimal temperature for humans is approximately 37°C, or 98.6°F. If this temperature is increased substantially, as in the case of heat stroke, your body can be shut down and loss of consciousness may result.



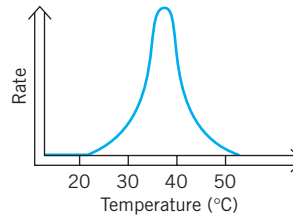
(a) The effect of enzyme concentration

As the enzyme concentration increases, the activity increases.



(b) The effect of substrate concentration

As the substrate concentration increases, the activity increases but levels off at high concentrations.



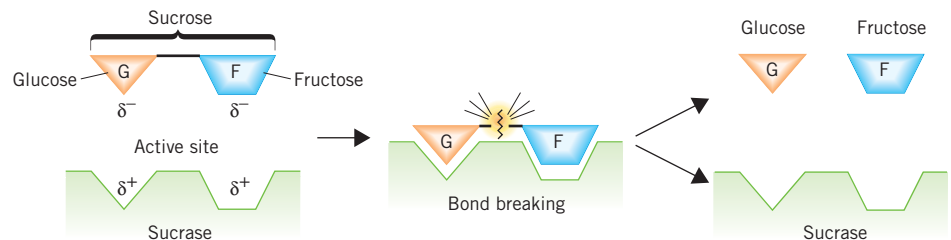
(c) The effect of temperature

There is a narrow range of temperature where activity occurs.

**FIGURE 18-15 Summary of Enzyme Activity** (a) The effect of enzyme concentration, (b) the effect of substrate concentration, and (c) the effect of temperature.

### 18-4.2 The Mechanism of Enzyme Activity

This discussion of factors affecting enzyme activity has left out one very important piece of information. How do enzymes function? At an introductory level, we will focus on one primary model of enzyme activity. *The lock-and-key model explains the specificity of an enzyme by comparing the enzyme active site to a lock and the substrate to a key specific for that lock.* The active site of an enzyme is the portion of the enzyme where catalysis occurs. The substrate is the reactant in a biological reaction that is modified in the presence of an enzyme to produce a product consistent with the enzyme function. An example



**FIGURE 18-16 Lock-and-Key Model** Enzymes catalyze the dissociation of a disaccharide into its two component monosaccharides.

of this would be the enzyme sucrase, mentioned in Section 18-2. Sucrase is an enzyme that will specifically catalyze the breaking of the ether bond in the disaccharide sucrose to produce D-fructose and D-glucose. In this reaction the enzyme is sucrase, the substrate is sucrose, and the products are D-fructose and D-glucose. This enzyme is specific for sucrose and will not catalyze the hydrolysis of any other substrate. (See Figure 18-16.)

#### EXERCISE 18-4(a) KNOWLEDGE: Fill in the blanks.

An enzyme is a \_\_\_\_\_ that serves as a \_\_\_\_\_ for bodily functions. The molecule that the enzyme works on is known as a \_\_\_\_\_. Enzymes in the body function at an optimal \_\_\_\_\_, \_\_\_\_\_, and substrate \_\_\_\_\_. The theory of how enzymes work is known as the \_\_\_\_\_ and-\_\_\_\_\_ model. This works on the \_\_\_\_\_ site of the substrate.

**ASSESSING THE OBJECTIVE FOR SECTION 18-4**

**EXERCISE 18-4(b) ANALYSIS:** The rate of chemical reactions increases as the temperature increases except for enzyme reactions. Why?

**EXERCISE 18-4(c) SYNTHESIS:** As the amount of CO<sub>2</sub> increases in the atmosphere, the pH of the oceans is decreasing. Why is this of environmental concern?

For additional practice, work chapter problems 18-24 and 18-25.

▶ **OBJECTIVES FOR SECTION 18-5**

(a) Describe the structure of DNA and RNA and the attractions between base pairs. (b) Describe the process of replication and transcription.

## 18-5 NUCLEIC ACIDS AND GENETICS



**LOOKING AHEAD!** In the past 60 years the amount of information that has become available about the chemistry of life has been phenomenal. The blueprint for our whole bodies is found in a huge, complex molecule known as DNA. How our DNA differs from that of chickens and how we differ from each other is now yielding to scientific research. We begin with the study of the polymers known as nucleic acids. ■

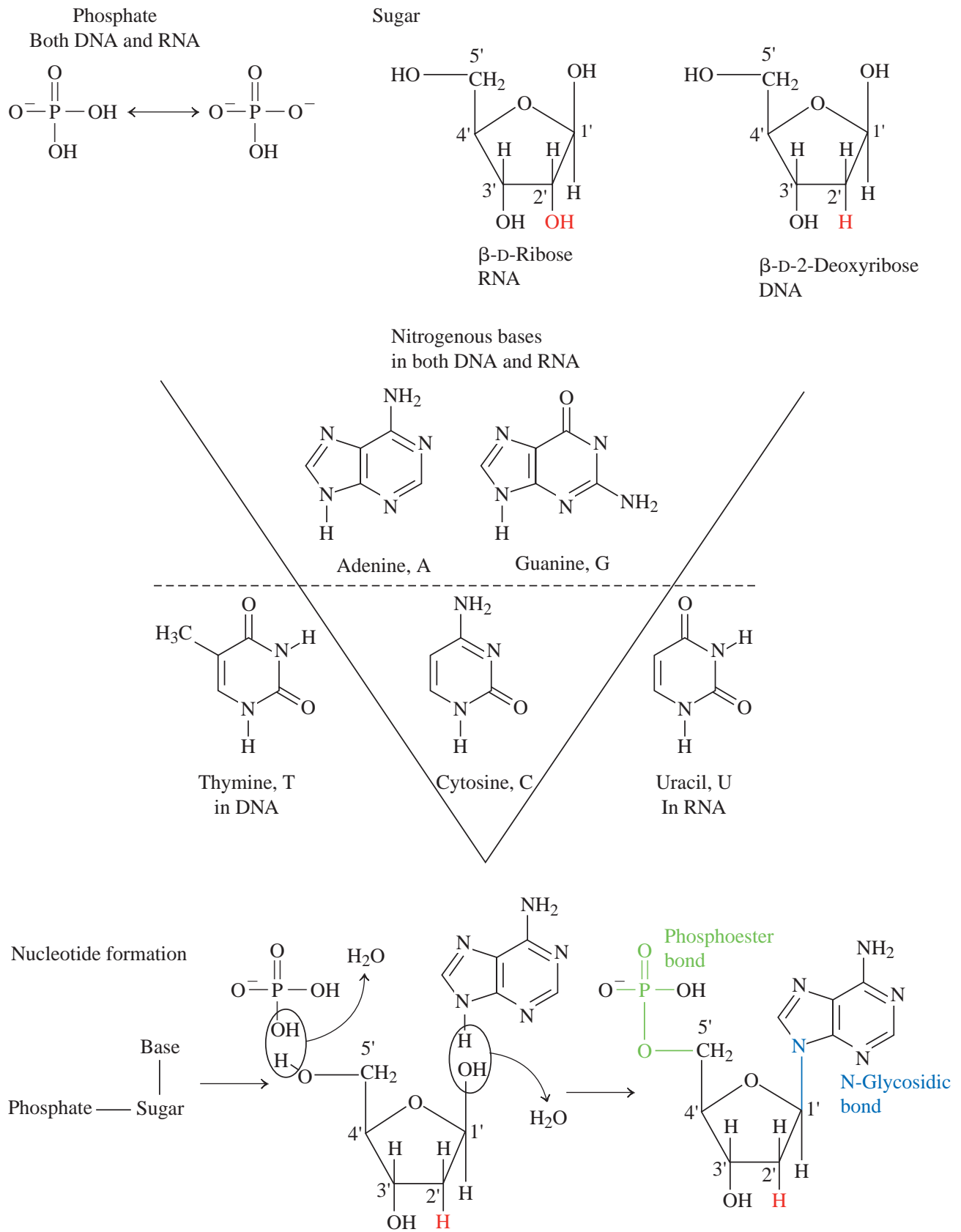
### 18-5.1 The Structure of DNA and RNA

A single DNA molecule in your body carries all of the genetic information for you as a unique individual as well as the code of the whole human race. This genetic code is contained in about 3 billion bits of information called base pairs. In 1990, the Human Genome Project was launched at a projected cost of \$250 million to sequence and record the complete order of these base pairs. In 2003, it was announced that the project was essentially finished, although there are still areas that have not been completed. We have already explored the depth of space but know we have just now deciphered the blueprint of a human being. The possibilities in curing and preventing diseases that are promised by this research are enormous. The story of this project began over 50 years ago with the discovery by Watson and Crick of the structure of the DNA molecule.

A **nucleic acid** is a biological polymer where the repeating monomer units are nucleotides. A **nucleotide** is a molecule consisting of a negatively charged phosphate, a pentose sugar, and a nitrogen-containing base. There are two types of nucleic acids, DNA and RNA. **Deoxyribonucleic acid (DNA)** is a nucleic acid where the nucleotides are made up of a negatively charged phosphate; the pentose sugar deoxyribose; and the nitrogen-containing bases adenine, guanine, thymine, and cytosine. DNA carries the hereditary information necessary for life. **Ribonucleic acid (RNA)** is a nucleic acid where the nucleotides are made up of a negatively charged phosphate; the pentose sugar ribose; and the nitrogen-containing bases adenine, guanine, uracil, and cytosine. (See Figure 18-17.)

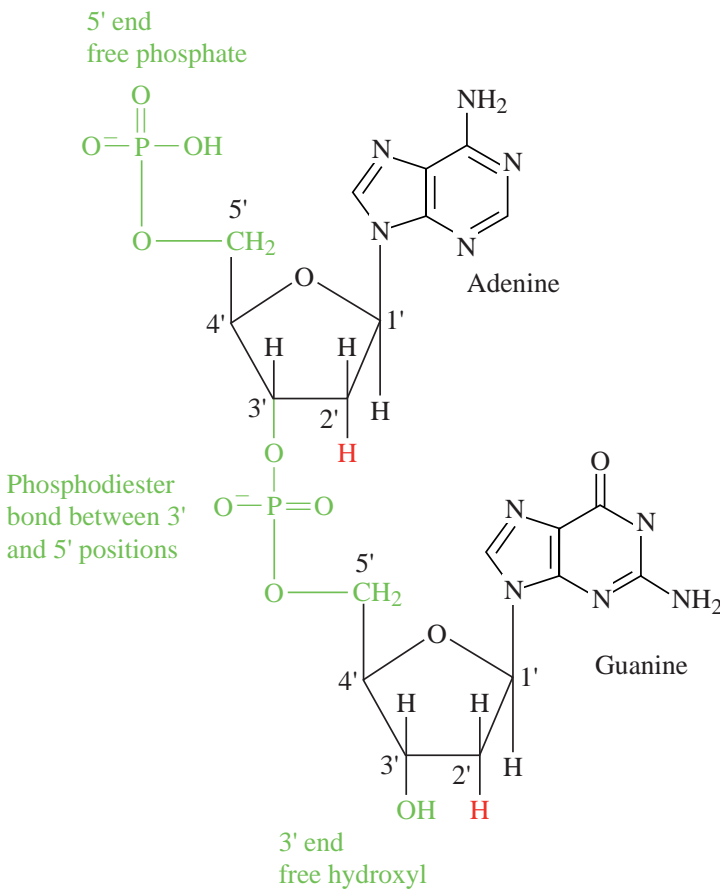
In the polymeric structure of DNA and RNA, the phosphate groups link two sugar molecules, each of which is attached to one of the nitrogen bases, as shown at the top in Figure 18-17a. In Figure 18-18 two actual bases in a sequence are shown. The phosphate at the top could bond to another sugar molecule, and the OH on the sugar at the bottom could bond to another phosphate to extend the DNA molecule in both directions. The alternating sugars and phosphates make up the backbone of the nucleic acids.

Recalling that the overall structure of a protein is predominantly dictated by the side-chain interactions, it is not too surprising that the nitrogen-containing bases play a significant role in the overall structure of the nucleic acids. An early discovery found that the chemical composition of DNA consisted of equal amounts of adenine and thymine. It was also discovered that the amount of cytosine and the amount of guanine are also always the same. It was not until Watson and Crick proposed the double-helical nature of DNA in 1953 that the secondary structure of DNA became clear. Watson and Crick discovered that the configuration for DNA was a double strand (i.e., a double helix) held together by hydrogen bonds. It was found that each one of the

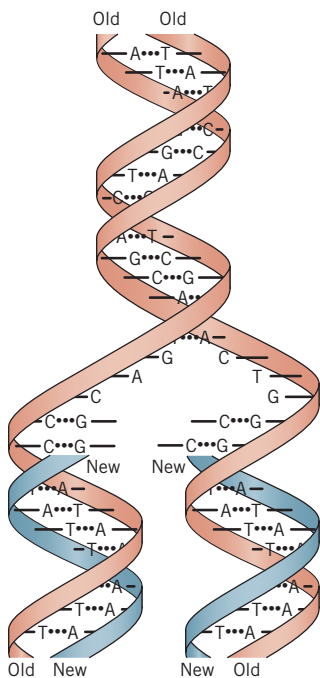


**FIGURE 18-17 The Structure and Components of Nucleotides** Nucleic acids are composed of phosphate, sugar, and nitrogenous bases.





**FIGURE 18-18** The Structure and Base Pairing in DNA  
Adenine and guanine can form two units of a strand of DNA.



**FIGURE 18-19** DNA and Replication  
DNA can unravel and the two strands can then form complementary copies of themselves.

four bases specifically hydrogen bonds with only one other. The bases adenine and thymine hydrogen bond to one another and the bases cytosine and guanine hydrogen bond to one another. These bonding partners are known as *complementary base pairs*. In the top part of Figure 18-19, the double helix of DNA is shown along with the base interactions between the two strands.

RNA has uracil as a base instead of thymine, as in DNA. Also, unlike DNA, RNA is composed of a single strand. The reason for this will make more sense once we gain a perspective on what biological role each nucleic acid plays. DNA contains all the hereditary information necessary for life. On a cellular level, this information is housed in the nucleus. DNA, as it exists in the nucleus of a cell, is wrapped around positively charged proteins called *histones*. A **chromosome** is the complex formed between the long DNA strand and the histones.

### 18-5.2 Replication of DNA

DNA can either replicate itself or have segments of information read and interpreted by RNA. **Replication** is the process by which DNA produces two identical copies of itself. In this process, specific enzymes unwind the DNA double helix to expose two single strands of nucleotides. A complementary strand for each of the two strands can then be constructed from free nucleotides, phosphates, and sugar molecules. When this happens, other enzymes link the free nucleotides

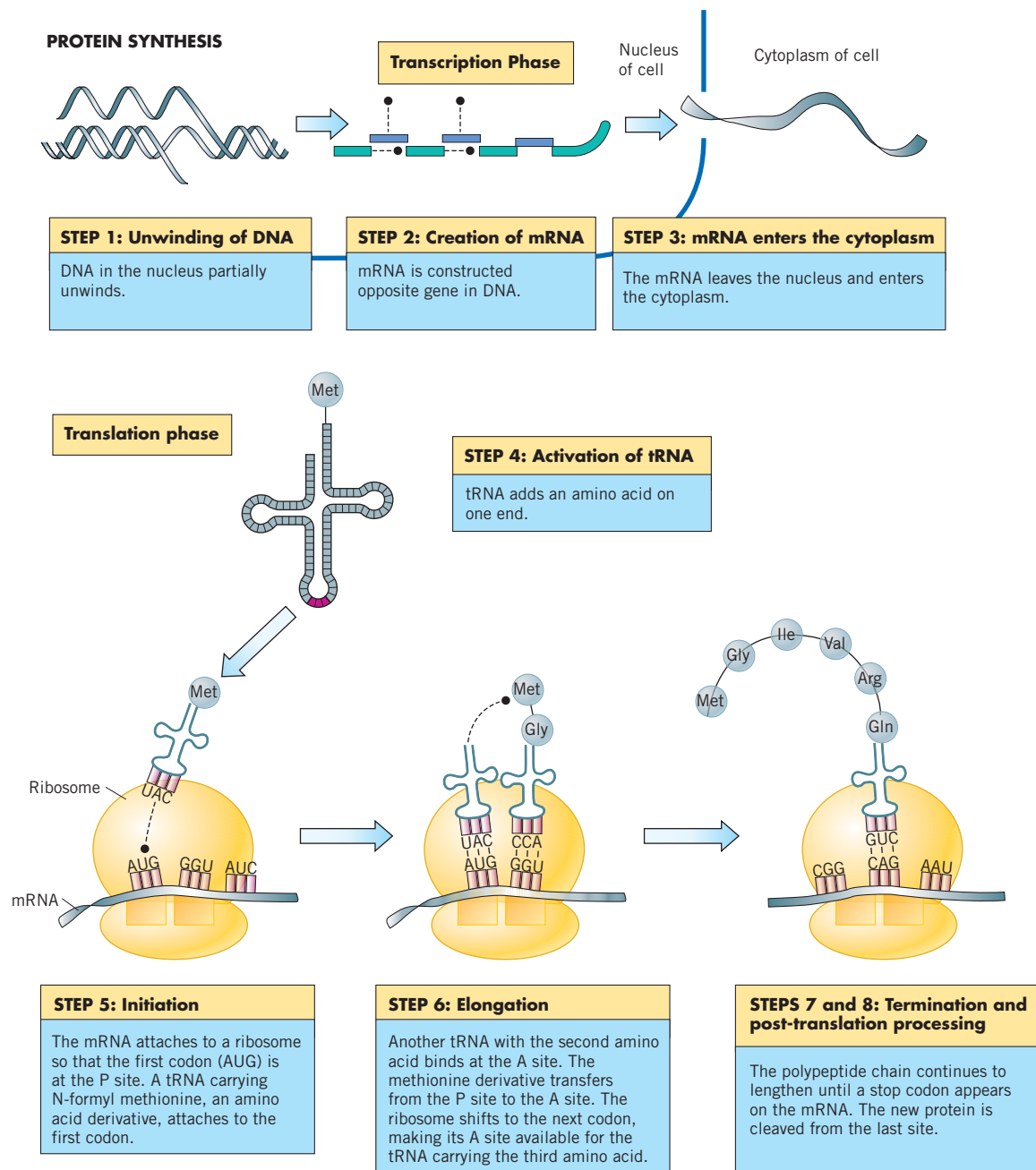
together to form new strands of nucleic acids. This entire process involving the enzymes and free nucleotides results in one parent strand of DNA forming two identical daughter strands of DNA. (See Figure 18-19.) Thus, the full genetic code in the DNA is exactly replicated. When you think of a developing child growing at an astronomical rate, consider that DNA replication is responsible for every new cell produced.

In order for our body to maintain a system that is in equilibrium, we require a regulatory mechanism. The enzymes in our body are the factory workers that keep our productivity where it needs to be. The more work we demand of our body, the more enzymes are produced to catalyze the biological reactions that generate the energy to maintain a healthy working system. DNA contains all the information necessary to make all the enzymes in your body.

### 18-5.3 Transcription and Translation

**Transcription** is the process by which a segment of DNA is copied by the formation of an RNA molecule that is eventually used for the synthesis of an enzyme or protein. The portion of the DNA that contains the specific nucleotide sequence is known as a **gene**. A gene contains the appropriate sequence of bases that codes for a specific protein. An enzyme causes the DNA to partially unwind, exposing the gene. The gene even has a sequence of bases that tells where the transcription begins and where it ends. **Messenger RNA (mRNA)** is constructed with a sequence of bases that are complementary to the gene. If you think of this in terms of cooking, DNA is like the master cookbook. The recipe in the cookbook is comparable to a gene on a chromosome. When we consult a cookbook, we transcribe the recipe to a piece of paper to use for the day. In the case of genes, information on the strand of DNA is transferred in the process called transcription.

**Translation** is the process by which two other types of RNA, **transfer RNA (tRNA)** and **ribosomal RNA (rRNA)**, in combination with proteins provide the site for protein synthesis. The mRNA travels from the nucleus out of the cell to the ribosomes. **Ribosomes** are made of proteins and rRNA. The ribosomes provide the site for protein synthesis. When mRNA attaches to the ribosome, the tRNA goes to work. This molecule uses a three-nucleotide code on one end (called a *codon*) and attaches to a specific amino acid on the other. It latches on to the three complementary bases on the mRNA, and an enzyme then forms a peptide bond with an adjacent amino acid held in place by another tRNA molecule. Amino acid by amino acid, eventually a complete protein with a specific primary structure is constructed. It is then cleaved from the ribosome and assumes its secondary and tertiary structures. It is now ready to go to work doing something important in our bodies. (See Figure 18-20.)



**FIGURE 18-20** Summary of Transcription and Translation.

Our DNA has all of the codes and information that describes us as human beings. Yet our individual DNA molecules are slightly different from anyone else's—except for identical twins, whose DNA is the same. Thus, we can be unambiguously identified by the sequence of bases in our individual DNA. The sequencing of DNA has become an important tool in identification of individuals in criminal cases and in identifying biological parents.

An understanding of the processes involved in protein production and DNA replication has led to cures for many common diseases. It promises to help researchers put an end to multiple sclerosis, Parkinson's disease, cancer, AIDS, diabetes, and many other ailments in the not-too-distant future.



## The Origin of Life



A simulation photo of ancient Earth with volcanoes, oceans, and bare land.

Somehow, somewhere, billions of years ago, the atoms of certain elements assembled themselves into a unique and spectacular compound. This compound did what no other compound could do. It was able to construct duplicates of itself from the ingredients of simpler compounds. This is what origin-of-life scientists refer to as *genesis*. From this start, the complex process that we call life eventually evolved.

At this time, researchers in this area still can't decide how

life began. Was it an unusual quirk present only on our planet, or is it a common feature of the entire universe? Life, as we know it, requires two basic ingredients: proteins and nucleic acids. However, we need the complex proteins of life to make nucleic acids, and vice versa. So which came first? Consider also that nucleic acids require the element phosphorus. But phosphorus was only present in the earth in minerals as highly insoluble calcium phosphate. So how did it originally get into a more soluble form so that it could be part of living cells? These are still some of the mysteries of the origin of life.

Some of the raw materials for life seem to be more plentiful in the universe than previously thought, however. Recent discoveries indicate that the universe contains vast amounts of organic compounds. For example, some meteorites that originated in deep space contain complex organic molecules, including amino acids. Also, many

simple organic compounds, such as formaldehyde, are found throughout the universe as components of huge clouds of interstellar gas. In fact, some suggest that the ingredients for life actually came from outer space in comets or asteroids.

One of the classic experiments that demonstrated how complex organic molecules such as amino acids could have originated from more fundamental compounds was performed in 1952 by Stanley Miller, then a graduate student at the University of Chicago. The original atmosphere on Earth was then thought to be composed of ammonia, methane, and hydrogen (compounds present in the atmospheres of Jupiter and Saturn today). Electric sparks were passed through a chamber containing these gases to simulate lightning. Within a week, the water and chamber were covered with tarry substances that contained many complex organic molecules, including amino acids. Some of these amino acids were exactly like those found in proteins, while others were not. It was immediately suggested that life emerged from simple chemical reactions in the "primordial soup" of organic compounds. Although most scientists now believe that the early atmosphere of Earth was mostly carbon dioxide and nitrogen, Miller made an important point—the organic compounds that are the basic building blocks of life are readily synthesized by natural phenomena.

Life is still a mystery, and we are still a long way from a provable theory. However, we have learned much in the last few years and we may yet determine an answer as to how it all got started. If we know that, we would have an idea about the likelihood of life elsewhere in the universe.

ASSESSING THE  
OBJECTIVES FOR  
SECTION 18-5**EXERCISE 18-5(a) KNOWLEDGE:** Fill in the blanks.

DNA and RNA are the two types of \_\_\_\_\_ acids. DNA is made of phosphate, nitrogen bases, and \_\_\_\_\_ sugar, while RNA uses \_\_\_\_\_ sugar. The \_\_\_\_\_ and the \_\_\_\_\_ form the backbone of these structures. DNA has a secondary structure composed of a \_\_\_\_\_ helix. The two strands are held together by \_\_\_\_\_ bonds with \_\_\_\_\_ bases opposite each other. The process whereby DNA creates a copy of itself is known as \_\_\_\_\_. A section of DNA that contains information about a specific enzyme is known as a \_\_\_\_\_. The process whereby a gene in DNA forms an mRNA molecule is known as \_\_\_\_\_. The formation of a protein or enzyme from this process is known as \_\_\_\_\_. Enzymes are constructed on \_\_\_\_\_ with the help of \_\_\_\_\_ and \_\_\_\_\_.

**EXERCISE 18-5(b) ANALYSIS:** If a gene has the partial sequence of bases TAAGC, what would be the complementary sequence of bases on the opposite strand of DNA? What would be the complementary sequence on a strand of mRNA?

**EXERCISE 18-5(c) SYNTHESIS:** What is a clone?

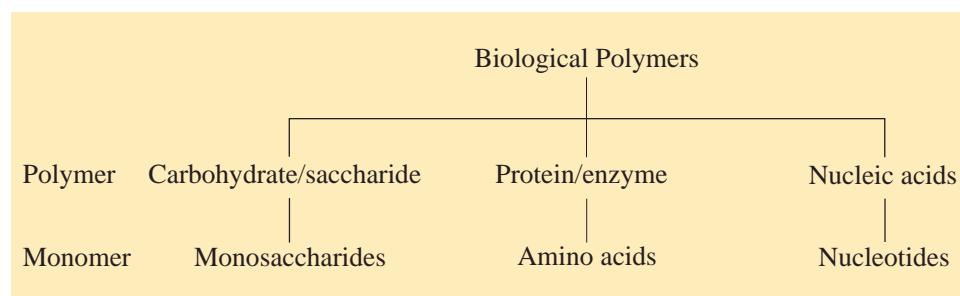
*For additional practice, work chapter problems 18-28, 18-30, and 18-34.*

PART B  
SUMMARY

## KEY TERMS

- 18-4** An **enzyme** is a catalyst that works on biological molecules. p. w-58
- 18-4.1** **Denaturation** refers to the destruction of the tertiary structure of a protein from heat. p. w-59
- 18-4.2** The **lock-and-key model** describes the mechanism where the **active site** of an enzyme attaches to a biological molecule called a **substrate**. p. w-59
- 18-5.1** A **nucleotide** is made up of a pentose sugar, a phosphate group, and a nitrogen base. A polymer of nucleotides is a **nucleic acid**. p. w-60
- 18-5.1** **DNA (deoxyribonucleic acid)** is a nucleic acid where the pentose sugar is deoxyribose. **RNA (ribonucleic acid)** is a nucleic acid where the pentose sugar is ribose. p. w-60
- 18-5.1** A **chromosome** is made up of a strand of DNA and a protein called a histone. p. w-62
- 18-5.2** **Replication** is the process whereby a strand of DNA makes copies of itself. p. w-62
- 18-5.3** The portion of DNA that undergoes **transcription** to form a particular protein is known as a **gene**. p. w-62
- 18-5.3** The production of a particular protein by DNA involves **messenger RNA (mRNA)**, **transfer RNA (tRNA)**, and **ribosomal RNA (rRNA)**. **Translation** provides the site where this process occurs. pp. w-62–w-63
- 18-5.3** A **ribosome** is a site outside of a cell where protein synthesis by transfer -RNA occurs. p. w-63

## SUMMARY CHART



## CHAPTER SUMMARY

*Biochemistry* is the study of the molecules and reactions that occur in living organisms. The major classes of biological molecules are the *lipids*, *carbohydrates*, *proteins*, and *nucleic acids*. An understanding of these classes leads to an introduction to amino acids, enzymes, and genetics. This chapter attempts to give a molecular perspective on key terms that you will encounter in your everyday life.

**Lipids** are unique in that they are nonpolar molecules that have a significant role in energy storage and protective coatings in an aqueous environment. Lipids can be broken down into simple and complex **saponifiable** fats and **nonsaponifiable steroids**. Complex lipids include **sphingolipids**, **glycolipids**, and **phospholipids**.

**Carbohydrates** serve as the most abundant and readily available source of energy for your body. Common **monosaccharides** are either **aldose** or **ketose** sugars and may also be identified by the number of carbon atoms as **pentose** and **hexose** sugars. Biologically important sugars include the aldopentoses **ribose** and **deoxyribose**, which serve as significant structural components of nucleotides. **Disaccharides** contain two sugar molecules attached by a **glycoside bond**. **Polysaccharides** are polymers composed of many sugar molecules.

**Amino acids** contain a basic and an acidic site. A **dipeptide** is composed of two amino acids connected by a **peptide bond**. **Proteins** are polymers composed of many amino acids. **Globular** are **fibrous** proteins exhibit different tertiary structure and have a number of functions that maintain proper working of a cell.

Specific proteins, known as **enzymes**, catalyze biological reactions. Enzymes are **denatured** by heat. Enzymes work by the **lock-and-key model** involving the **active site** on the enzyme and the **substrate** of the reactant molecule.

Proteins and enzymes are synthesized based on the information contained in the **nucleic acid** which is a polymer composed of **nucleotides**. Two types of nucleic acids are **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. DNA contains all of the hereditary information for an organism and is part of a **chromosome**. DNA has two main functions. It can undergo **replication**, or it can drive the production of proteins and enzymes. The principal role of RNA is to direct **transcription** from the **genes** and eventually **translation** to a specific protein. **Messenger DNA (mDNA)**, **transfer DNA (tDNA)**, and **ribosomal DNA (rDNA)** all play a roll in this process. The latter DNA, along with proteins, form **ribosomes**, which are also involved in transcription. The end result of these processes is the production of proteins and enzymes based on the information contained in DNA.

Many of the revolutionary advances in medicine rely on the basic principles presented in this chapter. Biochemistry covers everything from nutrition to medicine to gene manipulation and cloning. We live in a very exciting time for understanding how nature works and how we can manipulate our essence to live healthier lives. In our lifetime, we may see the end of many common diseases, and the length and quality of our lives will increase.

## OBJECTIVES

| SECTION | YOU SHOULD BE ABLE TO...   | EXERCISES      | CHAPTER PROBLEMS   |
|---------|--|----------------|--------------------|
| 18-1    | Describe the different types of lipids, their common properties, and their major uses or functions.        | 1a, 1b, 1c, 1d | 1, 2, 3, 5, 6      |
| 18-2    | Describe the different types of carbohydrates, their common properties, and their major uses or functions. | 2a, 2b, 2c     | 7, 8, 9, 10, 13    |
| 18-3    | Describe the different types of amino acids.   | 3a, 3b         | 17, 18, 19         |
|         | List and describe the four structures of proteins.   | 3a, 3c         | 20, 21, 23         |
| 18-4    | Describe the effects of conditions on enzymes and how they function.                                       | 4a, 4b, 4c     | 24, 25             |
| 18-5    | Describe the structure of DNA and RNA and the attractions between base pairs.                              | 5a, 5b         | 27, 28, 29         |
|         | Describe the process of replication and transcription.   | 5a, 5c         | 31, 32, 33, 34, 35 |



## ANSWERS TO ASSESSING THE OBJECTIVES

## PART A

## EXERCISES

**18-1(a)** When an alcohol and a carboxylic acid come together and water is lost, an ester bond will form. The difference between a fat and an oil is that a fat is solid at room temperature while an oil is liquid. A saponifiable lipid contains an ester linkage. A micelle is a cluster of fatty acid salts that surround a drop of oil and allow it to be soluble in water. Cholesterol is different from sphingolipids, glycolipids, and phospholipids because it is a nonsaponifiable lipid.

**18-1(b)** carboxylic acid (on left) and three double bonds

**18-1(c)**  $\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-$  (fatty acid anion) and  $\text{C}_2\text{H}_5\text{OH}$  (ethyl alcohol)

**18-1(d)** The product probably does contain some trans fat but in very low amounts. Just because it says “0 g trans fat” does not mean that there is not any trans fat. In fact, if there is less than 0.5 g of trans fat per serving, the FDA allows the product to be labeled “0 g”. Mono- and diglycerides have only one (mono) or two (di) of the three OH groups on glycerol substituted with fatty acids. Steroids do not contain an ester bond, which is necessary to make a lipid saponifiable.

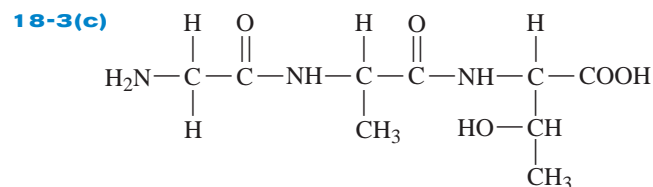
**18-2(a)** Ribose would be considered an aldopentose because it has an aldehyde functional group, has five carbon atoms, and is a simple sugar. Maltose, lactose, and sucrose contain two monosaccharides held together by a glycoside linkage. Starch and cellulose are both polymers of the monosaccharide glucose.

**18-2(b)** Maltose is composed of two glucose units, sucrose contains a glucose and a fructose, and lactose contains a glucose and a galactose sugar.

**18-2(c)** Both cellulose and starch are composed of large numbers of glucose units. The glucose units in starch, however, are all linked in the same geometry, while the glucose units in cellulose have alternating arrangements. The enzyme that breaks down starch into glucose units does not work on cellulose. Both table sugar and starch eventually provide the same source of energy, which is individual glucose units. Potatoes and pasta are mainly starch. One is not avoiding sugar by eating pasta since it breaks down to glucose.

**18-3(a)** The four classes of amino acids are nonpolar, polar neutral, acidic, and basic. The three types of protein secondary structure are primary, secondary, and tertiary. Hydrophobic interactions, electrostatic attraction, hydrogen bonding, and disulfide bonds are involved in stabilizing the tertiary structure of a protein.

**18-3(b)** (a) basic (b) nonpolar (c) polar neutral (d) acidic



Five other proteins can be made from these three amino acids: GTA, AGT, ATB, TAG, and TGA.

## PART B

## EXERCISES

**18-4(a)** An enzyme is a protein that serves as a catalyst for bodily functions. The molecule that the enzyme works on is known as a substrate. Enzymes in the body function at an optimal pH, temperature, and substrate concentration. The theory of how enzymes work is known as the lock-and-key model. This works on the active site of the substrate.

**18-5(b)** As the temperature increases, the tertiary structure of the protein enzyme is changed. Because of the change in geometry, the enzyme can no longer act as a catalyst.

**18-4(c)** Carbon dioxide is the anhydride of carbonic acid. As the concentration of carbon dioxide in water increases, so does the concentration of carbonic acid ( $\text{H}_2\text{CO}_3$ ). This leads to an increase in the  $\text{H}_3\text{O}^+$  concentration, which corresponds to a decrease in pH. This change in pH may begin to affect the function of enzymes that are involved in sea life.

**18-5(a)** DNA and RNA are the two types of nucleic acids. DNA is made of phosphate, nitrogen bases, and ribose sugar, while RNA uses deoxyribose sugar. The phosphate and the sugar form the backbone of these structures. DNA has a secondary structure composed of a double helix. The two strands are held together by hydrogen bonds with complementary bases opposite each other. The process whereby DNA creates a copy of itself is known as replication. A section of DNA that contains information about a specific enzyme is known as a gene. The process whereby a gene in DNA forms an mRNA molecule is known as transcription. The formation of a protein or enzyme from this process is known as translation. Enzymes are constructed on ribosomes with the help of tRNA and rRNA.

**18-5(b)** ATTCG on DNA, AUUCG on RNA

**18-5(c)** A clone is an exact replication of a member of a particular species. The nucleus of a viable egg, which contains the DNA, is removed. The DNA from the cell of another of the same species is removed and implanted in its place. The egg is implanted in a womb, but the fetus has the same DNA as the donor. The process is actually quite complex, and only a few species (e.g., dogs and sheep) have actually been cloned. Recently, however, researchers in California claimed to have cloned human cells, although the cells were destroyed after a few divisions.

## CHAPTER PROBLEMS

Answers to all of the following problems are found at the end of the Chapter.

## Lipids (SECTION 18-1)

**18-1.** A lipid is any substance of biological origin that is described by which of the following?

- (a) soluble in water, but insoluble in nonpolar solvents
- (b) insoluble in both water and nonpolar solvents
- (c) soluble in nonpolar solvents but insoluble in water
- (d) soluble in both water and nonpolar solvents

**18-2.** Which of the following types of compounds are expected products from the saponification of a fat?

- (a) glycerol and fatty acids
- (b) glycerol and fatty acid salts
- (c) fatty acids and fatty acid salts
- (d) glycerol, fatty acids, and fatty acid salts

**18-3.** Which of the following types of lipids would be soluble in water?

- (a) phosphoacylglycerols
- (b) sphingolipids
- (c) steroids
- (d) more than one correct response
- (e) no correct response

**18-4.** In which of the following types of lipids are both ester and amide linkages present?

- (a) sphingolipids
- (b) glycolipids
- (c) phospholipids
- (d) more than one correct response
- (e) no correct response

**18-5.** What is the physical and chemical difference between a saturated and an unsaturated lipid?

**18-6.** What are the products of the saponification of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ?

## Carbohydrates (SECTION 18-2)

**18-7.** What is the difference between an aldo and a keto sugar? What is the difference between a pentose and a hexose sugar?

**18-8.** What is the difference between L-glucose and D-glucose?

**18-9.** What is the difference between D-glucose and D-galactose?

**18-10.** What is the principal way monosaccharides are found in aqueous solution?

**18-11.** In which of the following pairs of carbohydrates are both members of the pair disaccharides?

- (a) glucose and fructose
- (b) sucrose and maltose
- (c) lactose and starch
- (d) cellulose and glycogen

**18-12.** What are the monosaccharide monomers that make up (a) sucrose, (b) maltose, (c) starch, (d) lactose, and (e) cellulose?

**18-13.** The major structural difference between cellulose and starch is found in which of the following?

- (a) the identity of the monosaccharide units present
- (b) the ring size of the monosaccharide units present
- (c) the linkages between the monosaccharide units present
- (d) the frequency of branching present

**18-14.** Which of the following monosaccharides has cyclic forms that involve a five-membered ring?

- (a) fructose
- (b) galactose
- (c) ribose
- (d) more than one correct response
- (e) no correct response

**18-15.** Which of the following disaccharides produces two of the same monosaccharide upon hydrolysis?

- (a) maltose
- (b) sucrose
- (c) lactose
- (d) more than one correct response
- (e) no correct response

**18-16.** Blood sugar is another name for

- (a) D-glucose
- (b) D-fructose
- (c) lactose
- (d) sucrose

## Amino Acids and Proteins (SECTION 18-3)

**18-17.** In the tetrapeptide Ala-Cys-Val-Leu, the C-terminal amino acid is

- (a) Ala
- (b) Cys
- (c) Val
- (d) Leu

**18-18.** Using the three-letter shorthand, write the sequences of proteins that can be made from valine, proline, and tryptophan.

**18-19.** The joining together of two amino acids to form a dipeptide involves the reaction between which of the following?

- (a) two amino groups
- (b) two carboxyl groups
- (c) an amino group and a carboxyl group
- (d) a carboxyl group and a hydroxyl group

**18-20.** Proteins are made from a mixture of which of the following?

- (a) polypeptides
- (b) free amino acids
- (c) polypeptides and free amino acids
- (d) dipeptides and free amino acids

**18-21.** How does the peptide linkage interact by hydrogen bonding with a different peptide linkage?

**18-22.** Nutrasweet, an artificial sweetener, is made from a dipeptide with the sequence AspPhe. Write the structure of

this compound. The sweetener itself is the methyl ester of this dipeptide. Write its structure.

**18-23.** Which of the following levels of protein structure is *not* disrupted when protein denaturation occurs?

- (a) primary structure
- (b) secondary structure
- (c) tertiary structure
- (d) more than one correct response
- (e) no correct response

### Enzymes (SECTION 18-4)

**18-24.** What is the function of enzymes within living systems?

- (a) structural elements
- (b) steroids
- (c) catalysts
- (d) energy usage

**18-25.** Which of the following statements concerning the effect of temperature change on an enzyme-catalyzed reaction is *correct*?

- (a) An increase in temperature can stop the reaction by denaturing the enzyme.
- (b) An increase in temperature can increase the reaction rate by increasing the speed at which molecules move.
- (c) An increase in temperature to the optimum temperature maximizes reaction rate.
- (d) more than one correct response
- (e) no correct response

### Nucleic Acids and Genetics (SECTION 18-5)

**18-26.** The region of a DNA strand carrying the information needed for synthesis of a specific protein is called what?

- (a) a histone
- (b) a chromosome
- (c) a gene
- (d) a complementary base pair

**18-27.** How do RNA molecules differ from DNA molecules?

- (a) They are single stranded rather than double stranded.
- (b) They contain five different bases instead of four.
- (c) They are much larger.
- (d) They contain 2-deoxyglucose rather than 2-deoxyribose.

**18-28.** In which of the following sets of nucleic acid building blocks are all members of the set possible components of a DNA molecule?

- (a) phosphate, ribose, and thymine
- (b) adenine, phosphate, and 2-deoxyribose
- (c) cytosine, guanine, and uracil
- (d) more than one correct response
- (e) no correct response

**18-29.** Which of the following elements is *not* present in the backbone of a nucleic acid molecule?

- (a) phosphorus
- (b) nitrogen
- (c) oxygen
- (d) more than one correct response
- (e) no correct response

**18-30.** Which of the following sets of base composition data is consistent with the double-helical nature of DNA molecules?

- (a) 35% T and 15% C
- (b) 35% A and 35% G
- (c) 15% C and 15% G
- (d) more than one correct response
- (e) no correct response

**18-31.** Which of the following is associated with the process of DNA transcription?

- (a) two DNA molecules from one DNA molecule and amino acids
- (b) one DNA molecule from a number of shorter RNA molecules
- (c) a tRNA molecule that contains the information from a gene
- (d) an mRNA molecule that contains the information from a gene

**18-32.** Which of the following is not necessary for protein synthesis at the time and place where synthesis occurs?

- (a) mRNA
- (b) tRNA
- (c) ribosomes
- (d) DNA

**18-33.** Which of the following events occurs during the *translation* phase of protein synthesis?

- (a) mRNA interacts with a chromosome.
- (b) tRNA brings amino acids to the ribosomes.
- (c) rRNAs carry amino acids to the site for protein synthesis.
- (d) more than one correct response
- (e) no correct response

**18-34.** The cookbook, recipe, ingredients, and crockpot correspond to these, respectively.

- (a) DNA, tRNA, amino acids, ribosome
- (b) gene, mRNA, tRNA, proteins
- (c) mRNA, tRNA, amino acid, rRNA
- (d) DNA, mRNA, tRNA, ribosome

**18-35.** Which of the following occur in translation?

- (a) The mRNA sequence is interpreted to produce an amino acid sequence.
- (b) Amino acids are linked together into a polypeptide chain.
- (c) All three types of RNA are used.
- (d) all of the above

## Answers to Chapter 18 Problems

18-1. C

18-2. C

18-3. E

18-4. D

18-5. Unsaturated lipids have double bonds in the fatty acid part whereas saturated lipids do not.

18-6.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

18-7. An aldo sugar has an aldehyde group whereas a keto sugar has a ketone group. A pentose sugar has five carbons and a hexose sugar has six carbons.

18-8. They have different orientations in space. That is, they are optical isomers.

18-9. The orientation of the OH group on the number-4 carbon has a different orientation in space.

18-10. They are found mostly in the cyclic form.

18-11. B

18-12. (a) sucrose—fructose and glucose (b) maltose—two glucose units (c) starch—glucose units (d) lactose—glucose and galactose (e) cellulose—glucose units

18-13. C

18-14. D

18-15. A

18-16. A

18-18. D

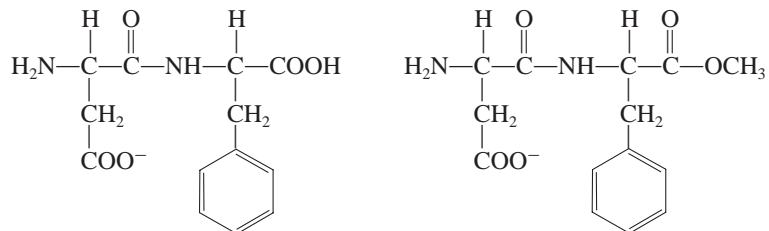
18-18. ValProTrp, ValTrpPro, ProValTrp, ProTrpVal, TrpValPro, TrpProVal

18-19. C

18-20. B

18-21. The  $\text{C}=\text{O}$  on one peptide linkage interacts with the  $\text{H}-\text{N}$  on another.

18-22.



18-23. A

18-24. C

18-25. D

18-26. C

18-27. A

18-28. B

18-29. B

18-30. D

18-31. D

18-32. D

18-33. D

18-34. D

18-35. D

## FOREWORD TO THE APPENDICES



*The successful athlete must be “in shape” physically. The successful chemistry student must be “in shape” mathematically.*

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**WHY** do some (one or two, anyway) students seem so self-assured in the study of chemistry and yet others (all the rest) seem so worried? Most likely, it has a lot to do with preparation. Preparation in this case probably does not mean a prior course in chemistry, but it does mean having a solid mathematical background. Most of the students using this text probably are a little rusty on at least some aspects of basic arithmetic, algebra, and scientific notation. There are several reasons for this. Some have not had a good secondary school background in math courses, and others have been away from their high school or college math courses for a number of years. It makes no difference—most students need access to a few reminders, hints, and review exercises to get in shape. The sooner students admit that they have forgotten some math, the faster they do something about it and start to enjoy chemistry. It is really difficult to appreciate the study of this science if math deficiencies get in the way.

**Appendix A** reviews some of the basic arithmetic concepts such as manipulation of fractions, expressing decimal fractions, and, very importantly, the expression and use of percent. **Appendix B** reviews the manipulation and solution of simple algebra equations, which are so important in the quantitative aspects of chemistry. **Appendix C** supplements the discussion of scientific notation in Chapter 1 with more examples and exercises. Also included in this appendix is a discussion of the concept of logarithms, which is a convenient way to express exponential numbers in certain situations. **Appendix D** is a brief discussion of graphing, an important tool of the social sciences as well as the natural sciences. **Appendix E** contains a discussion of the function of the more common type of calculator used by students in chemistry classes. **Appendix F** is a glossary of terms, and **Appendix G** contains answers to more than half of the exercises at the ends of the chapters.



# BASIC MATHEMATICS

- A-1 Addition and Subtraction**
- A-2 Multiplication**
- A-3 Roots of Numbers**
- A-4 Division, Fractions, and Decimal Numbers**
- A-5 Multiplication and Division of Fractions**
- A-6 Decimal Numbers and Percent**

The following is a quick (very quick) refresher of fundamentals of math. This may be sufficient to aid you if you are just a little rusty on some of the basic concepts. For more thorough explanations and practice, however, you are urged to use a more comprehensive math review workbook or consult with your instructor.

One may ask “Why not just use a calculator?” The answer is that serious science students need a “feeling” for the numbers they use. This can only be accomplished by understanding the calculations involved. Therefore, it is well worth the time to go through this appendix *without a calculator*. Being able to do these calculations on your own will certainly pay off.

## A-1 Addition and Subtraction

Since most calculations in this text use numbers expressed in decimal form, we will emphasize the manipulation of this type of number. In addition and subtraction, it is important to line up the decimal point carefully before doing the math.

Subtraction is simply the addition of a negative number. Remember that subtraction of a negative number changes the sign to a plus (two negatives make a positive). For example,  $4 - 7 = -3$ , but  $4 - (-7) = 4 + 7 = 11$ .

### EXAMPLE A-1

#### Addition and Subtraction

Carry out the following calculations.

(a)  $16.75 + 13.31 + 175.67$

$$\begin{array}{r} \downarrow \\ 16.75 \\ 13.31 \\ \underline{175.67} \\ \underline{205.73} \end{array}$$

(b)  $11.8 + 13.1 - 6.1$

$$\begin{array}{r} 11.8 \\ +13.1 \\ \hline 24.9 \end{array} \quad \begin{array}{r} \rightarrow \\ 24.9 \\ -6.1 \\ \hline 18.8 \end{array}$$

(c)  $47.82 - 111.18 - (-12.17)$

This is the same as  $47.82 - 111.18 + 12.17$ .

$$\begin{array}{r} 47.82 \\ +12.17 \\ \hline 59.99 \end{array} \quad \begin{array}{r} \rightarrow \\ -111.18 \\ +59.99 \\ \hline -51.19 \end{array}$$

**EXERCISES**

**A-1.** Carry out the following calculations.

- (a)  $47 + 1672$                       (e)  $0.897 + 1.310 - 0.063$   
 (b)  $11.15 + 190.25$                 (f)  $-0.377 - (-0.101) + 0.975$   
 (c)  $114 + 26 - 37$                 (g)  $17.489 - 318.112 - (-0.315) + (-3.330)$   
 (d)  $-97 + 16 - 118$

Answers: (a) 1719 (b) 201.40 (c) 103 (d) -199 (e) 2.144 (f) 0.699  
 (g) -303.638

**A-2 Multiplication**

Multiplication is expressed in various ways as follows:

$$13.7 \times 115.35 = 13.7 \cdot 115.35 = (13.7)(115.35) = 13.7(115.35)$$

If it is necessary to carry out the multiplication in longhand, you must be careful to place the decimal point correctly in the answer. Count the *total* number of digits to the right of the decimal point in both multipliers (three in this example). The answer has that number of digits to the right of the decimal point in the answer. Finally, round off to the proper number of significant figures.

$$\begin{array}{r}
 13.7 \times 2.15 = \qquad 13.7 \\
 \quad \underbrace{1 \quad + 2}_{\text{(decimal places)}} = \textcircled{3} \quad \times 2.15 \\
 \qquad \qquad \qquad \qquad \qquad \qquad \underline{685} \\
 \qquad \qquad \qquad \qquad \qquad \qquad 137 \\
 \qquad \qquad \qquad \qquad \qquad \qquad \underline{274} \\
 \qquad \qquad \qquad \qquad \qquad \qquad 29455 \\
 \qquad \qquad \qquad \qquad \qquad \qquad \textcircled{3} \quad = 29.455 = 29.5^*
 \end{array}$$

When a number (called a *base*) is multiplied by itself one or more times, it is said to be raised to a *power*. The power (called the *exponent*) indicates the number of bases multiplied. For example, the exact values of the following numbers raised to a power are

$$\begin{aligned}
 4^2 &= 4 \times 4 = 16 && \text{("four squared")} \\
 2^4 &= 2 \times 2 \times 2 \times 2 = 16 && \text{("two to the fourth power")} \\
 4^3 &= 4 \times 4 \times 4 = 64 && \text{("four cubed")} \\
 (14.1)^2 &= 14.1 \times 14.1 = 198.81 = 199^*
 \end{aligned}$$

In the calculations used in this book, most numbers have specific units. In multiplication, the units as well as the numbers are multiplied. For example,

$$\begin{aligned}
 3.7 \text{ cm} \times 4.61 \text{ cm} &= 17 (\text{cm} \times \text{cm}) = 17 \text{ cm}^2 \\
 (4.5 \text{ in.})^3 &= 91 \text{ in.}^3
 \end{aligned}$$

In the multiplication of a series of numbers, grouping is possible.

$$\begin{aligned}
 (a \times b) \times c &= a \times (b \times c) \\
 3.0 \text{ cm} \times 148 \text{ cm} \times 3.0 \text{ cm} &= (3.0 \times 3.0) \times 148 \times (\text{cm} \times \text{cm} \times \text{cm}) \\
 &= \underline{\underline{1300 \text{ cm}^3}}
 \end{aligned}$$

When multiplying signs, remember:

$$(+) \times (-) = - \quad (+) \times (+) = + \quad (-) \times (-) = +$$

For example,  $(-3) \times 2 = -6$ ;  $(-9) \times (-8) = +72$ .

\*Rounded off to three significant figures. See section 1-2.

**EXERCISES**

**A-2.** Carry out the following calculations. For (a) through (d) carry out the multiplications completely. For (e) through (h) round off the answer to the proper number of significant figures and include units.

- (a)  $16.2 \times (-118)$                       (d)  $(-47.8) \times (-9.6)$   
 (b)  $(4 \times 2) \times 879$                       (e)  $3.0 \text{ ft} \times 18 \text{ lb}$   
 (c)  $(-8) \times (-2) \times (-37)$             (f)  $17.7 \text{ in.} \times (13.2 \text{ in.} \times 25.0 \text{ in.})$

(g) What is the area of a circle where the radius is 2.2 cm? (Area =  $\pi r^2$ ,  $\pi = 3.14$ .)

(h) What is the volume of a cylinder 5.0 in. high with a cross-sectional radius of 0.82 in.? (Volume = area of cross section  $\times$  height.)

Answers: (a) -1911.6 (b) 7032 (c) -592 (d) 458.88 (e) 54 ft · lb  
 (f) 5840 in.<sup>3</sup> (g) 15 cm<sup>2</sup> (h) 11 in.<sup>3</sup>

**A-3 Roots of Numbers**

A root of a number is a fractional exponent. It is expressed as

$$\sqrt[x]{a} = a^{1/x}$$

If  $x$  is not shown (on the left), it is assumed to be 2 and is known as the *square root*. The square root is the number that when multiplied by itself gives the base  $a$ . For example,

$$\begin{aligned}\sqrt{4} &= 2 & (2 \times 2 &= 4) \\ \sqrt{9} &= 3 & (3 \times 3 &= 9)\end{aligned}$$

The square root of a number may have either a positive or a negative sign. Generally, however, we are interested only in the positive root in chemistry calculations.

If the square root of a number is not a whole number, it may be computed on a calculator or found in a table. Without these tools available, an educated approximation can come close to the answer. For example, the square root of 54 lies between 7 ( $7^2 = 49$ ) and 8 ( $8^2 = 64$ ) but closer to 7. An educated guess of 7.3 would be excellent.

The cube root of a number is expressed as

$$\sqrt[3]{b} = b^{1/3}$$

It is the number multiplied by itself two times that gives  $b$ . For example,

$$\begin{aligned}\sqrt[3]{27} &= 3.0 & (3 \times 3 \times 3 &= 27) \\ \sqrt[3]{64} &= 4.0 & (4 \times 4 \times 4 &= 64)\end{aligned}$$

A hand calculator (see Appendix E) is the most convenient source of roots of numbers.

**EXERCISES**

**A-3.** Find the following roots. If necessary, first approximate the answer, then check with a calculator.

- (a)  $\sqrt{25}$                       (b)  $\sqrt{36 \text{ cm}^2}$                       (c)  $\sqrt{144 \text{ ft}^4}$                       (d)  $\sqrt{40}$   
 (e)  $\sqrt{7.0}$                       (f)  $110^{1/2}$                       (g)  $100^{1/3}$                       (h)  $\sqrt[3]{50}$

(i) What is the radius of a circle that has an area of 150 ft<sup>2</sup>? (Area =  $\pi r^2$ )

(j) What is the radius of the cross section of a cylinder that has a volume of 320 m<sup>3</sup> and a height of 6.0 m? (Volume =  $\pi r^2 \times$  height)

Answers: (a) 5.0 (b) 6.0 cm (c) 12.0 ft<sup>2</sup> (d) 6.3 (e) 2.6 (f) 10.5 (g) 4.64  
 (h) 3.7 (i) 6.91 ft (j) 4.1 m

## A-4 Division, Fractions, and Decimal Numbers

Common fractions express ratios or portions of numbers. A *proper fraction* is less than one so it has a larger denominator than numerator. An *improper fraction* is greater than one so it has a smaller denominator than numerator. In chemistry most fractions are expressed as decimal numbers which show proper fractions less than 1.0 and improper fractions greater than 1.0. To convert a common fraction to a decimal number, the numerator is divided by the denominator. Consider the two fractions shown below where the decimal is shown to three digits.

|                          |          |                           |          |
|--------------------------|----------|---------------------------|----------|
| proper fraction          |          | improper fraction         |          |
| $7/8 = 7 \div 8 = 0.675$ |          | $11/9 = 11 \div 9 = 1.22$ |          |
| common                   | decimal  | common                    | decimal  |
| fraction                 | fraction | fraction                  | fraction |

Heaven forbid, but someday we may find ourselves in a test without a calculator. In that case, we may be well served by a review of long division. For example, consider the ratio  $88.8/2.44$ . It isn't necessary, but perhaps it is easier to remove the decimals in this ratio so that we are dealing only with whole numbers. As shown below, by multiplying both numerator and denominator by 100 we can move the decimal. Multiplying both numerator and denominator by the same number does not change the value of the fraction.

$$\frac{a}{b} = \frac{a \times c}{b \times c}$$

$$\frac{88.8}{2.44} = \frac{88.8 \times 100}{2.44 \times 100} = \frac{8880}{244} = \underline{36.4}$$

$$\begin{array}{r} 36.39 \\ 2.44 \overline{)88.800} = 244 \overline{)8880.00} = 36.4 \text{ (three significant figures)} \\ \underline{732} \\ 1560 \\ \underline{1464} \\ 960 \\ \underline{732} \\ 2280 \\ \underline{2196} \end{array}$$

Many divisions can be simplified by cancellation, which is the elimination of common factors in the numerator and denominator. This is possible because a number divided by itself is equal to unity (e.g.,  $25/25 = 1$ ). As in multiplication, all units also must be divided. If identical units appear in both numerator and denominator, they also can be canceled.

$$\frac{a \times c}{b \times c} = \frac{a}{b}$$

$$\frac{190 \times 4 \text{ torr}}{190 \text{ torr}} = \underline{4}$$

$$\frac{2500 \text{ cm}^3}{150 \text{ cm}} = \frac{50 \times 50 \text{ cm} \times \text{cm} \times \text{cm}}{50 \times 3 \text{ cm}} = \frac{50 \text{ cm}^2}{3} = \underline{17 \text{ cm}^2}$$

$$\frac{2800 \text{ mi}}{45 \text{ hr}} = \frac{8 \times 560 \text{ mi}}{8 \times 9 \text{ hr}} = \frac{62 \text{ mi}}{1 \text{ hr}} = \underline{62 \text{ mi/hr}}$$

This is read as 62 miles “per” one hour or simply 62 miles per hour. The word “per” implies a fraction or a ratio with the unit after “per” in the denominator. If a number is not written or read in the denominator with a unit, it is assumed that the number is unity and is known to as many significant figures as the number in the numerator (i.e., 62 miles per 1.0 hr).

### EXERCISES

**A-4.** Express the following in decimal form. Express (a)–(c) to three digits.

$$\begin{array}{llll} \text{(a)} \ 3/7 & \text{(d)} \ 892 \text{ mi} \div 41 \text{ hr} & \text{(g)} \ \frac{67.5 \text{ g}}{15.2 \text{ mL}} & \text{(j)} \ \frac{0.8772 \text{ ft}^3}{0.0023 \text{ ft}^2} \\ \text{(b)} \ 14/19 & \text{(e)} \ 982.6 \div 0.250 & \text{(h)} \ \frac{1890 \text{ cm}^3}{66 \text{ cm}} & \text{(k)} \ \frac{37.50 \text{ ft}}{0.455 \text{ sec}} \\ \text{(c)} \ 19/14 & \text{(f)} \ 195 \div 2650 & \text{(i)} \ \frac{146 \text{ ft} \cdot \text{hr}}{0.68 \text{ ft}} & \end{array}$$

*Answers:* (a) 0.429 (b) 0.737 (c) 1.36 (d) 22 mi/hr (e) 3930 (f) 0.0736  
(g) 4.44 g/mL (h) 29 cm<sup>2</sup> (i) 210 hr (j) 380 ft (k) 82.4 ft/sec

## A-5 Multiplication and Division of Fractions

When two or more fractions are multiplied, all numbers *and units* in both numerator and denominator can be combined into one fraction.

The division of one fraction by another is the same as the multiplication of the numerator by the *reciprocal* of the denominator. The reciprocal of a fraction is simply the fraction in an inverted form (e.g.,  $\frac{3}{5}$  is the reciprocal of  $\frac{5}{3}$ ).

$$\frac{a}{b/c} = a \times \frac{c}{b} \quad \frac{a/b}{c/d} = \frac{a}{b} \times \frac{d}{c} = \frac{a \times d}{b \times c}$$

### EXAMPLE A-2

#### Multiplication and Division

Carry out the following calculations. Round off the answer to two digits.

$$\text{(a)} \ \frac{3}{5} \times \frac{75}{4} \times \frac{16}{7} = \frac{3 \times 75 \times 16}{5 \times 4 \times 7} = \frac{3 \times \overset{15}{\cancel{75}} \times \overset{4}{\cancel{16}}}{\underset{1}{5} \times \underset{1}{4} \times 7} = \frac{180}{7} = \underline{\underline{26}}$$

$$\text{(b)} \ \frac{42 \text{ mi}}{\text{hr}} \times \frac{3}{7} \text{ hr} \times \frac{5280 \text{ ft}}{\text{mi}} = \frac{\overset{6}{\cancel{42}} \times 3 \times 5280 \text{ mi} \times \text{hr} \times \text{ft}}{7 \text{ hr} \times \text{mi}} = \underline{\underline{95,000 \text{ ft}}}$$

$$\text{(c)} \ \frac{3}{4} \text{ mol} \times \frac{0.75 \text{ g}}{\text{mol}} \times \frac{1 \text{ mL}}{19.3 \text{ g}} = \frac{3 \times 0.75 \times 1 \times \text{mol} \times \text{g} \times \text{mL}}{4 \times 1 \times 19.3 \times \text{mol} \times \text{g}} = \underline{\underline{0.029 \text{ mL}}}$$

$$\text{(d)} \ \frac{1650}{3/5} = 1650 \times \frac{5}{3} = \underline{\underline{2800}}$$

$$\text{(e)} \ \frac{145 \text{ g}}{7.5 \text{ g/mL}} = 145 \text{ g} \times \frac{1 \text{ mL}}{7.5 \text{ g}} = \underline{\underline{19 \text{ mL}}}$$



**EXERCISES**

**A-5.** Express the following answers in decimal form. If units are not used, round off the answer to three digits. If units are included, round off to the proper number of significant figures and include units in the answer.

(a)  $\frac{3}{8} \times \frac{4}{7} \times \frac{21}{20}$

(h)  $\frac{\left(-\frac{3}{7}\right)}{\left(-\frac{4}{9}\right)}$

(b)  $\frac{250}{273} \times \frac{175}{300} \times (-6)$

(i)  $\frac{\left(-\frac{17}{3}\right)}{\frac{8}{9}}$

(c)  $\frac{4}{9} \times \left(-\frac{5}{8}\right) \times \left(-\frac{3}{4}\right)$

(j)  $\frac{\frac{16}{9} \times \frac{10}{14}}{\frac{5}{6}}$

(d)  $195 \text{ g/mL} \times 47.5 \text{ mL}$

(k)  $\frac{75.2 \text{ torr}}{760 \text{ torr/atm}}$

(e)  $0.75 \text{ mol} \times 17.3 \text{ g/mol}$

(l)  $\frac{(55.0 \text{ mi/hr}) \times (5280 \text{ ft/mi}) \times (1 \text{ hr}/60 \text{ min})}{60 \text{ sec/min}}$

(f)  $(3.57 \text{ in.})^2 \times 0.85 \text{ in.} \times \frac{16.4 \text{ cm}^3}{\text{in.}^3}$

(m)  $\frac{305 \text{ K} \times 62.4 \frac{\text{L} \cdot \text{torr}}{\text{K} \cdot \text{mol}} \times 0.25 \text{ mol}}{650 \text{ torr}}$

(g)  $\frac{\frac{150}{350}}{\frac{25}{42}}$

*Answers:* (a) 0.225 (b) -3.21 (c) 0.208 (d) 9260 g (e) 13 g (f) 180 cm<sup>3</sup>  
 (g) 0.720 (h) 0.964 (i) -6.38 (j) 1.52 (k) 0.0989 atm (l) 80.7 ft/sec (m) 7.3 L

**A-6 Decimal Numbers and Percent**

In the examples of fractions thus far, we have seen that the units of the numerator can be profoundly different from those of the denominator (e.g., miles/hr, g/mL, etc.). In other problems in chemistry we use fractions to express a component part in the numerator to the total in the denominator. In most cases such fractions are expressed without units and in decimal form.

**EXAMPLE A-3****Decimal Numbers**

(a) A box of nails contains 985 nails; 415 of these are 6-in. nails, 375 are 3-in. nails, and the rest are roofing nails. What is the fraction of roofing nails in decimal form?

**SOLUTION**

$$\text{Roofing nails} = \text{total} - \text{others} = 985 - (415 + 375) = 195$$

$$\frac{\text{component}}{\text{total}} = \frac{195}{375 + 415 + 195} = \underline{\underline{0.198}}$$

- (b) A mixture contains 4.25 mol of  $N_2$ , 2.76 mol of  $O_2$ , and 1.75 mol of  $CO_2$ . What is the fraction of moles of  $O_2$  present in the mixture? (This fraction is known, not surprisingly, as “the mole fraction.” The mole is a unit of quantity, like dozen.)

**SOLUTION**

$$\frac{\text{component}}{\text{total}} = \frac{2.76}{4.25 + 2.76 + 1.75} = \underline{\underline{0.315}}$$

**EXERCISES**

**A-6.** A grocer has 195 dozen boxes of fruit; 74 dozen boxes are apples, 62 dozen boxes are peaches, and the rest are oranges. What is the fraction of the boxes that are oranges?

**A-7.** A mixture contains 9.85 mol of gas. A 3.18-mol quantity of the gas is  $N_2$ , 4.69 mol is  $O_2$ , and the rest is He. What is the mole fraction of He in the mixture?

**A-8.** The total pressure of a mixture of two gases,  $N_2$  and  $O_2$ , is 0.72 atm. The pressure due to  $O_2$  is 0.41 atm. What is the fraction of the pressure due to  $O_2$ ?

Answers: **A-6** 0.30    **A-7** 0.201    **A-8** 0.57

The decimal numbers that have just been discussed are frequently expressed as percentages. Percent simply means parts per 100. Percent is obtained by multiplying a fraction in decimal form by 100%.

**EXAMPLE A-4****Expressing Percent**

If 57 out of 180 people at a party are women, what is the percent women?

**SOLUTION**

The fraction of women in decimal form is

$$\frac{57}{180} = 0.317$$

The percent women is

$$0.317 \times 100\% = \underline{\underline{31.7\% \text{ women}}}$$

The general method used to obtain percent is

$$\frac{\text{component}}{\text{total}} \times 100\% = \text{_____}\% \text{ of component}$$

To change from percent back to a decimal number, divide the percent by 100%, which moves the decimal to the left two places.

$$86.2\% = \frac{86.2\%}{100\%} = 0.862 \text{ (fraction in decimal form)}$$

**EXERCISES**

**A-9.** Express the following fractions or decimal numbers as percents:  $\frac{1}{4}$ ,  $\frac{3}{8}$ ,  $\frac{9}{8}$ ,  $\frac{55}{25}$ , 0.67, 0.13, 1.75, 0.098.

**A-10.** A bushel holds 198 apples, 27 of which are green. What is the percent of green apples?

**A-11.** A basket contains 75 pears, 8 apples, 15 oranges, and 51 grapefruit. What is the percent of each?

Answers: A-9  $\frac{1}{4} = 25\%$ ,  $\frac{3}{8} = 37.5\%$ ,  $\frac{9}{8} = 112.5\%$ ,  $\frac{55}{25} = 220\%$ ,  $0.67 = 67\%$ ,  
 $0.13 = 13\%$ ,  $1.75 = 175\%$ ,  $0.098 = 9.8\%$  A-10 13.6% A-11 50.3% pears, 5.4%  
 apples, 10.1% oranges, 34.2% grapefruit

We have seen how the percent is calculated from the total and the component part. We now consider problems where percent is given and we calculate either the component part as in Example A-5(a) or the total as in Example A-5(b). Such problems can be solved in two ways. The method we employ here uses the percent as a conversion factor, and the problems are solved by the factor-label method. (See section 1-5.) They also can be solved algebraically as is done in Appendix B.

### EXAMPLE A-5

#### Using Percent in Calculations

- (a) A crowd at a rock concert was composed of about 87% teenagers. If the crowd totaled 586 people, how many were teenagers?

#### PROCEDURE

Remember that percent means "per 100." In this case it means 87 teenagers per 100 people or, in fraction form,

$$\frac{87 \text{ teenagers}}{100 \text{ people}}$$

If this fraction is then multiplied by the number of people, the result is the component part or the number of teenagers.

$$586 \text{ people} \times \frac{87 \text{ teenagers}}{100 \text{ people}} = (586 \times 0.87) = \underline{510 \text{ teenagers}}$$

- (b) A professional baseball player got a hit 28.7% of the times he batted. If he got 246 hits, how many times did he bat?

#### PROCEDURE

The percent can be written in fraction form and then inverted. It thus relates the total at bats to the number of hits:

$$28.7\% = \frac{28.7 \text{ hits}}{100 \text{ at bats}} \text{ or } \frac{100 \text{ at bats}}{28.7 \text{ hits}}$$

If this is now multiplied by the number of hits, the result is the total number of at bats.

$$246 \text{ hits} \times \frac{100 \text{ at bats}}{28.7 \text{ hits}} = \frac{246}{0.287} = \underline{857 \text{ at bats}}$$

### EXERCISES

- A-12. In a certain audience, 45.9% were men. If there were 196 people in the audience, how many women were present?
- A-13. In the alcohol molecule, 34.8% of the mass is due to oxygen. What is the mass of oxygen in 497 g of alcohol?
- A-14. The cost of a hamburger in 2003 is 216% of the cost in 1970. If hamburgers cost \$0.75 each in 1970, what do they cost in 2003?
- A-15. In a certain audience, 46.0% are men. If there are 195 men in the audience, how large is the audience?
- A-16. If a solution is 23.3% by mass HCl and it contains 14.8 g of HCl, what is the total mass of the solution?
- A-17. An unstable isotope has a mass of 131 amu. This is 104% of the mass of a stable isotope. What is the mass of the stable isotope?

Answers: A-12 106 women A-13 173 g A-14 \$1.62 A-15 424 people  
 A-16 63.5 g A-17 126 amu

## BASIC ALGEBRA

- B-1 Operations of Basic Equations
- B-2 Word Problems and Algebra Equations
- B-3 Direct and Inverse Proportionalities

There are two aspects to the use of algebra that affect chemistry students. First is the actual skill and application of basic concepts and second is the ability to translate words or quantitative concepts into a proper algebraic relationship. In the first section, we will concentrate on the algebra equation itself and how it can be manipulated. In the two sections following this we will concentrate on how we can express quantitative concepts as equations.

## B-1 Operations of Basic Equations

Many of the quantitative problems of chemistry require the use of basic algebra. As an example of a simple algebra equation we use

$$x = y + 8$$

In any algebraic equation the equality remains valid when identical operations are performed on both sides of the equation. The following operations illustrate this principle.

1. A quantity may be added to or subtracted from both sides of the equation.

$$\text{(add 8)} \quad x + 8 = y + 8 + 8 \quad x + 8 = y + 16$$

$$\text{(subtract 8)} \quad x - 8 = y + 8 - 8 \quad x - 8 = y$$

2. Both sides of the equation may be multiplied or divided by the same quantity.

$$\text{(multiply by 4)} \quad 4x = 4(y + 8) = 4y + 32$$

$$\text{(divide by 2)} \quad \frac{x}{2} = \frac{(y + 8)}{2} \quad \frac{x}{2} = \frac{y}{2} + 4$$

3. Both sides of the equation may be raised to a power, or a root of both sides of an equation may be taken.

$$\text{(equation squared)} \quad x^2 = (y + 8)^2$$

$$\text{(square root taken)} \quad \sqrt{x} = \sqrt{y + 8}$$

4. Both sides of an equation may be inverted.

$$\frac{1}{x} = \frac{1}{y + 8}$$

In addition to operation on both sides of an equation, two other points must be recalled.

1. As in any fraction, identical factors in the numerator and the denominator in an algebraic equation may be canceled.

$$\frac{\cancel{4}x}{\cancel{4}} = x = y + 8 \quad \text{or} \quad x = \frac{\cancel{z}(y + 8)}{\cancel{z}} = y + 8$$

2. Quantities equal to the same quantity are equal to each other. Thus substitutions for equalities may be made in algebraic equations.

$$\begin{aligned}x &= y + 8 \\x &= 27\end{aligned}$$

Therefore, since  $x = x$ ,

$$y + 8 = 27$$

We can use these basic rules to solve algebraic equations. Usually, we need to isolate one variable on the left-hand side of the equation with all other numbers and variables on the right-hand side of the equations. The operations previously listed can be simplified for this purpose in two ways.

In practice, a number or a variable may be moved to the other side of an equation with a change of sign. For example, if

$$x + z = y$$

then subtracting  $z$  from both sides, in effect, gives us

$$x = y - z$$

Also, the numerator of a fraction on the left becomes the denominator on the right. The denominator of a fraction on the left becomes the numerator on the right. For example, consider the following two cases.

$$\text{If } xz = y$$

then by dividing both sides by  $z$ , in effect, gives us

$$\begin{aligned}xz &= y \\x &= \frac{y}{z}\end{aligned}$$

$$\text{If } \frac{x}{k+5} = B,$$

then multiplying both sides by  $k+5$

$$\begin{aligned}\frac{x}{k+5} &= B \\x &= B(k+5)\end{aligned}$$

The following examples illustrate the isolation of one variable ( $x$ ) on the left-hand side of the equation.

### EXAMPLE B-1

#### Solving Algebra Equations for a Variable

- (a) Solve for  $x$  in  $x + y + 8 = z + 6$ .

#### SOLUTION

Move  $+y$  and  $+8$  to the right by changing signs.

$$\begin{aligned}x &= z + 6 - y - 8 \\&= z - y + 6 - 8 = \underline{\underline{z - y - 2}}\end{aligned}$$

- (b) Solve for  $x$  in

$$\frac{x+8}{y} = z$$

#### SOLUTION

First, move  $y$  to the right by multiplying both sides by  $y$ .

$$y \cdot \frac{x+8}{y} = z \cdot y$$

This leaves

$$x + 8 = zy$$

Subtract 8 from both sides to obtain the final answer.

$$\underline{\underline{x = zy - 8}}$$

(c) Solve for  $x$  in

$$\frac{4x + 2}{3 + x} = 7$$

### SOLUTION

First, multiply both sides by  $(3 + x)$  to clear the fraction.

$$(\cancel{3 + x}) \cdot \frac{4x + 2}{(\cancel{3 + x})} = 7(3 + x)$$

This leaves

$$4x + 2 = 21 + 7x$$

To move integers to the right and the  $x$  variable to the left, subtract  $7x$  and  $2$  from both sides of the equation. This leaves

$$-3x = 19$$

Finally, divide both sides by  $-3$  to move the  $-3$  to the right.

$$x = -\frac{19}{3} = \underline{\underline{-6.33}}$$

(d) Solve for  $T_2$  in

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

### SOLUTION

To move  $T_2$  to the left, multiply both sides by  $T_2$ .

$$T_2 \cdot \frac{P_1 V_1}{T_1} = T_2 \cdot \frac{P_2 V_2}{T_2} = P_2 V_2$$

Move  $P_1 V_1$  to the right by dividing by  $P_1 V_1$ .

$$\frac{T_2}{P_1 V_1} \cdot \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

Finally, move  $T_1$  to the right by multiplying both sides by  $T_1$ .

$$T_2 = \underline{\underline{\frac{T_1 P_2 V_2}{P_1 V_1}}}$$

(e) Solve the following equation for  $y$ .

$$\frac{2y}{3} + x = 9z + 4$$

### SOLUTION

First, to clear the fraction, multiply both sides by  $3$ . This leaves

$$2y + 3x = 27z + 12$$

Subtract  $3x$  from both sides, which leaves

$$2y = 27z + 12 - 3x$$

Finally, divide both sides by  $2$ , which leaves

$$y = \frac{27z + 12 - 3x}{2}$$



**EXERCISES****B-1.** Solve for  $x$  in  $17x = y - 87$ .**B-2.** Solve for  $x$  in

$$\frac{y}{x} + 8 = z + 16$$

**B-3.** Solve for  $T$  in  $PV = (\text{mass}/MM)RT$ .**B-4.** Solve for  $x$  in

$$\frac{7x - 3}{6 + 2x} = 3r$$

**B-5.** Solve for  $x$  in  $18x - 27 = 2x + 4y - 35$ . If  $y = 3x$ , what is the value of  $x$ ?**B-6.** Solve for  $x$  in

$$\frac{x}{4y} + 18 = y + 2$$

**B-7.** Solve for  $x$  in  $5x^2 + 12 = x^2 + 37$ .**B-8.** Solve for  $r$  in

$$\frac{80}{2r} + \frac{y}{r} = 11$$

What is the value of  $r$  if  $y = 14$ ?*Answers:* **B-1**  $x = (y - 87)/17$  **B-2**  $x = y/(8 + z)$  **B-3**  $T = PV \cdot MM/\text{mass} \cdot R$ **B-4**  $x = 3(6r + 1)/(7 - 6r)$  **B-5**  $x = (y - 2)/4$ . When  $y = 3x$ , $x = -2$ . **B-6**  $x = 4y(y - 16)$  **B-7**  $x = \pm 2.5$  **B-8**  $r = (40 + y)/11$ . When $y = 14$ ,  $r = \frac{54}{11}$ **B-2 Word Problems and Algebra Equations**

Eventually, a necessary skill in chemistry is the ability to translate word problems into algebra equations and then solve. The key is to assign a variable (usually  $x$ ) to be equal to a certain quantity and then to treat the variable consistently throughout the equation. Again, examples are the best way to illustrate the problems.

**EXAMPLE B-2****Solving Abstract Word Equations**

Translate each of the following to an equation.

**(a)** A number  $x$  is equal to a number that is 4 larger than  $y$ .

$$\underline{\underline{x = y + 4}}$$

**(b)** A number  $z$  is equal to three-fourths of  $u$ .

$$\underline{\underline{z = \frac{3}{4}u}}$$

**(c)** The square of a number  $r$  is equal to 16.9% of the value of  $w$ .

$$\underline{\underline{r^2 = 0.169w}} \quad (\text{change percent to a decimal number})$$

**(d)** A number  $t$  is equal to 12 plus the square root of  $q$ .

$$\underline{\underline{t = 12 + \sqrt{q}}}$$

## EXERCISES

**B-9.** Write algebraic equations for the following:

- (a) A number  $n$  is equal to a number that is 85 smaller than  $m$ .
- (b) A number  $y$  is equal to one-fourth of  $z$ .
- (c) Fifteen percent of a number  $k$  is equal to the square of another number  $d$ .
- (d) A number  $x$  is equal to 14 more than the square root of  $v$ .
- (e) Four times the sum of two numbers,  $q$  and  $w$ , is equal to 68.
- (f) Five times the product of two variables,  $s$  and  $t$ , is equal to 16 less than the square of  $s$ .
- (g) Five-ninths of a number  $C$  is equal to 32 less than a number  $F$ .

Answers: (a)  $n = m - 85$  (b)  $y = z/4$  (c)  $0.15k = d^2$  (d)  $x = \sqrt{v} + 14$   
 (e)  $4(q + w) = 68$  (f)  $5st = s^2 - 16$  (g)  $\frac{5}{9}C = F - 32$

We now move from the abstract to the real. In the following examples it is necessary to translate the problem into an algebraic expression, as in the previous examples. There are two types of examples that we will use. The first you will certainly recognize, but the second type may be unfamiliar, especially if you have just begun the study of chemistry. However, it is *not* important that you understand the units of chemistry problems at this time. What *is* important is for you to notice that the problems are worked in the same manner regardless of the units.

## EXAMPLE B-3

## Solving Concrete Word Equations

- (a) John is 2 years more than twice as old as Mary. The sum of their ages is 86. How old is each?

## SOLUTION

Let  $x$  = age of Mary. Then  $2x + 2$  = age of John.

$$\begin{aligned}x + (2x + 2) &= 86 \\3x &= 84 \\x &= \underline{28} \quad (\text{age of Mary}) \\2(28) + 2 &= \underline{58} \quad (\text{age of John})\end{aligned}$$

- (b) One mole of  $\text{SF}_6$  has a mass 30.0 g less than four times the mass of 1 mol of  $\text{CO}_2$ . The mass of 1 mol of  $\text{SF}_6$  plus the mass of 1 mol of  $\text{CO}_2$  is equal to 190 g. What is the mass of 1 mol of each?

## SOLUTION

Let  $x$  = mass of 1 mol of  $\text{CO}_2$ . Then  $4x - 30$  = mass of 1 mol of  $\text{SF}_6$ .

$$\begin{aligned}x + (4x - 30) &= 190 \\x &= \underline{44 \text{ g}} \quad (\text{mass of 1 mol of } \text{CO}_2) \\4(44) - 30 &= \underline{146 \text{ g}} \quad (\text{mass of 1 mol of } \text{SF}_6)\end{aligned}$$

- (c) Two students took the same test, and their percent scores differed by 10%. If there were 200 points on the test and the total of their point scores was 260 points, what was each student's percent score?

## PROCEDURE

Set up an equation relating each person's percent scores to their total points (260).

$$\begin{aligned}\text{Let } x &= \text{percent score of higher test.} \\ \text{Then } x - 10 &= \text{percent score of lower test.}\end{aligned}$$

The points that each person scores is the percent in fraction form multiplied by the points on the test.

$$\frac{\% \text{ grade}}{100\%} \times (\text{points on test}) = \text{points scored}$$

**SOLUTION**

$$\left[ \frac{x}{100}(200 \text{ points}) \right] + \left[ \frac{x-10}{100}(200 \text{ points}) \right] = 260 \text{ points}$$

$$200x + 200x - 2000 = 26,000$$

$$400x = 28,000$$

$$x = 70$$

$$\text{higher score} = \underline{70\%} \quad \text{lower score} = 70 - 10 = \underline{60\%}$$

(d) If an 8.75-g quantity of sugar represents 65.7% of a mixture, what is the mass of the mixture?

**SOLUTION**

Let  $x$  = mass of the mixture. Then

$$\frac{65.7}{100}x = 0.657x = 8.75$$

$$x = \frac{8.75}{0.657} = \underline{13.3 \text{ g}}$$

(e) A used car dealer has Fords, Chevrolets, and Hondas. There are 120 Fords, 152 Chevrolets, and the rest are Hondas. If the fraction of Fords is 0.310, how many Hondas are on the lot?

**SOLUTION**

Let  $x$  = number of Hondas.

$$\text{fraction of Fords} = \frac{\text{number of Fords}}{\text{total number of cars}} = 0.310$$

$$\frac{120}{120 + 152 + x} = 0.310$$

$$120 = 0.310(272 + x)$$

$$120 = 84.3 + 0.310x$$

$$x = \underline{115 \text{ Hondas}}$$

(f) There is a 0.605-mol quantity of  $\text{N}_2$  present in a mixture of  $\text{N}_2$  and  $\text{O}_2$ . If the mole fraction of  $\text{N}_2$  is 0.251, how many moles of  $\text{O}_2$  are present?

**SOLUTION**

Let  $x$  = number of moles of  $\text{O}_2$ . Then

$$\text{mole fraction } \text{N}_2 = \frac{\text{mol of } \text{N}_2}{\text{total mol present}} = 0.251$$

$$\frac{0.605}{0.605 + x} = 0.251$$

$$0.605 = 0.251(0.605 + x)$$

$$x = \underline{1.80 \text{ mol}}$$

In the following exercises, a problem concerning an everyday situation is followed by one or more closely analogous problems concerning a chemistry situation. In both cases the mechanics of the solution are similar. Only the units differ.

**EXERCISES**

**B-10.** The total length of two boards is 18.4 ft. If one board is 4.0 ft longer than the other, what is the length of each board?

**B-11.** An isotope of iodine has a mass 10 amu less than two-thirds the mass of an isotope of thallium. The total mass of the two isotopes is 340 amu. What is the mass of each isotope?

**B-12.** An isotope of gallium has a mass 22 amu more than one-fourth the mass of an isotope of osmium. The difference in the two masses is 122 amu. What is the mass of each?

**B-13.** An oil refinery held 175 barrels of oil. When refined, each barrel yields 24 gallons of gasoline. If 3120 gallons of gasoline were produced, what percentage of the original barrels of oil was refined?

**B-14.** A solution contained 0.856 mol of a substance  $A_2X$ . In solution some of the  $A_2X$ s break up into As and Xs. (Note that each mole of  $A_2X$  yields 2 mol of A.) If 0.224 mol of A is present in the solution, what percentage of the moles of  $A_2X$  dissociated (broke apart)?

**B-15.** In Las Vegas, a dealer starts with 264 decks of cards. If 42.8% of the decks were used in an evening, how many jacks (four per deck) were used?

**B-16.** A solution originally contains a 1.45-mol quantity of a compound  $A_3X_2$ . If 31.5% of the  $A_3X_2$  dissociates (three As and two Xs per  $A_3X_2$ ), how many moles of A are formed? How many moles of X? How many moles of undissociated  $A_3X_2$  remain? How many moles of particles (As, Xs, and  $A_3X_2$ s) are present in the solution?

**B-17.** The fraction of kerosene that can be recovered from a barrel of crude oil is 0.200. After a certain amount of oil was refined, 8.90 gal of kerosene, some gasoline, and 18.6 gal of other products were produced. How many gallons of gasoline were produced?

**B-18.** The fraction of moles (mole fraction) of gas A in a mixture is 0.261. If the mixture contains 0.375 mol of gas B and 0.175 mol of gas C as well as gas A, how many moles of gas A are present?

*Answers:* **B-10** 7.2 ft, 11.2 ft **B-11** thallium, 210 amu; iodine, 130 amu

**B-12** gallium, 70 amu; osmium, 192 amu **B-13** 74.3% **B-14** 13.1% **B-15** 452 jacks **B-16** 1.37 mol of A, 0.914 mol of X, 0.99 mol of  $A_3X_2$ , 3.27 mol total

**B-17** 17.0 gal **B-18** 0.195 mol

### B-3 Direct and Inverse Proportionalities

There is one other point that should be included in a review on algebra—direct and inverse proportionalities. We use these often in chemistry.

When a quantity is directly proportional to another, it means that an increase in one variable will cause a corresponding increase of the same percent in the other variable. A direct proportionality is shown as

$$A \propto B \quad (\propto \text{ is the proportionality symbol})$$

which is read “A is directly proportional to B.” A proportionality can be easily converted to an algebraic equation by the introduction of a constant (in our examples designated  $k$ ), called a constant of proportionality. Thus the proportion becomes

$$A = kB$$

or, rearranging,

$$\frac{A}{B} = k$$

Note that  $k$  is not a variable but has a certain numerical value that does not change as do  $A$  and  $B$  under experimental conditions.

A common, direct proportionality that we will study relates Kelvin temperature  $T$  and volume  $V$  of a gas at constant pressure. This is written as

$$V \propto T \quad V = kT \quad \frac{V}{T} = k$$

(This is known as Charles’s law.)

In a hypothetical case,  $V = 100 \text{ L}$  and  $T = 200 \text{ K}$ . From this information we can calculate the value of the constant  $k$ .

$$\frac{V}{T} = \frac{100 \text{ L}}{200 \text{ K}} = 0.50 \text{ L/K}$$

A change in volume or temperature requires a corresponding change in the other *in the same direction*. For example, if the temperature of the gas is changed to  $300 \text{ K}$ , we can see that a corresponding change in volume is required from the following calculation.

$$V = kT = 0.50 \text{ L/K} \times 300 \text{ K} = \underline{150 \text{ L}}$$

When a quantity is inversely proportional to another quantity, an increase in one brings about a corresponding *decrease* in the other. An inverse proportionality between  $A$  and  $B$  is written as

$$A \propto \frac{1}{B}$$

As before, the proportionality can be written as an equality by the introduction of a constant (which has a value different from the example above).

$$A = \frac{k}{B} \quad \text{or} \quad AB = k$$

A common inverse proportionality that we use relates the volume  $V$  of a gas to the pressure  $P$  at a constant temperature. This is written as

$$V \propto \frac{1}{P} \quad V = \frac{k}{P} \quad PV = k$$

(This is known as Boyle's law.)

In a hypothetical case,  $V = 100 \text{ L}$  and  $P = 1.50 \text{ atm}$ . From this information we can calculate the value of the constant  $k$ .

$$PV = k = 1.50 \text{ atm} \times 100 \text{ L} = 150 \text{ atm} \cdot \text{L}$$

A change in volume or pressure requires a corresponding change in the other *in the opposite direction*. For example, if the pressure on the gas is changed to  $3.00 \text{ atm}$ , we can see that a corresponding change in volume is required.

$$V = \frac{k}{P} = \frac{150 \text{ atm} \cdot \text{L}}{3.00 \text{ atm}} = \underline{50.0 \text{ L}}$$

When one variable (e.g.,  $x$ ) is directly proportional to two other variables (e.g.,  $y$  and  $z$ ), the proportionality can be written as the product of the two.

$$\text{If } x \propto y \text{ and } x \propto z, \text{ then} \\ x \propto yz$$

When one variable, (e.g.,  $a$ ) is directly proportional to one variable, (e.g.,  $b$ ) and inversely proportional to another (e.g.,  $c$ ), the proportionality can be written as the ratio of the two.

$$\text{If } a \propto b \text{ and } a \propto \frac{1}{c}, \text{ then} \\ a \propto \frac{b}{c}$$

Quantities can be directly or inversely proportional to the square, square root, or any other function of another variable or number, as illustrated by the examples that follow.

**EXAMPLE B-4****Solving Equations with Proportionalities**

- (a) A quantity  $C$  is directly proportional to the square of  $D$ . Write an equality for this statement and explain how a change in  $D$  affects the value of  $C$ .

**SOLUTION**

The equation is

$$\underline{C = kD^2}$$

Note that a change in  $D$  will have a significant effect on the value of  $C$ . For example,

$$\text{If } D = 1, \text{ then } C = k$$

$$\text{If } D = 2, \text{ then } C = 4k$$

$$\text{If } D = 3, \text{ then } C = 9k$$

Note that when the value of  $D$  is doubled, the value of  $C$  is increased *fourfold*.

- (b) A variable  $X$  is directly proportional to the square of the variable  $Y$  and inversely proportional to the square of another variable  $Z$ . Write an equality for this statement.

**SOLUTION**

This can be written as two separate equations if it is assumed that  $Y$  is constant when  $Z$  varies and vice versa.

$$X = k_1 Y^2 \quad (Z \text{ constant})$$

$$X = k_2 / Z^2 \quad (Y \text{ constant})$$

$k_1$  and  $k_2$  are different constants. This relationship can be combined into one equation when both  $Y$  and  $Z$  are variables.

$$X = \frac{k_3 Y^2}{Z^2}$$

$k_3$  is a third constant that is a combination of  $k_1$  and  $k_2$ .

**EXERCISES**

**B-19.** Write equalities for the following relations.

- (a)  $X$  is inversely proportional to  $Y + Z$ .  
 (b)  $[\text{H}_3\text{O}^+]$  is inversely proportional to  $[\text{OH}^-]$ .  
 (c)  $[\text{H}_2]$  is directly proportional to the square root of  $r$ .  
 (d)  $B$  is directly proportional to the square of  $y$  and the cube of  $z$ .  
 (e) The pressure  $P$  of a gas is directly proportional to the number of moles  $n$  and the temperature  $T$ , and inversely proportional to the volume  $V$ .

Answers: (a)  $X = k/(Y + Z)$  (b)  $[\text{H}_3\text{O}^+] = k/[\text{OH}^-]$  (c)  $[\text{H}_2] = k\sqrt{r}$   
 (d)  $B = ky^2z^3$  (e)  $P = knT/V$



## APPENDIX C

# SCIENTIFIC NOTATION

- C-1 Review of Scientific Notation
- C-2 Addition and Subtraction
- C-3 Multiplication and Division
- C-4 Powers and Roots
- C-5 Logarithms

Although this topic was first introduced in section 1-3 in this text, we will focus on a review of the mathematical manipulation of numbers expressed in scientific notation in this appendix. Specifically, addition, multiplication, division, and taking the roots of numbers expressed in scientific notation are covered. We conclude this section with how we can simplify the expression of numbers in scientific notation with the use of logarithms. As mentioned in Chapter 1, scientific notation makes use of powers of 10 to express awkward numbers that employ more than two or three zeros that are not significant figures. The exponent of 10 simply indicates how many times we should multiply or divide a number (called the coefficient) by 10 to produce the actual number. For example,  $8.9 \times 10^3 = 8.9$  (the coefficient) multiplied by 10 *three* times, or

$$8.9 \times 10 \times 10 \times 10 = 8900$$

Also,  $4.7 \times 10^{-3} = 4.7$  (the coefficient) divided by 10 *three* times, or

$$\frac{4.7}{10 \times 10 \times 10} = 0.0047$$

## C-1 Review of Scientific Notation

The method for expressing numbers in scientific notation was explained in section 1-3. However, to simplify a number or to express it in the standard form with one digit to the left of the decimal point in the coefficient, it is often necessary to change a number already expressed in scientific notation. If this is done in a hurry, errors may result. Thus it is worthwhile to practice moving the decimal point of numbers expressed in scientific notation.

### EXAMPLE C-1

#### Changing Normal Numbers to Scientific Notation

Change the following numbers to the standard form in scientific notation.

- (a)  $489 \times 10^4$       (b)  $0.00489 \times 10^8$

#### PROCEDURE

All you need to remember is to raise the power of 10 one unit for each place the decimal point is moved to the left, and lower the power of 10 one unit for each place that the decimal point is moved to the right in the coefficient.

#### SOLUTION

(a)  $489 \times 10^4 = (489) \times 10^4 = 4.89 \times 10^{4+2} = 4.89 \times 10^6$

(b)  $0.00489 \times 10^8 = (0.00489) \times 10^8 = 4.89 \times 10^{8-3} = 4.89 \times 10^5$

As an aid to remembering whether you should raise or lower the exponent as you move the decimal point, it is suggested that you write (or at least imagine) the coefficient on a slant. For each place that you move the decimal point *up*, add one to the exponent. For each place that you move the decimal point *down*, subtract one from the exponent. Note that the exponent moves up or down with the decimal point. It may be easier to recall “up or down” rather than “right or left.”

**EXAMPLE C-2****Changing the Decimal Point in the Coefficient**

Change the following numbers to the standard form in scientific notation.

(a)  $4223 \times 10^{-7}$       (b)  $0.00076 \times 10^{18}$

**SOLUTION**

$$(a) \quad 4223 \times 10^{-7} = \left[ \begin{array}{c} 4 \leftarrow +3 \\ 2 \leftarrow +2 \\ 2 \leftarrow +1 \\ 3 \leftarrow +1 \end{array} \right] \times 10^{-7} = 4.223 \times 10^{-7+3} = \underline{\underline{4.223 \times 10^{-4}}}$$

$$(b) \quad 0.00076 \times 10^{18} = \left[ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 7 \leftarrow -4 \\ 6 \leftarrow -4 \end{array} \right] \times 10^{18} = 7.6 \times 10^{18-4} = \underline{\underline{7.6 \times 10^{14}}}$$

**EXERCISES**

**C-1.** Change the following numbers to standard scientific notation with one digit to the left of the decimal point in the coefficient.

(a)  $787 \times 10^{-6}$       (c)  $0.015 \times 10^{-16}$       (e)  $49.3 \times 10^{15}$   
 (b)  $43.8 \times 10^{-1}$       (d)  $0.0037 \times 10^9$       (f)  $6678 \times 10^{-16}$

**C-2.** Change the following numbers to a number with two digits to the left of the decimal point in the coefficient.

(a)  $9554 \times 10^4$       (c)  $1 \times 10^6$       (e)  $0.023 \times 10^{-1}$   
 (b)  $1.6 \times 10^{-5}$       (d)  $116.5 \times 10^4$       (f)  $0.005 \times 10^{23}$

*Answers:* **C-1:** (a)  $7.87 \times 10^{-4}$       (b)  $4.38$       (c)  $1.5 \times 10^{-18}$       (d)  $3.7 \times 10^6$   
 (e)  $4.93 \times 10^{16}$       (f)  $6.678 \times 10^{-13}$       **C-2:** (a)  $95.54 \times 10^6$       (b)  $16 \times 10^{-6}$   
 (c)  $10 \times 10^5$       (d)  $11.65 \times 10^5$       (e)  $23 \times 10^{-4}$       (f)  $50 \times 10^{19}$

**C-2 Addition and Subtraction**

Addition or subtraction of numbers in scientific notation can be accomplished only when all coefficients have the same exponent of 10. When all the exponents are the same, the coefficients are added and then multiplied by the power of 10. The correct number of places to the right of the decimal point, as discussed in section 1-2, must be shown.

**EXAMPLE C-3****Addition of Numbers in Scientific Notation**

(a) Add the following numbers:  $3.67 \times 10^{-4}$ ,  $4.879 \times 10^{-4}$ , and  $18.2 \times 10^{-4}$ .

**SOLUTION**

$$\begin{array}{r} 3.67 \times 10^{-4} \\ 4.879 \times 10^{-4} \\ 18.2 \times 10^{-4} \\ \hline 26.749 \times 10^{-4} = \underline{26.7 \times 10^{-4}} = \underline{2.67 \times 10^{-3}} \end{array}$$

(b) Add the following numbers:  $320.4 \times 10^3$ ,  $1.2 \times 10^5$ , and  $0.0615 \times 10^7$ .

**SOLUTION**

Before adding, change all three numbers to the same exponent of 10.

$$\begin{array}{r} 320.4 \times 10^3 = 3.204 \times 10^5 \\ 1.2 \times 10^5 = 1.2 \times 10^5 \\ 0.0615 \times 10^7 = 6.15 \times 10^5 \\ \hline 10.554 \times 10^5 = \underline{10.6 \times 10^5} = \underline{1.06 \times 10^6} \end{array}$$

**EXERCISES**

**C-3.** Add the following numbers. Express the answer to the proper decimal place.

- (a)  $152 + (8.635 \times 10^2) + (0.021 \times 10^3)$   
 (b)  $(10.32 \times 10^5) + (1.1 \times 10^5) + (0.4 \times 10^5)$   
 (c)  $(1.007 \times 10^{-8}) + (118 \times 10^{-11}) + (0.1141 \times 10^{-6})$   
 (d)  $(0.0082) + (2.6 \times 10^{-4}) + (159 \times 10^{-4})$

**C-4.** Carry out the following calculations. Express your answer to the proper decimal place.

- (a)  $(18.75 \times 10^{-6}) - (13.8 \times 10^{-8}) + (1.0 \times 10^{-5})$   
 (b)  $(1.52 \times 10^{-11}) + (17.7 \times 10^{-12}) - (7.5 \times 10^{-15})$   
 (c)  $(481 \times 10^6) - (0.113 \times 10^9) + (8.5 \times 10^5)$   
 (d)  $(0.363 \times 10^{-6}) + (71.2 \times 10^{-9}) + (519 \times 10^{-12})$

Answers: **C-3:** (a)  $1.037 \times 10^3$  (b)  $1.18 \times 10^6$  (c)  $1.254 \times 10^{-7}$   
 (d)  $2.44 \times 10^{-2}$  **C-4:** (a)  $2.9 \times 10^{-5}$  (b)  $3.29 \times 10^{-11}$  (c)  $3.69 \times 10^8$   
 (d)  $4.35 \times 10^{-7}$

**C-3 Multiplication and Division**

When numbers expressed in scientific notation are multiplied, the exponents of 10 are *added*. When the numbers are divided, the exponent of 10 in the denominator (the divisor) is subtracted from the exponent of 10 in the numerator (the dividend).

**EXAMPLE C-4****Multiplication and Division**

(a) Carry out the following calculation.

$$(4.75 \times 10^6) \times (3.2 \times 10^5)$$

**SOLUTION**

In the first step, group the coefficients and the powers of 10. Carry out each step separately.

$$\begin{aligned} (4.75 \times 3.2) \times (10^6 \times 10^5) &= 15.200 \times 10^{6+5} \\ &= 15 \times 10^{11} = \underline{1.5 \times 10^{12}} \end{aligned}$$

(b) Carry out the following calculation.

$$(1.62 \times 10^{-8}) \div (8.55 \times 10^{-3})$$

### SOLUTION

$$\begin{aligned} \frac{1.62 \times 10^{-8}}{8.55 \times 10^{-3}} &= \frac{1.62}{8.55} \times \frac{10^{-8}}{10^{-3}} = 0.189 \times 10^{-8-(-3)} \\ &= 0.189 \times 10^{-5} = \underline{\underline{1.89 \times 10^{-6}}} \end{aligned}$$

### EXERCISES

**C-5.** Carry out the following calculations. Express your answer to the proper number of significant figures with one digit to the left of the decimal point.

- (a)  $(7.8 \times 10^{-6}) \times (1.12 \times 10^{-2})$   
 (b)  $(0.511 \times 10^{-3}) \times (891 \times 10^{-8})$   
 (c)  $(156 \times 10^{-12}) \times (0.010 \times 10^4)$   
 (d)  $(16 \times 10^9) \times (0.112 \times 10^{-3})$   
 (e)  $(2.35 \times 10^3) \times (0.3 \times 10^5) \times (3.75 \times 10^2)$   
 (f)  $(6.02 \times 10^{23}) \times (0.0100)$

**C-6.** Follow the instructions in Problem C-5.

- (a)  $(14.6 \times 10^8) \div (2.2 \times 10^8)$       (d)  $(0.0221 \times 10^3) \div (0.57 \times 10^{18})$   
 (b)  $(6.02 \times 10^{23}) \div (3.01 \times 10^{20})$       (e)  $238 \div (6.02 \times 10^{23})$   
 (c)  $(0.885 \times 10^{-7}) \div (16.5 \times 10^3)$

**C-7.** Follow the instructions in Problem C-5.

- (a)  $[(8.70 \times 10^6) \times (3.1 \times 10^8)] \div (5 \times 10^{-3})$   
 (b)  $(47.9 \times 10^{-6}) \div [(0.87 \times 10^6) \times (1.4 \times 10^2)]$   
 (c)  $1 \div [(3 \times 10^6) \times (4 \times 10^{10})]$   
 (d)  $1.00 \times 10^{-14} \div [(6.5 \times 10^5) \times (0.32 \times 10^{-5})]$   
 (e)  $[(147 \times 10^{-6}) \div (154 \times 10^{-6})] \div (3.0 \times 10^{12})$

Answers: **C-5:** (a)  $8.7 \times 10^{-8}$     (b)  $4.55 \times 10^{-9}$     (c)  $1.6 \times 10^{-8}$   
 (d)  $1.8 \times 10^6$     (e)  $3 \times 10^{10}$     (f)  $6.02 \times 10^{21}$     **C-6:** (a) 6.6    (b)  $2.00 \times 10^3$   
 (c)  $5.36 \times 10^{-12}$     (d)  $3.9 \times 10^{-17}$     (e)  $3.95 \times 10^{-22}$     **C-7:** (a)  $5 \times 10^{17}$   
 (b)  $3.9 \times 10^{-13}$     (c)  $8 \times 10^{-18}$     (d)  $4.8 \times 10^{-15}$     (e)  $3.2 \times 10^{-13}$

## C-4 Powers and Roots

When a number expressed in scientific notation is raised to a power, the coefficient is raised to the power and the exponent of 10 is *multiplied* by the power.

For a number expressed in scientific notation, we take the root of the coefficient and *divide* the exponent by the root. (A square root is the same as raising the number to the  $1/2$  power, a cube root to the  $1/3$  power, etc.) In the interest of easy viewing in the exercises, we will adjust the number so that division of the exponent by the root produces a whole number. It is not necessary to adjust the number when using a calculator.

### EXAMPLE C-5

#### Powers and Roots

(a) Carry out the following calculation.

$$\begin{aligned} (3.2 \times 10^3)^2 &= (3.2)^2 \times 10^{3 \times 2} \\ &= 10.24 \times 10^6 = \underline{\underline{1.0 \times 10^7}} \end{aligned}$$

$$[(10^3)^2 = 10^3 \times 10^3 = 10 \times 10 \times 10 \times 10 \times 10 \times 10 = 10^6]$$

(b) Carry out the following calculation.

$$\begin{aligned}(1.5 \times 10^{-3})^3 &= (1.5)^3 \times 10^{-3 \times 3} \\ &= \underline{\underline{3.4 \times 10^{-9}}}\end{aligned}$$

(c) Carry out the following calculation.

$$\sqrt{2.9 \times 10^5}$$

### SOLUTION

It is easier to see and do (even if using a calculator) if you first adjust the number so that the exponent of 10 is divisible by 2.

$$\begin{aligned}\sqrt{2.9 \times 10^5} &= \sqrt{29 \times 10^4} = \sqrt{29} \times \sqrt{10^4} = \sqrt{29} \times 10^{4/2} \\ &= \underline{\underline{5.4 \times 10^2}}\end{aligned}$$

(d) Carry out the following calculation.

$$\sqrt[3]{6.9 \times 10^{-8}}$$

### SOLUTION

Adjust the number so that the exponent of 10 is divisible by 3.

$$\begin{aligned}\sqrt[3]{6.9 \times 10^{-8}} &= \sqrt[3]{69 \times 10^{-9}} = \sqrt[3]{69} \times \sqrt[3]{10^{-9}} \\ &= 4.1 \times 10^{-9/3} = \underline{\underline{4.1 \times 10^{-3}}}\end{aligned}$$

## EXERCISES

**C-8.** Carry out the following operations.

(a)  $(6.6 \times 10^4)^2$       (d)  $(0.035 \times 10^{-3})^3$

(b)  $(0.7 \times 10^6)^3$       (e)  $(0.7 \times 10^7)^4$

(c)  $(1200 \times 10^{-5})^2$  (It will be easier to square if you change the number to  $1.2 \times 10^2$  first.)

**C-9.** Take the following roots. Approximate the answer if necessary.

(a)  $\sqrt{36 \times 10^4}$       (c)  $\sqrt{64 \times 10^9}$       (e)  $\sqrt{81 \times 10^{-7}}$

(b)  $\sqrt[3]{27 \times 10^{12}}$       (d)  $\sqrt[3]{1.6 \times 10^5}$       (f)  $\sqrt{180 \times 10^{10}}$

Answers: **C-8:** (a)  $4.4 \times 10^9$       (b)  $3 \times 10^{17}$       (c)  $1.4 \times 10^{-4}$       (d)  $4.3 \times 10^{-14}$

(e)  $2 \times 10^{27}$       **C-9:** (a)  $6.0 \times 10^2$       (b)  $3.0 \times 10^4$       (c)  $2.5 \times 10^5$       (d) 54

(e)  $2.8 \times 10^{-3}$       (f)  $1.3 \times 10^6$

## C-5 Logarithms

Scientific notation is particularly useful in expressing very large or very small numbers. In certain areas of chemistry, however, such as in the expression of  $\text{H}_3\text{O}^+$  concentration, even the repeated use of scientific notation becomes tedious. In this situation, it is convenient to express the concentration as simply the *exponent of 10*. The exponent to which 10 must be raised to give a certain number is called its **common logarithm**. With common logarithms (or just logs) it is possible to express both the coefficient and the exponent of 10 as one number.

Since logarithms are simply exponents of 10, logs of exact multiples of 10 such as 100 can be easily determined. Note that 100 can be expressed as  $10^2$ , so that the log of 100 is exactly 2. Other examples of simple logs of numbers (that we assume to be exact) are

|               |                 |                    |                    |
|---------------|-----------------|--------------------|--------------------|
| $1 = 10^0$    | $\log 1 = 0$    | $0.1 = 10^{-1}$    | $\log 0.1 = -1$    |
| $10 = 10^1$   | $\log 10 = 1$   | $0.01 = 10^{-2}$   | $\log 0.01 = -2$   |
| $100 = 10^2$  | $\log 100 = 2$  | $0.001 = 10^{-3}$  | $\log 0.001 = -3$  |
| $1000 = 10^3$ | $\log 1000 = 3$ | $0.0001 = 10^{-4}$ | $\log 0.0001 = -4$ |

There are two general rules regarding logarithms.

1.  $\log(A \times B) = \log A + \log B$
2.  $\log(A/B) = \log A - \log B$

We can see how these rules apply when we multiply and divide multiples of ten.

|                | Exponents                                 | Logarithms   |
|----------------|---|--|
| multiplication | $10^4 \times 10^3 = 10^{4+3}$<br>$= 10^7$ | $\log(10^4 \times 10^3) = \log 10^4 + \log 10^3$<br>$= 4 + 3 = 7$        |
| division       | $\frac{10^{10}}{10^4} = 10^{10-4} = 10^6$ | $\log \frac{10^{10}}{10^4} = \log 10^{10} - \log 10^4$<br>$= 10 - 4 = 6$ |

Although we will use the calculator (see Appendix E) to determine the logs of numbers that are not simple multiples of ten, such as those above, it is helpful to have a sense of how the log of a specific number will appear. The log of a number has two parts. *The number to the left of the decimal is known as the **characteristic** and represents the exact exponent of 10 in the exponential number. The number to the right of the decimal is known as the **mantissa** and is the log of the coefficient in the exponential number.* For example, consider the log of the following exponential number.

$$\begin{array}{l} \text{Exponential number } 5.7 \times 10^6 \\ (\log 10^6 = 6) + (\log 5.7 = 0.76) \\ \log(5.7 \times 10^6) = \boxed{6.76} \\ \text{characteristic} \qquad \qquad \qquad \text{mantissa} \end{array}$$

Notice that the mantissa should be expressed with the same number of significant figures as the coefficient of the original exponential number. In this case, that is two significant figures.

Logs of numbers between one and ten are positive numbers where the characteristic is a zero (i.e.,  $5.8 = 5.8 \times 10^0$ ). For example,

$$\log 5.8 = \underline{0.76}$$

Logs of numbers greater than ten have a characteristic greater than zero. For example,

$$\log 4.7 \times 10^3 = \underline{3.67}$$

Logs of numbers that are less than one have a negative value since the exponent is a negative value. For example,

|        |   |   |
|--------|---|---|
| number | $0.66 = 6.6 \times 10^{-1}$                   | $7.3 \times 10^{-4}$                                      |
|        | $\log 6.6 + \log 10^{-1}$                     | $\log 7.3 + \log 10^{-4}$                                 |
|        | $\log 0.66 = 0.82 + (-1) = \underline{-0.18}$ | $\log(7.3 \times 10^{-4}) = 0.86 - 4 = \underline{-3.14}$ |

The *antilog* or *inverse log* is the opposite of a logarithm. It is the number whose log has a certain value. For example, consider the antilog ( $x$ ) of 2.

$$\log x = 2 \quad x = \underline{10^2} \quad \text{since } \log 10^2 = 2$$

Since the log of a number between one and ten is a positive number with zero as the characteristic, then the antilog of a number with zero as a characteristic is between one and ten. If the characteristic of a positive number is greater than zero, that number is the exponent of ten and the antilog of the mantissa is the coefficient. For example,

$$\text{antilog } 0.62 = \underline{4.2} \quad \text{antilog } 6.62 = \underline{4.2} \times 10^6$$



The antilog of a negative number is somewhat different. The calculator can only take the antilog of a mantissa with a positive value. To change a mantissa with a negative value to one with a positive value requires a mathematical manipulation. The negative number is separated into its two parts, the mantissa and the characteristic. A value of one is added to the mantissa and a value of one is subtracted from the characteristic. For example, consider the antilogs of  $-3.28$  and  $-0.18$ .

$$\begin{array}{r} \text{Separate} \\ -3.28 = \overbrace{-0.28 - 3} = \overbrace{(-0.28 + 1)} \quad - \quad \overbrace{3 - 1} = +0.72 - 4 \\ \text{Add 1 to} \\ \text{mantissa} \\ \text{Subtract} \\ \text{1 from} \\ \text{characteristic} \end{array}$$

$$\begin{array}{r} -0.18 = -0.18 - 0 = \overbrace{(-0.18 + 1)} \quad - \quad \overbrace{0 - 1} = +0.82 - 1 \end{array}$$

The antilog of the positive number becomes the coefficient of the exponential number, and the antilog of the negative integer becomes the negative exponent of ten. Thus,

$$\begin{aligned} \text{antilog}(-3.28) &= \text{antilog}(0.72) + \text{antilog}(-4) = 5.2 \times 10^{-4} \\ \text{antilog}(-0.18) &= \text{antilog}(0.82) + \text{antilog}(-1) = 6.6 \times 10^{-1} = \underline{0.66} \end{aligned}$$

In the following examples and exercises, we will test our understanding of logs by concentrating on the characteristic of the log or the exponent of ten for an antilog. It is suggested that you do this without the benefit of a calculator. You can then plug the number or the log into your calculator to get the actual answer.

### EXAMPLE C-6

#### Logs

Give the value of the characteristic in the logarithm for each of the following numbers. Use  $xx$  as the mantissa.

- |     |                      |   |   |
|-----|----------------------|---|---|
| (a) | 5.8                  | number between one and ten  | $\log = \underline{0.xx}$                     |
| (b) | $4.7 \times 10^3$    | number greater than ten   | $\log = \underline{3.xx}$                     |
| (c) | 0.085                | number less than one expressed in scientific notation as $8.5 \times 10^{-2}$ | $\log 8.5 + \log 10^{-2} = +0.yy - 2 = -1.xx$ |
| (d) | $8.7 \times 10^{-7}$ | number less than one  | $\log = \underline{-6.xx}$                    |

### EXAMPLE C-7

#### Antilogs

Give the value of the exponent of ten for the number (expressed in scientific notation) whose log is the following. Use  $z.z$  as the value of the coefficient.

- |     |        |  |               |   |
|-----|--------|--|---------------|---|
| (a) | 0.84   | antilog between zero and one               | exponent = 0  | $z.z \times 10^0 = \underline{z.z}$     |
| (b) | 4.65   | antilog greater than one                   | exponent = 4  | $\underline{z.z} \times 10^4$           |
| (c) | -0.020 | antilog less than zero (antilog 0.080 - 1) | exponent = -1 | $z.z \times 10^{-1} = \underline{0.zz}$ |
| (d) | -4.54  | antilog less than zero (antilog 0.46 - 5)  | exponent = -5 | $\underline{z.z} \times 10^{-5}$        |

**EXERCISES**

**C-10.** Give the value of the characteristic in the logarithm for each of the following numbers. Use  $xx$  as the mantissa.

(a) 7.4    (b) 0.087    (c) 1700    (d)  $7.3 \times 10^4$     (e)  $32 \times 10^{-5}$     (f)  $32 \times 10^5$

**C-11.** Give the value of the exponent of ten for the number (expressed in scientific notation) whose log is the following. Use  $z.z$  for the value of the coefficient.

(a) 0.34    (b) -5.48    (c) -0.070    (d) 8.40    (e) 10.94    (f) -2.60

*Answers:* **C-10:** (a) 0.xx    (b) -1.xx    (c) 3.xx    (d) 4.xx    (e) -3.xx

(f) 6.xx    **C-11:** (a)  $z.z$     (b)  $z.z \times 10^{-6}$     (c) 0.zz    (d)  $z.z \times 10^8$

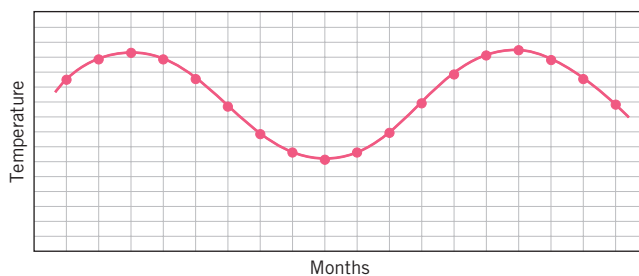
(e)  $z.z \times 10^{10}$     (f)  $z.z \times 10^{-3}$

## GRAPHS

## D-1 Direct Linear Relationships

## D-2 Nonlinear Relationships

The graphical representation of data is important in all branches of science, social as well as natural. Trends and cycles in data may be obscure when presented in a table but become immediately apparent in graphical form. For example, consider a graph in which the average monthly temperature (represented on the vertical axis) is plotted as a function of the month (represented on the horizontal axis). The graph is constructed by marking the temperature for each month and drawing a smooth curve through the points. A quick look at the graph tells us what we already knew—the temperature cycles up and down throughout the seasons.



Useful graphs of this nature were constructed in the Chapter 8 Student Workshop, *Plotting Periodic Trends*. The two graphs illustrate the periodic nature of atomic radius and ionization energy as atomic number increases.

## D-1 Direct Linear Relationships

Other types of graphs can be useful in predicting data as well as simply illustrating measurements. For example, in Appendix B we discussed proportionalities. In a proportionality a variable ( $x$ ) is related to another variable ( $y$ ) by some mathematical operation (a power, a root, a reciprocal, etc.). A graph translates a proportionality into a line that illustrates the relationship of  $x$  to  $y$ . There are two types of graphs: linear and nonlinear. A linear graph is represented by a straight line and is a result of a direct, first-power proportionality between the variables  $x$  and  $y$ . This is expressed as

$$x \propto y$$

Such a graph is illustrated in Figure 10-8, which relates the volume of a gas to the Celsius temperature. Since the data points fall in a straight line, the line can be extended to provide data points beyond the limits of the experiments. (We say the line has been extrapolated.) Using a linear graph, as few as two experiments can be used to predict the results of other measurements.

The relationship between the volume ( $V$ ) of a gas at constant pressure and the Kelvin temperature ( $T$ ) can be expressed as

$$V \propto T$$

We will use this direct relationship to construct a linear graph. The following two experiments provide the information necessary to construct such a graph.

**Experiment 1** At a temperature of 350°C, the volume was 12.5 L.

**Experiment 2** At a temperature of 250°C, the volume was 10.5 L.

Actually, it is always risky to assume that only two experiments provide an accurate graph or give all of the needed information, but for simplicity we will assume that it is valid in this case. We will check the graph with an additional experiment later.

To record this information on a graph, we first need some graph paper with regularly spaced divisions. On the vertical axis (called the ordinate or  $y$  axis) we put temperature. Pick divisions on the graph paper that spread out the range of temperatures as much as possible. In our example, the temperatures range between 250°C and 350°C, or 100 degrees. Note that the two axes do not need to intersect at  $x = y = 0$ . We then plot the volume on the horizontal axis (called the abscissa or  $x$  axis). The volumes range between 12.5 L and 10.5 L, or 2.0 L.

The graph is shown in Figure D-1. Dots mark the locations of the two points from the experiments, and a straight line has been drawn between them.

We can now check the accuracy of our graph. A third experiment tells us that at  $T = 300^\circ\text{C}$ ,  $V = 11.5$  L. Refer back to the graph. Locate 300°C on the ordinate and trace that line to where it intersects the vertical line representing the volume of 11.5 L. Since the point of intersection is right on the line, we have confirmation of the accuracy of the original plot. *Normally, four or five measurements are required to provide enough points on the graph so that a line can be drawn through or as near as many points as possible.*

A straight line graph can be expressed by the linear algebraic equation

$$y = mx + b$$

where  $y$  = a value on the ordinate

$x$  = the corresponding value on the abscissa

$b$  = the point on the  $y$  axis or ordinate where the straight line intersects the axis

$m$  = the slope of the line

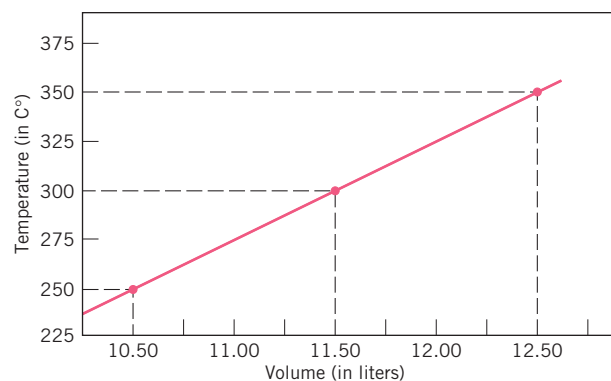
The slope of a line is the ratio of the change on the ordinate to the change on the abscissa. It is determined by choosing two widely spaced points on the line ( $x_1, y_1$  and  $x_2, y_2$ ). The slope is the difference in  $y$  divided by the difference in  $x$ .

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

The larger the slope *for a particular graph*, the steeper the straight line. For the graph shown in Figure D-1, if we pick point 1 to be  $x_1 = 10.50$ ,  $y_1 = 250$  and point 2 to be  $x_2 = 12.50$ ,  $y_2 = 350$ , then

$$m = \frac{350 - 250}{12.50 - 10.50} = \frac{100}{2.00} = 50.0$$

The value for  $b$  cannot be determined directly from Figure D-1. The value for  $b$  is found by determining the point on the  $y$  axis where the line intersects when  $x = 0$ .



**Figure D-1**  
The Volume of a Gas as a Function of Temperature.

If we plotted the data on such a graph, we would find that  $b = -273^{\circ}\text{C}$ . Therefore, the linear equation for this line is

$$y = 50.0x - 273$$

From this equation we can determine the value for  $y$  (the temperature) by substitution of any value for  $x$  (the volume).

### EXERCISES

**D-1.** A sample of water was heated at a constant rate, and its temperature was recorded. The following results were obtained.

| Experiment | Temp ( $^{\circ}\text{C}$ ) | Time (min) |
|------------|-----------------------------|------------|
| 1          | 10.0                        | 0          |
| 2          | 20.0                        | 4.5        |
| 3          | 30.0                        | 7.5        |
| 4          | 55.0                        | 17.8       |
| 5          | 85.0                        | 30.0       |

- Construct a graph that includes all of the information above with temperature on the ordinate and time on the abscissa.
- Calculate the slope of the line and the linear equation  $y = mx + b$  for the line.
- From the graph find the temperature at 11.0 min and compare it with the value calculated from the equation.
- From the graph find the time when the temperature is  $65.0^{\circ}\text{C}$  and compare it with the value calculated from the equation.

*Answers:* (a) Draw the line touching or coming close to as many points as possible. Note that the straight line does not go through all points. (b)  $m = 2.5$ ,  $y = 2.5x + 10$  (c) From the equation, when  $x = 11.0$ ,  $y = 2.5 \cdot 11.0 + 10$ , so  $y = 37.5^{\circ}\text{C}$ . The graph agrees. (d) From the equation, when  $y = 65$ ,  $65 = 2.5x + 10$ , and  $x = 22.0$  min. The graph agrees.

## D-2 Nonlinear Relationships

Nonlinear graphs are represented by a curved line and result from an inverse proportionality, or any type of proportionality other than direct. Examples of such relationships can be expressed as

$$x \propto y^2 \quad \text{and} \quad x \propto \frac{1}{y}$$

An example of an inverse relationship that produces a curve when plotted is the relationship between volume of a gas ( $V$ ) at constant temperature and the pressure ( $P$ ). The relationship is

$$V \propto \frac{1}{P}$$

In the following experiments the pressure on a volume of gas was varied and the volume was measured at constant temperature.

| Experiment | Pressure (torr) | Volume (L) |
|------------|-----------------|------------|
| 1          | 500             | 15.2       |
| 2          | 600             | 12.6       |
| 3          | 760             | 10.0       |
| 4          | 900             | 8.44       |
| 5          | 1200            | 6.40       |
| 6          | 1600            | 4.80       |

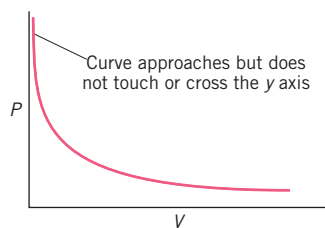


Figure D-3

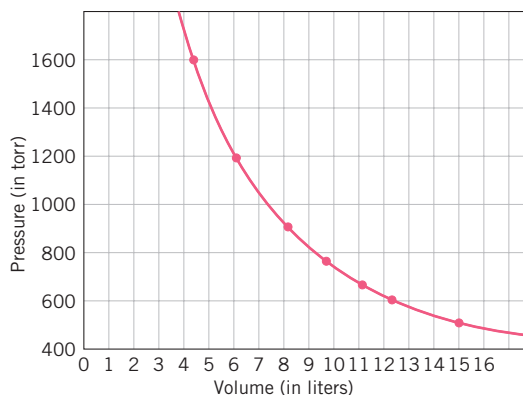


Figure D-2 An Inverse Relationship—The Volume of a Gas as a Function of Pressure

This information has been graphed in Figure D-2. Note that the line has a gradually changing slope, starting with a very steep slope on the left and going to a small slope on the right of the graph. We can interpret this. In the region of the steep slope, the increase in pressure causes little decrease in volume compared with the part of the curve with the small slope to the right. Note that this is a plot of an inverse relationship. That is, the higher the pressure, the lower the volume. If we regraph the information and include much higher pressures and the corresponding volumes, as shown in Figure D-3, we see that *the curve approaches the y axis but never actually touches it*, no matter how high the pressure. Such a curve is said to approach the axis **asymptotically**. In our example, the curve would eventually appear to change to a vertical line parallel to the y axis.

### EXERCISES

**D-2.** Construct a graph from the following experimental information. Plot the time on the abscissa and the concentration on the ordinate. Describe what this graph tells you about the change in concentration of HI as a function of (how it varies with) the time.

| Experiment | Time (min) | Concentration of HI (mol/L) |
|------------|------------|-----------------------------|
| 1          | 0.0        | $2.50 \times 10^{-2}$       |
| 2          | 5.0        | $1.50 \times 10^{-2}$       |
| 3          | 10.0       | $0.90 \times 10^{-2}$       |
| 4          | 15.0       | $0.65 \times 10^{-2}$       |
| 5          | 20.0       | $0.55 \times 10^{-2}$       |
| 6          | 35.0       | $0.50 \times 10^{-2}$       |

- (a) From the graph, find the concentration of HI at 12.0 min and at 25 min.  
 (b) From the graph, find the times at which the concentration of HI is  $2.00 \times 10^{-2}$  and  $0.75 \times 10^{-2}$ .

*Answers:* The concentration decreases rapidly at the start (the curve has a large slope) but then changes little after about 25 min. At that point the curve appears to change to a straight line parallel to the x axis. (a) At 12.0 min, the concentration is  $0.80 \times 10^{-2}$  mol/L; at 25 min, the concentration is about  $0.52 \times 10^{-2}$  mol/L. (b) When the concentration is  $2.00 \times 10^{-2}$  mol/L, the time is 2.4 min; when the concentration is  $0.75 \times 10^{-2}$  mol/L, the time is 13.0 min.



## CALCULATORS

## E-1 Addition, Subtraction, Multiplication, and Division

## E-2 Chain Calculations

## E-3 Scientific Notation

## E-4 Powers, Roots, Logs, and Antilogs

An inexpensive hand calculator has become a necessity for almost all chemistry students. The convenience of this handy instrument is undeniable. Calculations are easy, quick, and accurate. In a way, however, use of calculators creates the risk that we may lose the ability to add, multiply, and divide simple numbers on our own. It is sad for an instructor to see students pull out their calculators when the only exercise is to multiply a number by 10. This appendix is included last because it is hoped that students will first review math operations, scientific notation, and logs before using the calculator. Obviously, it is easy to become overly dependent on the calculator, but it is here to stay.

There are two basic types of hand calculators. Almost all inexpensive hand calculators now in use have a logic system known as Algebraic Operating System (AOS). A few students may have calculators that use a system called Reverse Polish Notation (RPN). Calculators using this system have a key labeled “ENTER.” In this appendix, we will describe use of the more common AOS system. If your calculator uses the RPN system, consult your instruction book.

Different brands of calculators vary as to the number of digits shown in the answer, the labeling of some functions, and, of course, the number of functions available. You should consult the instruction booklet for more details. In this appendix, we concentrate on the types of calculations that you will encounter in general chemistry courses. This should save time and confusion when reading through an often complicated instruction booklet. Calculations encountered in chemistry include powers, logs, and scientific notation. Recall that the calculator usually gives at least six digits in an answer. This is almost always far too many for the result of a chemical calculation. You must know how to express the answer to the proper number of significant figures (see section 1-2). A chemistry teacher is not impressed with a student who reports a pH of 8.678346 for a calculation made from a two-significant-figure number. Reporting more numbers than necessary makes an answer look worse, not better.

## E-1 Addition, Subtraction, Multiplication, and Division

In one-step calculations, you simply enter one number and then tell the calculator what you want it to do with the next number (i.e., +, −, ×, or ÷). You then enter the next number and ask for the answer (i.e., press the = key). The following examples illustrate simple one-step calculations.

## EXAMPLE E-1

## One-Step Calculations

(a)  $6.368 + 43.852$

(b)  $0.0835 \div 37.2$

| Enter  | Display | Enter  | Display                  |
|--------|---------|--------|--------------------------|
| 6.368  | 6.368   | 0.0835 | 0.0835                   |
| +      | 6.368   | ÷      | 0.0835                   |
| 43.852 | 43.852  | 37.2   | 37.2                     |
| =      | 50.22   | =      | 2.2446237 <sup>-03</sup> |

The answer in (a) should be reported as 50.220 to indicate the proper number of decimal places. A calculator does not include zeros that are to the right of the last digit. Our calculator did not realize that the last zero is significant.

The answer in (b) includes a superscript  $-03$ , which is the power of 10. We should report this answer to three significant figures in the form  $2.24 \times 10^{-3}$  or 0.00224.

## E-2 Chain Calculations

One of the most convenient features of the modern hand calculator allows us to do a series of calculations without pausing. For example, many gas law problems require successive calculations as illustrated in the following example.

### EXAMPLE E-2

#### Chain Calculations

(a) Solve the following problem.

$$n = \frac{PV}{RT} = \frac{0.749 \times 7.22}{0.0821 \times 312} = \text{_____ mol}$$

| Enter  | Display                |
|--------|------------------------|
| 0.749  | 0.749                  |
| ×      | 0.749                  |
| 7.22   | 7.22                   |
| ÷      | 5.40778                |
| 0.0821 | 0.0821                 |
| ÷      | 65.86821               |
| 312    | 0.211116               |
|        | Report as <u>0.211</u> |

You can do this problem in other sequences. For example, you could just as easily carry out the calculation in the following sequence:  $(0.749 \div 0.0821) \times 7.22 \div 312 = 0.211$ . One sequence that you *cannot do* is to multiply the numerator ( $0.74 \times 7.22$ ) and then divide by 0.0821 *times* 312. The final calculation must again be a division by 312. To calculate the formula weight of a compound, the atomic masses are multiplied by the number of atoms and the masses totaled. This is illustrated as follows.

(b) Find the formula weight of  $B_2O_3$ .

$$\text{Formula weight} = (2 \times 10.8) + (3 \times 16.0) = \text{_____ amu.}$$

| Enter | Display     |
|-------|-------------|
| 2     | 2           |
| ×     | 2           |
| 10.8  | 10.8        |
| +     | 21.6        |
| 3     | 3           |
| ×     | 3           |
| 16.0  | 16.0        |
| =     | <u>69.6</u> |

When a negative number is part of a calculation (i.e.,  $2 \times -6$ ), the  $+/-$  key or equivalent must be pressed after the 6 is entered. The display should now read  $-6$ , and you can proceed with the calculation.

Some calculations require the use of the parentheses functions which are included on most calculators. These usually involve summations of other operations or summations in a numerator or denominator. For example, consider the following calculation.

$$\frac{7 + 5 + 6}{8}$$

First, press “(” or “[(-” then  $7 + 5 + 6$  followed by “)” or “—]”. Next press “ $\div$ ” then 8 then “=” or “exe” to obtain the answer of 2.25.

Next, consider the calculation

$$(37 \times 56) + \frac{150 \times 10}{2}$$

Each operation must be included within a parenthesis. Carry out the calculation in the order “ $(37 \times 56)$ ” + “ $(\frac{150 \times 10}{2})$ ” = 2822.

## EXERCISES

**E-1.** Perform the following calculations.

(a)  $0.662 \times 7.99$

(b)  $73.8 + 0.27 + 45.8$

(c)  $43.8 - 178.34$

(d)  $7.3 + 8.5 - (-3.4)$

(e)  $\frac{46.8 \times 23.4}{0.00786}$

(f)  $\frac{172 + 67 - 89}{55}$

(g)  $(4 \times 14.006) + (3 \times 15.998) + (6 \times 1.008)$

(h)  $(0.810 \times 102.99) + (0.190 \times 104.88)$

Answers: (a) 5.29 (b) 119.9 (c)  $-134.5$  (d) 19.2 (e) 139000 (f) 2.7

(g) 110.066 (h) 103

## E-3 Scientific Notation

Most calculators have the capacity to easily handle scientific notation. This is done with a key marked EE, EXP, or EEX. The coefficient is entered first; then the exponent key is pressed and the exponent entered. If it is a negative exponent, one must press the  $+/-$  key to change the sign. The following examples illustrate the use of scientific notation in typical calculations.

### EXAMPLE E-3

#### Scientific Notation

Carry out the following calculations.

(a)  $\frac{0.250 \times (6.02 \times 10^{23})}{1.55}$

(b)  $\frac{3.76 \times 10^{-18}}{0.862 \times 10^6}$

| Enter | Display                         |    | Enter | Display                          |     |
|-------|---------------------------------|----|-------|----------------------------------|-----|
| 0.250 | 0.250                           |    | 3.76  | 3.76                             |     |
| ×     | 0.25                            |    | EXP   | 3.76                             | 00  |
| 6.02  | 6.02                            |    | 18    | 3.76                             | 18  |
| EXP   | 6.02                            | 00 | +/-   | 3.76                             | -18 |
| 23    | 6.02                            | 23 | ÷     | 3.76                             | -18 |
| ÷     | 1.505                           | 23 | 0.862 | 0.862                            |     |
| 1.55  | 1.55                            |    | EXP   | 0.862                            | 00  |
| =     | 9.71                            | 22 | 6     | 0.862                            | 06  |
|       | <u>(9.71 × 10<sup>22</sup>)</u> |    | =     | 4.36                             | -24 |
|       |                                 |    |       | <u>(4.36 × 10<sup>-24</sup>)</u> |     |

## E-4 Powers, Roots, Logs, and Antilogs

These are all one-step calculations that require a special function on the calculator. On some calculators a direct key function is not available. However, notice that there are other functions listed above the key that are accessed by pressing the inverse (INV) or second (2nd) keys. For example, an  $x^2$  key is not available on some calculators, but the function is obtained by pressing the INV key first and then the  $\sqrt{x}$  key. The square is the inverse of the square root. On one calculator, the cube root of a number  $\sqrt[3]{x}$  is the inverse of the +/- key. On this calculator, the cube of the number must be obtained by first squaring the number, then multiplying the number again. On another calculator, taking the cube root is the same as raising the number to the 1/3 power. There are several variations of how cube functions are presented, and you should experiment with your own calculator in this regard.

There is also variation in the order of operations. For example, some calculators require that you press the " $\sqrt{\quad}$ " (square root) or the "log" signs first, then the number, followed by "=" or "exe."

### EXAMPLE E-4

#### Roots and Powers

Carry out the following calculations.

(a)  $(6.2)^2$

(b)  $(6.2)^3$

(c)  $\sqrt{6.2}$

(d)  $\sqrt[3]{6.2}$

| Enter      | Display      | Enter | Display        | Enter      | Display     | Enter | Display      |
|------------|--------------|-------|----------------|------------|-------------|-------|--------------|
| 6.2        | 6.2          | 6.2   | 6.2            | 6.2        | 6.2         | 6.2   | 6.2          |
| INV        | 6.2          | $x^y$ | 6.2            | $\sqrt{x}$ | <u>2.49</u> | INV*  | 6.2          |
| $\sqrt{x}$ | <u>38.44</u> | 3     | 3              |            |             | $x^y$ | 6.2          |
|            |              | =     | <u>238.328</u> |            |             | 3     | 3            |
|            |              |       |                |            |             | =     | <u>1.837</u> |

\*INV  $x^y$  is the same as  $x^{1/y}$

**EXAMPLE E-5****Logs and Antilogs**

Find the following logs (common) and antilogs.

**(a)**  $\log 35.6$

**(b)**  $\log 4.88 \times 10^{-9}$

**(c)** the antilog of  $-3.876$

| Enter | Display     |
|-------|-------------|
| 35.6  | 35.6        |
| log   | <u>1.55</u> |

| Enter | Display       |
|-------|---------------|
| 4.88  | 4.88          |
| EXP   | 4.88 00       |
| 9     | 4.88 09       |
| +/-   | 4.88 -09      |
| log   | <u>-8.312</u> |

| Enter | Display                                    |
|-------|--|
| 3.876 | 3.876                                      |
| +/-   | -3.876                                     |
| INV   | -3.876                                     |
| log   | 0.000133 or<br><u>1.3304<sup>-04</sup></u> |

**EXERCISES****E-2.** Perform the following calculations on your calculator.

**(a)**  $0.230^2$

**(g)** the log of 0.0257

**(b)**  $\sqrt{6.80 \times 10^{-3}}$

**(h)** the log of 567

**(c)**  $\sqrt[3]{0.986}$

**(i)** the antilog of 0.665

**(d)**  $(3.60)^4$

**(j)** the antilog of 2.977

**(e)**  $\sqrt[5]{4.32 \times 10^6}$

**(k)** the antilog of  $-4.005$

**(f)** the log of 8.33

*Answers:* (given to three significant figures): **(a)** 0.0529 **(b)** 0.0825 **(c)** 0.995

**(d)** 168 **(e)** 21.2 **(f)** 0.921 **(g)**  $-1.590$  **(h)** 2.754 **(i)** 4.62 **(j)** 948

**(k)**  $9.89 \times 10^{-5}$

## GLOSSARY

The numbers in parentheses at the end of each entry refer to the chapter in which the entry is first discussed plus any chapter in which the topic is discussed in detail.

## A

- absolute zero.** The lowest possible temperature. The temperature at which translational motion ceases. Defined as zero on the Kelvin scale. (1, 10)
- accuracy.** How close a measurement is to the true value. (1)
- acid.** A compound that increases the  $\text{H}^+$  concentration in aqueous solution. In the Brønsted definition, an acid is a proton donor. (4, 5, 13, 15)
- acid anhydride.** A molecular oxide that dissolves in water to form an oxyacid. (13)
- acid ionization constant ( $K_a$ ).** The equilibrium constant specifically for the ionization of a weak acid. The magnitude of the constant relates to the strength of the acid. (15)
- acid salt.** An ionic compound containing one or more acidic hydrogens on the anion. (13)
- acidic solution.** A solution with  $\text{pH} < 7$  or  $[\text{H}_3\text{O}^+] > 10^{-7}$  M. (13)
- actinide.** One of the 14 elements between Ac and Rf. An element whose  $5f$  subshell is filling. (4, 8)
- activated complex.** The transition state formed at the instant of maximum impact between reacting molecules. (15)
- activation energy.** The minimum energy needed by reactant molecules to form an activated complex so that a reaction may occur. It is the difference in potential energy between the reactants and the activated complex. (15)
- activity series.** The ability of metals to replace other metal ions can be compared and ranked in an activity series. (5)
- actual yield.** The measured amount of product in a chemical reaction. (7)
- alkali metal.** An element in Group IA in the periodic table (except H). Elements with the electron configuration  $[\text{NG}]ns^1$ . (4, 8)
- alkaline earth metal.** An element in Group IIA in the periodic table. Elements with the electron configuration  $[\text{NG}]ns^2$ . (4, 8)
- allotropes.** Different forms of the same element. (9)
- alloy.** A homogeneous mixture of metallic elements in one solid phase. (3)

- alpha ( $\alpha$ ) particle.** A helium nucleus ( $\frac{4}{2}\text{He}^{2+}$ ) emitted from a radioactive nucleus. (2, 16)
- amorphous solid.** A solid without a defined shape. The molecules in such a solid do not occupy regular, symmetrical positions. (11)
- amphiprotic.** Refers to a molecule or ion that has both a conjugate acid and a conjugate base. (13)
- anion.** A negatively charged ion. (2)
- anode.** The electrode at which oxidation takes place. (14)
- atmosphere.** The sea of gases above the surface of Earth. Also, the average pressure of the atmosphere at sea level, which is defined as the standard pressure and is abbreviated atm. (10)
- atom.** The smallest fundamental particle of an element that has the properties of that element. (2)
- atomic mass.** The weighted average of the isotopic masses of all of the naturally occurring isotopes of an element. The mass of an “average” atom of a naturally occurring element compared to  $^{12}\text{C}$ . (2)
- atomic mass unit (amu).** A mass that is exactly one-twelfth of the mass of an atom of  $^{12}\text{C}$ , which is defined as exactly 12 amu. (2)
- atomic number.** The number of protons (positive charge) in the nuclei of the isotopes of a particular element. (2)
- atomic radius.** The distance from the nucleus of an atom to the outermost electron. (8)
- atomic theory.** A theory first proposed by John Dalton in 1803 that holds that the basic components of matter are atoms. (2)
- Aufbau principle.** A rule that states that electrons fill the lowest available energy level first. (8)
- autoionization.** The dissociation of a solvent to produce positive and negative ions. (13)
- Avogadro's law.** A law that states that the volume of a gas is directly proportional to the number of moles of gas present at constant temperature and pressure (i.e.,  $V = kn$ ). (10)
- Avogadro's number.** The number of objects or particles in one mole, which is  $6.022 \times 10^{23}$ . (6)

## B

- balanced equation.** A chemical equation that has the same number and type of atoms on both sides of the equation. (5)
- barometer.** A device that measures the atmospheric pressure. (10)



**base.** A compound that increases the  $\text{OH}^-$  concentration in aqueous solution. In the Brønsted definition, a base is a proton acceptor. (5, 13)

**base anhydride.** An ionic oxide that dissolves in water to form an ionic hydroxide. (13)

**base ionization constant ( $K_b$ ).** An equilibrium constant specifically for the ionization of a weak base. The magnitude of the constant relates to the strength of the base. (15)

**basic solution.** A solution with  $\text{pH} > 7$  or  $[\text{OH}^-] > 10^{-7}$  M. (13)

**battery.** One or more voltaic cells joined together as a single unit. (14)

**beta ( $\beta$ ) particle.** A high-energy electron emitted from a radioactive nucleus. (16)

**binary acid.** An acid composed of hydrogen and one other element. (4)

**Bohr model.** A model of the atom in which electrons orbit around a central nucleus in discrete energy levels. (8)

**boiling point.** The temperature at which a pure substance changes from the liquid to the gaseous state. (3) It is the temperature at which the vapor pressure equals the restraining pressure. (11, 12)

**box diagram.** See *orbital diagram*.

**Boyle's law.** A law that states that the volume of a gas is inversely proportional to the pressure at constant temperature (i.e.,  $PV = k$ ). (10)

**Brønsted-Lowry definition.** Acids are proton donors and bases are proton acceptors. (13)

**buffer solution.** A solution that resists changes in pH from the addition of limited amounts of strong acid or base. Made from a solution of a weak acid and a salt containing its conjugate base, or a weak base and a salt containing its conjugate acid. (13)

## C

**calorie.** The amount of heat required to raise the temperature of one gram of water one degree Celsius. Equal to exactly 4.184 joules. (3)

**catalyst.** A substance that is not consumed in a reaction but whose presence increases the rate of the reaction. A catalyst lowers the activation energy. (15)

**cathode.** The electrode at which reduction takes place. (14)

**cation.** A positively charged ion. (2)

**Celsius.** A temperature scale with 100 equal divisions between the freezing and boiling points of water at average sea level pressure, with exactly zero assigned to the freezing point of water. (1)

**chain reaction.** A self-sustaining reaction. In a nuclear chain reaction, one reacting neutron produces between two and three other neutrons that in turn cause reactions. (16)

**Charles's law.** A law that states that the volume of a gas is directly proportional to the Kelvin temperature at constant pressure (i.e.,  $V = kT$ ). (10)

**chemical change.** A change in a substance to another substance or substances. (3)

**chemical equation.** The representation of a chemical reaction using the symbols of the elements and the formulas of compounds. (5)

**chemical property.** The property of a substance relating to its tendency to undergo chemical changes. (3)

**chemical thermodynamics.** The study of heat and its relationship to chemical changes. (7)

**chemistry.** The branch of science dealing with the nature, composition, and structure of matter and the changes it undergoes. (3)

**coefficient.** The number in scientific notation which is raised to a power of ten. (1) The number before an element or compound in a balanced chemical equation indicating the number of molecules or moles of that substance. (7)

**colligative property.** A property that depends only on the relative amounts of solute and solvent present, not on their identities. (12)

**collision theory.** A theory that states that chemical reactions are brought about by collisions of molecules. (15)

**combination reaction.** A chemical reaction whereby one compound is formed from two elements and/or compounds. (5)

**combined gas law.** A law that relates the pressure, volume, and temperature of a gas (i.e.,  $PV = kT$ ). (10)

**combustion reaction.** A chemical reaction whereby an element or compound reacts with elemental oxygen. (5)

**compound.** A pure substance composed of two or more elements that are chemically combined in fixed proportions. (2)

**concentrated solution.** A solution containing a relatively large amount of a specified solute per unit volume. (12)

**concentration.** The amount of solute present in a specified amount of solvent or solution. (12)

**condensation point.** The temperature at which a pure substance changes from the gas to the liquid or solid state. (3, 11)

**conductor.** A substance that allows a flow of electricity. (12)

**conjugate acid.** An acid formed by addition of one  $\text{H}^+$  to a base. (13)

**conjugate base.** A base formed by removal of one  $\text{H}^+$  from an acid. (13)

**conservation of energy.** A law that states that energy is neither created nor destroyed but can be transformed from one form to another. (3)

**conservation of mass.** A law that states that matter is neither created nor destroyed in a chemical reaction. (3)

**continuous spectrum.** The visible spectrum where one color blends gradually into another. A spectrum containing all wavelengths of visible light. (8)

**conversion factor.** A relationship between two units or quantities expressed in fractional form. (1)

**covalent bond.** The force that bonds two atoms together by a shared pair or pairs of electrons. (2, 9)

**crystal lattice.** See *lattice*.

**crystalline solid.** A solid with a regular, symmetrical shape where the molecules or ions occupy set positions in the crystal lattice. (11)

## D

**Dalton's law.** A law that states that the total pressure of a gas in a system is the sum of the partial pressures of all component gases. (10)

**Daniell cell.** A voltaic cell made up of zinc and copper electrodes immersed in solutions of their respective ions that are connected by a salt bridge. (14)

**decomposition reaction.** A chemical reaction whereby one compound decomposes to two or more elements and/or compounds. (5)

**density.** The ratio of the mass (usually in grams) to the volume (usually in milliliters or liters) of a substance. (3)

**diffusion.** The mixing of one gas or liquid into others. (10)

**dilute solution.** A solution containing a relatively small amount of a specified solute per unit volume. (12)

**dilution.** The preparation of a dilute solution from a concentrated solution by the addition of more solvent. (12)

**dimensional analysis.** See *factor-label method*.

**dipole.** Two poles—one positive and one negative—that may exist in a bond or molecule. (9)

**dipole–dipole attractions.** The force of attraction between a dipole on one polar molecule and a dipole on another polar molecule. (11)

**diprotic acid.** An acid that can produce two  $H^+$  ions per molecule. (13)

**discrete spectrum.** A spectrum containing specific wavelengths of light originating from the hot gaseous atoms of an element. (8)

**distillation.** A laboratory procedure where a solution is separated into its components by boiling the mixture and condensing the vapor to form a liquid. (3)

**double bond.** The sharing of two pairs of electrons between two atoms. (8)

**double-replacement reaction.** A chemical reaction whereby the cations and anions in two compounds exchange, leading to formation of either a precipitate or a molecular compound such as water. (5)

**dry cell.** A voltaic cell composed of zinc and graphite electrodes immersed in an aqueous paste of  $NH_4Cl$  and  $MnO_2$ . (14)

**dynamic equilibrium.** See *point of equilibrium*.

## E

**effusion.** The movement of gases through an opening or hole. (10)

**electricity.** A flow of electrons through a conductor. (14)

**electrode.** A surface in a cell where the oxidation or reduction reaction takes place. (14)

**electrolysis.** The process of forcing electrical energy through an electrolytic cell, thereby causing a chemical reaction. (14)

**electrolyte.** A solute whose aqueous solution or molten state conducts electricity. (12)

**electrolytic cell.** A voltaic cell that converts electrical energy into chemical energy by means of a nonspontaneous reaction. (14)

**electron.** A negatively charged particle in an atom, with a comparatively very small mass. (2)

**electron capture.** The capture of an orbital electron by a radioactive isotope. (16)

**electron configuration.** The designation of all of the electrons in an atom into specific shells and subshells. (8)

**electronegativity.** The ability of the atoms of an element to attract electrons in a covalent bond. (7)

**electrostatic forces.** The forces of attraction between unlike charges and of repulsion by like charges. (2)

**element.** A pure substance that cannot be broken down into simpler substances. The most basic form of matter existing under ordinary conditions. (2)

**empirical formula.** The simplest whole-number ratio of atoms in a compound. (6)

**endothermic reaction.** A chemical reaction that absorbs heat from the surroundings. (3, 7, 15)

**energy.** The capacity or the ability to do work. It has several different forms (e.g., light and heat) and two types (kinetic and potential). (3)

**equilibrium.** See *point of equilibrium*.

**equilibrium constant.** A number that defines the position of equilibrium for a particular reaction at a specified temperature. (15)

**equilibrium constant expression.** The ratio of the concentrations of products to reactants, each raised to the power corresponding to its coefficient in the balanced equation. (15)

**equilibrium vapor pressure.** The pressure exerted by a vapor above a liquid at a certain temperature. (11)

**evaporation.** The vaporization of a liquid below its boiling point. (11)

**exact number.** A number that results from a definition or an actual count. (1)

**excited state.** An energy level higher than the lowest available energy level. (8)

**exothermic reaction.** A chemical reaction that occurs with the evolution of heat to the surroundings. (3, 7, 15)

**exponent.** In scientific notation, it is the power to which ten is raised. (1)

## F

**factor-label method.** A problem-solving technique that converts from one unit to another by use of conversion factors. (1)

**Fahrenheit.** A temperature scale with 180 divisions between the freezing and boiling points of water, with exactly 32 assigned to the freezing point of water. (1)

**family.** See *group*.

**filtration.** A laboratory procedure where solids are removed from liquids by passing the heterogeneous mixture through a filter. (3)

**fission.** The splitting of a large, unstable nucleus into two smaller nuclei of similar size, resulting in the production of energy. (16)

**formula.** The symbols of the elements and the number of atoms of each element that make up a compound. (2)

**formula unit.** The simplest whole-number ratio of ions in an ionic compound. (2)

**formula weight.** The mass of a compound (in amu), which is determined from the number of atoms and the atomic masses of the elements indicated by the formula. (6)

**freezing point.** The temperature at which a pure substance changes from the liquid to the solid state. (3, 12)

**fuel cell.** A voltaic cell that can generate a continuous flow of electricity from the reaction of hydrogen and oxygen to produce water. (14)

**fusion (nuclear).** The combination of two small nuclei to form a larger nucleus, resulting in the production of energy. (16)

## G

**gamma ( $\gamma$ ) ray.** A high-energy form of light emitted from a radioactive nucleus. (16)

**gas.** A physical state that has neither a definite volume nor a definite shape and fills a container uniformly. (3, 10)

**gas constant.** The constant of proportionality ( $R$ ) in the ideal gas law. (10)

**gas law.** A law governing the behavior of gases that is consistent with the kinetic molecular theory as applied to gases. (10)

**Gay-Lussac's law.** A law that states that the pressure of a gas is directly proportional to the Kelvin temperature at constant volume (i.e.,  $P = kT$ ). (10)

**Graham's law.** A law that states that the rates of diffusion of gases are inversely proportional to the square root of their molar masses. (10)

**ground state.** The lowest available energy level in an atom. (8)

**group.** A vertical column of elements in the periodic table. (4)

## H

**half-life.** The time required for one-half of a given sample of an isotope to undergo radioactive decay. (16)

**half-reaction.** The oxidation or reduction process in a redox reaction written separately. (14)

**halogen.** An element in Group VIIA in the periodic table. Elements with the electron configuration  $[\text{NG}] ns^2 np^5$ . (4, 8)

**heat of fusion.** The amount of heat in calories or joules required to melt one gram of a substance. (11)

**heat of reaction.** The amount of heat energy absorbed or evolved in a specified chemical reaction. (7)

**heat of vaporization.** The amount of heat in calories or joules required to vaporize one gram of the substance. (11)

**heating curve.** The graphical representation of the temperature as a solid is heated through two phase changes, plotted as a function of the time of heating. (11)

**Henderson-Hasselbalch equation.** Equations that are used to calculate the pH of buffer solutions

$$\left( \text{i.e., } \text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}; \text{pOH} = \text{p}K_b + \log \frac{[\text{acid}]}{[\text{base}]} \right). \quad (15)$$

**heterogeneous mixture.** A nonuniform mixture containing two or more phases with definite boundaries between phases. (3)

**homogeneous mixture.** A mixture that is the same throughout and contains only one phase. (3)

**Hund's rule.** A rule that states that electrons occupy separate orbitals with parallel spins if possible. (8)

**hydrogen bonding.** A force of attraction between a N, O, or F atom on one molecule and a hydrogen bonded to a N, O, or F atom on another. (11)

**hydrolysis reaction.** The reaction of an anion as a base with water or a cation as an acid. (13)

**hydronium ion.** A representation of the hydrogen ion in aqueous solution ( $\text{H}_3\text{O}^+$ ). (13)

**hypothesis.** A tentative explanation of related data. It can be used to predict results of more experiments. (Prologue)

## I

**ideal gas.** A hypothetical gas whose molecules are considered to have no volume or interactions with each other. An ideal gas would obey the ideal gas law under all conditions. (10)

**ideal gas law.** A relationship between the pressure, volume, temperature, and number of moles of gas (i.e.,  $PV = nRT$ ). (10)

**immiscible liquids.** Two liquids that do not mix and thus form a heterogeneous mixture. (12)

**improper fraction.** A fraction whose numerator is larger than the denominator and thus has a value greater than one. (Appendix A)

**infrared light.** Light with wavelengths somewhat longer than those of red light in the visible spectrum. (8)

**inner transition element.** Either a lanthanide, where the  $4f$  subshell is filling, or an actinide, where the  $5f$  subshell is filling. (4, 8)

**insoluble compound.** A compound that does not dissolve to any appreciable amount in a solvent. (5)

**insulator.** See *nonconductor*.

**intermolecular forces.** The attractive forces between molecules. (11)

**ion.** An atom or group of covalently bonded atoms that has a net electrical charge. (2)

**ion product ( $K_w$ ).** The equilibrium expression of the anion and the cation of water (i.e.,  $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$ ). (13)

**ion-dipole force.** The force between an ion and the dipole of a polar molecule. (12)

**ion-electron method.** A method of balancing oxidation-reduction reactions where two half-reactions are balanced separately and then added. (14)

**ionic bond.** The electrostatic force holding the positive and negative ions together in an ionic compound. (2, 9)

**ionic compound.** Compounds containing positive and negative ions. (2)

**ionic solid.** A solid where the crystal lattice positions are occupied by ions. (11)

**ionization.** The process of forming an ion or ions from a molecule or atom. (8, 12, 13, 16)

**ionization energy.** The energy required to remove an electron from a gaseous atom or ion. (8)

**isotopes.** Atoms having the same atomic number but different mass numbers. (2)

**isotopic mass.** The mass of an isotope compared to  $^{12}\text{C}$ , which is defined as having a mass of exactly 12 amu. (2)

## J

**joule.** The SI unit for measurement of heat energy. (3)

## K

**Kelvin scale.** A temperature scale in which 0 K is the lowest possible temperature.  $T(\text{K}) = T(^{\circ}\text{C}) + 273$ . (1, 10)

**kinetic energy.** Energy as a result of motion; equal to  $\frac{1}{2}mv^2$  (3, 11)

**kinetic molecular theory.** A theory advanced in the late 1800s to explain the nature of gases. (10)

## L

**lanthanide.** One of fourteen elements between La and Hf. Elements whose 4f subshell is filling. (4, 8)

**lattice.** A three-dimensional array of ions or molecules in a solid crystal. (9)

**law.** A concise statement or mathematical relationship that describes some behavior of matter. (Prologue)

**Law of conservation of energy.** A law that states that energy cannot be created or destroyed but only transformed from one form to another. (3)

**Law of conservation of mass.** A law that states that matter is neither created nor destroyed in a chemical reaction. (3)

**lead-acid battery.** A rechargeable voltaic battery composed of lead and lead dioxide electrodes in a sulfuric acid solution. (14)

**Le Châtelier's principle.** A principle that states that when stress is applied to a system at equilibrium, the system reacts in such a way as to counteract the stress. (15)

**Lewis dot symbols.** The representation of an element by its symbol with its valence electrons as dots. (9)

**Lewis structure.** The representation of a molecule or ion showing the order and arrangement of the atoms as well as the bonded pairs and unshared electrons of all of the atoms. (9)

**limiting reactant.** The reactant that produces the least amount of product when that reactant is completely consumed. (7)

**liquid.** A physical state that has a definite volume but not a definite shape. Liquids take the shape of the bottom of the container. (3, 11)

**London forces.** The instantaneous dipole-induced dipole forces between molecules caused by an instantaneous imbalance of electrical charge in a molecule. The force is dependent on the size of the molecule. (11)

## M

**main group element.** See *representative element*.

**mass.** The quantity of matter (usually in grams or kilograms) in a sample. (1)

**mass number.** The number of nucleons (neutrons and protons) in a nucleus. (2)

**matter.** Anything that has mass and occupies space. (2)

**measurement.** The quantity, dimensions, or extent of something, usually in comparison to a specific unit. (1)

**melting point.** The temperature at which a pure substance changes from the solid to the liquid state. (3)

**metal.** An element with a comparatively low ionization energy that forms positive ions in compounds. Generally, metals are hard, lustrous elements that are ductile and malleable. (4, 8)

**metallic solid.** A solid made of metals where positive metal ions occupy regular positions in the crystal lattice with the valence electrons moving freely among these positive ions. (11)

**metalloid.** Elements with properties intermediate between metals and nonmetals. Many of the elements on the metal-nonmetal borderline in the periodic table. (4)

**metallurgy.** The conversion of metal ores into metals. (Prologue)

**metric system.** A system of measurement based on multiples of 10. (1)

**miscible liquids.** Two liquids that mix or dissolve in each other to form a solution. (12)

**model.** A description or analogy used to help visualize a phenomenon. (8)

**molality.** A temperature independent unit of concentration that relates the moles of solute to the mass (kg) of solvent. (12)

**molar mass.** The atomic mass of an element or the formula weight of a compound expressed in grams. (8)



**molar volume.** The volume of one mole of a gas at STP, which is 22.4 L. (10)

**molarity.** A unit of concentration that relates moles of solute to volume (in liters) of solution. (12)

**mole.** A unit of  $6.022 \times 10^{23}$  atoms, molecules, or formula units. It is the same number of particles as there are atoms in exactly 12 grams of  $^{12}\text{C}$ . It also represents the atomic mass of an element or the formula weight of a compound expressed in grams. (8)

**mole ratio.** The ratios of moles from a balanced equation that serve as conversion factors in stoichiometry calculations. (7)

**molecular compound.** A compound composed of discrete molecules. (2)

**molecular dipole.** The combined or net effect of all of the bond dipoles in a molecule as determined by the molecular geometry. (9)

**molecular equation.** A chemical equation showing all reactants and products as neutral compounds. (5)

**molecular formula.** See *formula*.

**molecular geometry.** The geometry of a molecule or ion described by the bonded atoms. It does not include the unshared pairs of electrons. (9)

**molecular solid.** A solid where the individual molecules in the crystal lattice are held together by London forces, dipole–dipole attractions, or hydrogen bonding. (11)

**molecular weight.** The formula weight of a molecular compound. (8)

**molecule.** The basic unit of a molecular compound, which is two or more atoms held together by covalent bonds. (2)

**monoprotic acid.** An acid that can produce one  $\text{H}^+$  ion per molecule. (13)

**N**

**net ionic equation.** A chemical equation shown in ionic form with spectator ions eliminated. (5)

**network solid.** A solid where the atoms are covalently bonded to each other throughout the entire crystal. (11)

**neutral.** Pure water or a solution with  $\text{pH} = 7$ . (13)

**neutralization reaction.** A reaction whereby an acid reacts with a base to form a salt and water. The reaction of  $\text{H}^+$  (*aq*) with  $\text{OH}^-$  (*aq*). (5, 13)

**neutron.** A particle in the nucleus with a mass of about 1 amu and no charge. (2)

**noble gas.** An element with a full outer *s* and *p* subshell. Group VIIIA in the periodic table. (4, 8)

**nonconductor.** A substance that does not conduct electricity. (12)

**nonelectrolyte.** A solute whose aqueous solution or molten state does not conduct electricity. (12)

**nonmetal.** Elements to the right in the periodic table. These elements generally lack metallic properties. They have relatively high ionization energies. (4, 8)

**nonpolar bond.** A covalent bond in which electrons are shared equally. (9)

**normal boiling point.** The temperature at which the vapor pressure of a liquid is equal to exactly one atmosphere pressure. (11)

**nuclear equation.** A symbolic representation of the changes of a nucleus or nuclei into other nuclei and particles. (16)

**nuclear reactor.** A device that can maintain a controlled nuclear fission reaction. Used either for research or generation of electrical power. (16)

**nucleons.** The protons and neutrons that make up the nucleus of the atom. (2, 16)

**nucleus.** The core of the atom containing neutrons, protons, and most of the mass. (2, 16)

**O**

**octet rule.** A rule that states that atoms of representative elements form bonds so as to have access to eight electrons. (9)

**orbital.** A region of space where there is the highest probability of finding a particular electron. There are four types of orbitals; each has a characteristic shape. (8)

**orbital diagram.** The representation of specific orbitals of a subshell as boxes and the electrons as arrows in the boxes. (8)

**osmosis.** The tendency of a solvent to move through a semipermeable membrane from a region of low concentration to a region of high concentration of solute. (12)

**osmotic pressure.** The pressure needed to counteract the movement of solvent through a semipermeable membrane from a region of low concentration of solute to a region of high concentration. (12)

**oxidation.** The loss of electrons as indicated by an increase in oxidation state. (14)

**oxidation–reduction reaction.** A chemical reaction involving an exchange of electrons. (14)

**oxidation state (number).** The charge on an atom in a compound if all atoms were present as monatomic ions. The electrons in bonds are assigned to the more electronegative atom. (14)

**oxidation state method.** A method of balancing oxidation–reduction reactions that focuses on the atoms of the elements undergoing a change in oxidation state. (14)

**oxidizing agent.** The element, compound, or ion that oxidizes another reactant. It is reduced. (14)

**oxyacid.** An acid composed of hydrogen and an oxyanion. (4)

**oxyanion.** An anion composed of oxygen and one other element. (4)

**P**

**partial pressure.** The pressure of one component in a mixture of gases. (10)

**parts per billion (ppb).** A unit of concentration obtained by multiplying the ratio of the mass of solute to the mass of solution by  $10^9$  ppb. (12)

**parts per million (ppm).** A unit of concentration obtained by multiplying the ratio of the mass of solute to the mass of solution by  $10^6$  ppm. (12)

**Pauli exclusion principle.** A rule that states that no two electrons can have the same spin in the same orbital. (8)

**percent by mass.** The mass of solute expressed as a percent of the mass of solution. (3,12)

**percent composition.** The mass of each element expressed per 100 mass units of the compound. (8)

**percent yield.** The actual yield in grams or moles divided by the theoretical yield in grams or moles and multiplied by 100%. (9)

**period.** A horizontal row of elements between noble gases in the periodic table. (4)

**periodic law.** A law that states that the properties of elements are periodic functions of their atomic numbers. (4)

**periodic table.** An arrangement of elements in order of increasing atomic number. Elements with the same number of outer electrons are arranged in vertical columns. (4, 8)

**pH.** The negative of the common logarithm of the  $\text{H}_3\text{O}^+$  concentration. (13)

**phase.** A homogeneous state (solid, liquid, or gas) with distinct boundaries and uniform properties. (3)

**physical change.** A change in physical state or dimensions of a substance that does not involve a change in composition. (3)

**physical properties.** Properties that can be observed without changing the composition of a substance. (3)

**physical states.** The physical condition of matter—solid, liquid, or gas. (3)

**pOH.** The negative of the common logarithm of the  $\text{OH}^-$  concentration. (13)

**point of equilibrium.** The point at which the forward and reverse reactions in a reversible reaction occur at the same rate so that the concentrations of both reactants and products remain constant. (15)

**polar covalent bond.** A covalent bond that has a partial separation of charge due to the unequal sharing of electrons. (9)

**polyatomic ion.** A group of atoms covalently bonded to each other that have a net electrical charge. (2)

**polyprotic acid.** An acid that can produce more than one  $\text{H}^+$  ion per molecule. (13)

**positron.** A positively charged electron emitted from a radioactive isotope. (16)

**potential energy.** Energy as a result of position or composition. (3, 15)

**precipitate.** A solid compound formed in a solution. (5)

**precipitation reaction.** A type of double-replacement reaction in which an insoluble ionic compound is formed by an exchange of ions in the reactants. (5)

**precision.** The reproducibility of a measurement as indicated by the number of significant figures expressed. (1)

**pressure.** The force per unit area. (10)

**principal quantum number ( $n$ ).** A number that corresponds to a particular shell occupied by the electrons in an atom. (8)

**product.** An element or compound in an equation that is formed as a result of a chemical reaction. (5)

**proper fraction.** A fraction whose numerator is smaller than the denominator and thus has a value less than one. (Appendix A)

**property.** A particular characteristic or trait of a substance. (2, 3)

**proton.** A particle in the nucleus with a mass of about 1 amu and a charge of +1. (2)

**pure substance.** A substance that has a definite composition with definite and unchanging properties (i.e., elements and compounds). (3)

## Q

**quantized energy level.** An energy level with a definite and measurable energy. (8)

## R

**radiation.** Particles or high-energy light rays that are emitted by an atom or a nucleus of an atom. (16)

**radioactive decay series.** A series of elements formed from the successive emission of alpha and beta particles starting from a long-lived isotope and ending with a stable isotope. (16)

**radioactivity.** The emission of energy or particles from an unstable nucleus. (16)

**rate of reaction.** A measure of the increase in concentration of a product or the decrease in concentration of a reactant per unit time. (15)

**reactant.** An element of compound in an equation that undergoes a chemical reaction. (5)

**recrystallization.** A laboratory procedure whereby a solid compound is purified by saturating a solution at a high temperature and then forming a precipitate at a lower temperature. (12)

**redox reaction.** See *oxidation-reduction reaction*.

**reducing agent.** An element, compound, or ion that reduces another reactant. It is oxidized. (14)

**reduction.** The gain of electrons as indicated by a decrease in the oxidation state. (14)

**representative element.** Elements whose outer  $s$  and  $p$  subshells are filling. The A Group elements in the periodic table (except for VIIIA). (4, 8)

**resonance hybrid.** The actual structure of the molecule as implied by the resonance structures. (9)

**resonance structure.** A Lewis structure showing one of two or more possible Lewis structures. (9)



**reversible reaction.** A reaction where both a forward reaction (forming products) and a reverse reaction (reforming reactants) can occur. (15)

**room temperature.** The standard reference temperature for physical state, which is usually defined as 25°C. (4)

## S

**salt.** An ionic compound formed by the combination of most cations and anions. Also, the compound that forms from the cation of a base and the anion of an acid. (4, 5, 13)

**salt bridge.** An aqueous gel that allows anions to migrate between compartments in a voltaic cell. (14)

**saturated solution.** A solution containing the maximum amount of dissolved solute at a specific temperature. (12)

**scientific method.** The method whereby modern scientists explain the behavior of nature with hypotheses and theories, or describe the behavior of nature with laws. (Prologue)

**scientific notation.** A number expressed with one nonzero digit to the left of the decimal point multiplied by 10 raised to a given power. (1, Appendix C)

**semimetal.** See *metalloid*.

**shell.** The principal energy level which contains one or more subshells. (8)

**SI units.** An international system of units of measurement. (1)

**significant figure.** A digit or number in a measurement that is either reliably known or is estimated. (1)

**single-replacement reaction.** A chemical reaction whereby a free element substitutes for another element in a compound. (5)

**solid.** A physical state with both a definite shape and a definite volume. (3, 11)

**solubility.** The maximum amount of a solute that dissolves in a specific amount of solvent at a certain temperature. (12)

**solubility product constant ( $K_{sp}$ ).** The equilibrium constant associated with the solution of ionic compounds. (15)

**soluble compound.** A compound that dissolves to an appreciable extent in a solvent. (5)

**solute.** A substance that dissolves in a solvent. (5, 12)

**solution.** A homogeneous mixture with one phase. It is composed of a solute dissolved in a solvent. (3, 5, 12)

**solvent.** A medium, usually a liquid, that disperses a solute to form a solution. (5, 12)

**specific gravity.** The ratio of the mass of a substance to the mass of an equal volume of water under the same conditions. (3)

**specific heat.** The amount of heat required to raise the temperature of one gram of a substance one degree Celsius. (3)

**spectator ion.** An ion that is in an identical state on both sides of an equation. (5)

**spectrum.** The separate color components of a beam of light. (8)

**standard temperature and pressure (STP).** The defined standard conditions for a gas, which are exactly 0°C and one atmosphere pressure. (10)

**Stock method.** A method used to name metal–nonmetal or metal–polyatomic ion compounds where the charge on the metal is indicated by Roman numerals enclosed in parentheses. (4)

**stoichiometry.** The quantitative relationship among reactants and products. (7)

**strong acid (base).** An acid (or base) that is completely ionized in aqueous solution. (5, 13)

**structural formula.** Formulas written so that the order and arrangement of specific atoms are shown. (2, 9)

**sublimation.** The vaporization of a solid. (11)

**subshell.** The orbitals of the same type within a shell. The subshells are named for the types of orbitals, that is, *s*, *p*, *d*, or *f*. (8)

**substance.** A form of matter. Usually thought of as either an element or a compound. (3)

**supersaturated solution.** A solution containing more than the maximum amount of solute indicated by the compound's solubility at that temperature. (12)

**surface tension.** The forces of attraction between molecules that cause a liquid surface to contract. (11)

**symbol.** One or two letters from an element's English or, in some cases, Latin name. (2)

## T

**temperature.** A measure of the intensity of heat of a substance. It relates to the average kinetic energy of the substance. (1, 10)

**theoretical yield.** The calculated amount of product that would be obtained if all of a reactant were converted to a certain product. (9)

**theory.** A hypothesis that withstands the test of time and experiments designed to test the hypothesis. (Prologue)

**thermochemical equation.** A balanced equation that includes the amount of heat energy. (9)

**thermometer.** A device that measures temperature. (1)

**torr.** A unit of gas pressure equivalent to the height of one millimeter of mercury. (10)

**total ionic equation.** A chemical equation showing all soluble compounds that exist primarily as ions in aqueous solution as separate ions. (5)

**transition element.** Elements whose outer *s* and *d* subshells are filling. The B Group elements in the periodic table. (4, 8)

**transmutation.** The changing of one element into another by a nuclear reaction. (16)

**triple bond.** The sharing of three pairs of electrons in a bond between two atoms. (9)

**triprotic acid.** An acid that can produce three  $\text{H}^+$  ions per molecule. (13)

**U**

**ultraviolet light.** Light with wavelengths somewhat shorter than those of violet light. (8)

**unit.** A definite quantity adapted as a standard of measurement. (1)

**unit factor.** A fractional expression that relates a quantity in a certain unit to “one” of another unit. (1)

**unit map.** A shorthand representation of the procedure for solving a problem that indicates the conversion of units in one or more steps. (1, 6, 7)

**unsaturated solution.** A solution that contains less than the maximum amount of solute indicated by the compound’s solubility at that temperature. (12)

**V**

**valence electron.** An outer *s* or *p* electron in the atom of a representative element. (8)

**valence shell electron-pair repulsion theory (VSEPR).** A theory that predicts that electron pairs either unshared or in a bond repel each other to the maximum extent. (9)

**vapor pressure.** See *equilibrium vapor pressure*.

**viscosity.** A measure of the resistance of a liquid to flow. (11)

**volatile.** Refers to a liquid or solid with a significant vapor pressure. (11)

**voltaic cell.** A spontaneous oxidation-reduction reaction that can be used to produce electrical energy. (14)

**volume.** The space that a certain quantity of matter occupies. (1)

**W**

**wavelength ( $\lambda$ ).** The distance between two adjacent peaks in a wave. (8)

**wave mechanics.** A complex mathematical approach to the electrons in an atom that considers the electron as having both a particle and a wave nature. (8)

**weak acid (base).** An acid (or base) that is only partially ionized in aqueous solution. (13)

**weak electrolyte.** A solute whose aqueous solution allows only a limited amount of electrical conduction. (12)

**weight.** A measure of the attraction of gravity for a sample of matter. (1)

ANSWERS TO  
CHAPTER PROBLEMS

CHAPTER 1

- 1-1. (b) 74.212 gal (the most significant figures)
- 1-2. A device used to produce a measurement may provide a reproducible answer to several significant figures, but if the device itself is inaccurate (such as a ruler with the tip broken off) the measurement is inaccurate.
- 1-4. (a) three (b) two (c) three (d) one (e) four (f) two (g) two (h) three
- 1-6. (a)  $\pm 10$  (b)  $\pm 0.1$  (c)  $\pm 0.01$  (d)  $\pm 0.01$  (e)  $\pm 1$  (f)  $\pm 0.001$  (g)  $\pm 100$  (h)  $\pm 0.00001$
- 1-8. (a) 16.0 (b) 1.01 (c) 0.665 (d) 489 (e) 87,600 (f) 0.0272 (g) 301
- 1-10. (a) 0.250 (b) 0.800 (c) 1.67 (d) 1.17
- 1-12. (a)  $\pm 0.1$  (b)  $\pm 1000$  (c)  $\pm 1$  (d)  $\pm 0.01$
- 1-14. (a) 188 (b) 12.90 (c) 2300 (d) 48 (e) 0.84
- 1-16. 37.9 qt
- 1-18. (a) 7.0 (b) 137 (c) 192 (d) 0.445 (e) 3.20 (f) 2.9
- 1-20. (a) two (b) three (c) two (d) one
- 1-23. (a) 6.07 (b) 6.049 (c) 8.62 (d) 7 (e) 3.98 (f) 3.973 (g) 0.5098
- 1-26. (a)  $(63) + 75.0 = 138$   
(b)  $(45) \times 25.6 = 1200$   
(c)  $(2.7) \times (10.52) = 28$
- 1-28. (a)  $1.57 \times 10^2$  (b)  $1.57 \times 10^{-1}$  (c)  $3.00 \times 10^{-2}$  (d)  $4.0 \times 10^7$  (e)  $3.49 \times 10^{-2}$  (f)  $3.2 \times 10^4$  (g)  $3.2 \times 10^{10}$  (h)  $7.71 \times 10^{-4}$  (i)  $2.34 \times 10^3$
- 1-30. (a)  $9 \times 10^7$  (b)  $8.7 \times 10^7$  (c)  $8.70 \times 10^7$
- 1-32. (a) 0.000476 (b) 6550 (c) 0.0078 (d) 48,900 (e) 4.75 (f) 0.0000034
- 1-34. (a)  $4.89 \times 10^{-4}$  (b)  $4.56 \times 10^{-5}$  (c)  $7.8 \times 10^3$  (d)  $5.71 \times 10^{-2}$  (e)  $4.975 \times 10^8$  (f)  $3.0 \times 10^{-4}$
- 1-36. (b) < (f) < (g) < (d) < (a) < (e) < (c)
- 1-38. (a)  $1.597 \times 10^{-3}$  (b)  $2.30 \times 10^7$  (c)  $3.5 \times 10^{-5}$  (d)  $2.0 \times 10^{14}$
- 1-40. (a)  $10^7$  (b)  $10^0 = 1$  (c)  $10^{29}$  (d)  $10^9$
- 1-42. (a)  $3.1 \times 10^{10}$  (b)  $2 \times 10^9$  (c)  $4 \times 10^{13}$  (d) 14 (e)  $2.56 \times 10^{-14}$
- 1-44. (a)  $2.0 \times 10^{12}$  (b)  $3.7 \times 10^{16}$  (c)  $6.0 \times 10^2$  (d)  $2 \times 10^{12}$  (e)  $1.9 \times 10^8$
- 1-45. (a)  $1.225 \times 10^7$  (b)  $9.00 \times 10^{-12}$  (c)  $3.0 \times 10^{-24}$  (d)  $9 \times 10^4$  (e)  $1 \times 10^{10}$

- 1-47. (a) milliliter (mL) (b) hectogram (hg) (c) nanojoule (nJ) (d) centimeter (cm) (e) microgram ( $\mu\text{g}$ ) (f) decipascal (dPa)
- 1-49. (a) 720 cm, 7.2 m,  $7.2 \times 10^{-3}$  km  
(b)  $5.64 \times 10^4$  mm, 5640 cm, 0.0564 km  
(c)  $2.50 \times 10^5$  mm,  $2.50 \times 10^4$  cm, 250 m
- 1-50. (a) 8.9 g,  $8.9 \times 10^{-3}$  kg  
(b)  $2.57 \times 10^4$  mg, 0.0257 kg  
(c)  $1.25 \times 10^6$  mg, 1250 g
- 1-52. (a) 12 = 1 doz (c) 3 ft = 1 yd (e)  $10^3$  m = 1 km
- 1-54. (a)  $\frac{1 \text{ g}}{10^3 \text{ mg}}$  (b)  $\frac{1 \text{ km}}{10^3 \text{ m}}$  (c)  $\frac{1 \text{ L}}{100 \text{ cL}}$   
(d)  $\frac{1 \text{ m}}{10^3 \text{ mm}}, \frac{1 \text{ km}}{10^3 \text{ m}}$
- 1-56. (a)  $\frac{1 \text{ ft}}{12 \text{ in.}}$  (b)  $\frac{2.54 \text{ cm}}{\text{in.}}$  (c)  $\frac{5280 \text{ ft}}{\text{mi}}$   
(d)  $\frac{1.057 \text{ qt}}{\text{L}}$  (e)  $\frac{1 \text{ qt}}{2 \text{ pt}}, \frac{1 \text{ L}}{1.057 \text{ qt}}$
- 1-58. (a) 47 L (b) 98 cm (c) 1.85 mi (d) 51.56 yd (e) 92 m (f) 10.27 bbl (g) 32 Gg
- 1-60. (a) 7.8 km, 4.8 mi,  $6 \times 10^4$  ft  
(b) 2380 ft, 0.724 km, 724 m  
(c) 1.70 mi, 2.74 km, 2740 m  
(d) 4.21 mi,  $2.22 \times 10^4$  ft, 6780 m
- 1-61. (a) 25.7 L, 27.2 qt (b) 630 L, 170 gal (c)  $8.12 \times 10^3$  qt,  $2.03 \times 10^3$  gal
- 1-63. 55.3 kg
- 1-65.  $28.0 \text{ m} \times \frac{10^2 \text{ cm}}{\text{m}} \times \frac{1 \text{ in.}}{2.54 \text{ cm}} \times \frac{1 \text{ ft}}{12 \text{ in.}} \times \frac{1 \text{ yd}}{3 \text{ ft}}$   
 $= 30.6 \text{ yd}$  (New punter is needed.)
- 1-67. 0.355 L
- 1-69. 6 ft 10 1/2 in. = 82.5 in.  
 $82.5 \text{ in.} \times \frac{2.54 \text{ cm}}{\text{in.}} \times \frac{1 \text{ m}}{10^2 \text{ cm}} = 2.10 \text{ m}$   
 $212 \text{ lb} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} = 96.1 \text{ kg}$
- 1-70. 14.5 gal
- 1-72.  $0.200 \text{ gal} \times \frac{4 \text{ qt}}{\text{gal}} = 0.800 \text{ qt}$   
 $0.800 \text{ qt} \times \frac{1 \text{ L}}{1.057 \text{ qt}} \times \frac{1 \text{ mL}}{10^{-3} \text{ L}} = 757 \text{ mL}$   
There is slightly more in a "fifth" than in 750 mL.

1-74. 105 km/hr

$$1-78. \frac{\$0.899}{\text{gal}} \times \frac{1 \text{ gal}}{4 \text{ qt}} \times \frac{1.057 \text{ qt}}{\text{L}} = \$0.238/\text{L}$$

$$80.0 \text{ L} \times \frac{\$0.238}{\text{L}} = \underline{\$19.04}$$

In 2008, the cost was  $\$79.44$ 1-79.  $\$98.63$  (551 mi),  $\$53.62$  (482 km)

1-80. 674 km

1-83. 382 nails

1-84.  $\$28.20$ 1-85.  $\$52.06$  (the hybrid);  $\$108.35$  (the SUV)

1-88. 3.31 hr

1-89. (a) 7.28 euro (b)  $\$11.29$  (c)  $\$22.75$ 

1-90. 0.864 pound/euro, 21,600 pound

1-93. 2100 s, 0.58 hr

1-94.  $572^\circ\text{F}$ 1-95.  $24^\circ\text{C}$ 1-97.  $-38^\circ\text{F}$ 1-99.  $95.0^\circ\text{F}$ 1-100. (a)  $-98^\circ\text{C}$  (b)  $22^\circ\text{C}$  (c)  $27^\circ\text{C}$  (d)  $-48^\circ\text{C}$   
(e)  $600^\circ\text{C}$ 1-101. (a) 320 K (b) 296 K (c) 200 K (d) 261 K  
(e) 291 K (f) 244 K1-103. Since  $T(^{\circ}\text{C}) = T(^{\circ}\text{F})$  substitute  $T(^{\circ}\text{C})$  for  $T(^{\circ}\text{F})$   
and set the two equations equal.

$$[T(^{\circ}\text{C}) \times 1.8] + 32 = \frac{T(^{\circ}\text{C}) - 32}{1.8}$$

$$(1.8)^2 T(^{\circ}\text{C}) - T(^{\circ}\text{C}) = -32 - 32(1.8)$$

$$T(^{\circ}\text{C}) = -40^\circ\text{C}$$

1-104. (a)  $3 \times 10^2$  (b)  $8.26 \text{ g} \cdot \text{cm}$  (c)  $5.24 \text{ g/mL}$   
(d) 19.1

$$1-105. \text{(a)} \frac{1 \text{ g}}{10^3 \text{ mg}}, \frac{1 \text{ lb}}{453.6 \text{ g}} \quad \text{(b)} \frac{1.057 \text{ qt}}{\text{L}}, \frac{2 \text{ pt}}{\text{qt}}$$

$$\text{(c)} \frac{1 \text{ km}}{10 \text{ hm}}, \frac{1 \text{ mi}}{1.609 \text{ km}} \quad \text{(d)} \frac{1 \text{ in.}}{2.54 \text{ cm}}, \frac{1 \text{ ft}}{12 \text{ in.}}$$

$$1-106. 5.34 \times 10^{10} \text{ ng} \times \frac{10^{-9} \text{ g}}{\text{ng}} \times \frac{1 \text{ lb}}{453.6 \text{ g}} = \underline{0.118 \text{ lb}}$$

1-108.  $\$23,300$ 

$$1-109. \frac{247 \text{ lb}}{82.3 \text{ doz}} = \frac{3.00 \text{ lb/doz}}{247 \text{ lb}} \frac{82.3 \text{ doz}}{247 \text{ lb}} = \underline{0.333 \text{ doz/lb}}$$

$$1-110. 12.0 \text{ fms} \times \frac{1 \text{ mi}}{8 \text{ fms}} \times \frac{5280 \text{ ft}}{\text{mi}} \times \frac{12 \text{ in.}}{\text{ft}} \times \frac{1 \text{ hand}}{4 \text{ in.}} \\ = \underline{2.38 \times 10^4 \text{ hands}}$$

1-112. 1030 pkgs, 1.41 years

1-113. 5.02 L

$$1-115. 5.4 \times 10^7 \text{ F} \quad 3.0 \times 10^7 \text{ C} + 273 = 3.0 \times 10^7 \text{ K}$$

1-117. 4.65 ton

## CHAPTER 2

2-2. cadmium, Cd calcium, Ca californium, Cf carbon, C  
cerium, Ce cesium, Cs chlorine, Cl chromium, Cr cobalt,  
Co copper, Cu curium, Cm

2-5. (a) Ba (b) Ne (c) Cs (d) Pt (e) Mn (f) W

2-7. (a) boron (b) bismuth (c) germanium  
(d) uranium (e) cobalt (f) mercury (g) beryllium  
(h) arsenic

2-8. (b) and (e)

2-9. (c)

2-12. (a) 21 p, 21 e, 24 n (b) 90 p, 90 e, 142 n (c) 87 p,  
87 e, 136 n (d) 38 p, 38 e, 52 n

2-14.

| Isotope Name     | Isotope Notation       | Atomic Number | Mass Number | p  | n   | e  |
|------------------|------------------------|---------------|-------------|----|-----|----|
| (a) silver-108   | $^{108}_{47}\text{Ag}$ | 47            | 108         | 47 | 61  | 47 |
| (b) silicon-28   | $^{28}_{14}\text{Si}$  | 14            | 28          | 14 | 14  | 14 |
| (c) potassium-39 | $^{39}_{19}\text{K}$   | 19            | 39          | 19 | 20  | 19 |
| (d) cerium-140   | $^{140}_{58}\text{Ce}$ | 58            | 140         | 58 | 82  | 58 |
| (e) iron-56      | $^{56}_{26}\text{Fe}$  | 26            | 56          | 26 | 30  | 26 |
| (f) tin-110      | $^{110}_{50}\text{Sn}$ | 50            | 110         | 50 | 60  | 50 |
| (g) iodine-118   | $^{118}_{53}\text{I}$  | 53            | 118         | 53 | 65  | 53 |
| (h) mercury-196  | $^{196}_{80}\text{Hg}$ | 80            | 196         | 80 | 116 | 80 |

2-16.  $^{59}\text{Co}$ 2-18. (a) The identity of a specific element is determined  
by its atomic number. An element is a basic form of matter  
and its atomic number relates to the number of protons in  
the nuclei of its atoms.(b) Both relate to the particles in the nucleus of the atoms  
of an element. The atomic mass is the mass of an average  
atom since elements are usually composed of more than  
one isotope. The atomic number is the number of protons.(c) Both relate to the number of particles in a nucleus.  
The mass number relates to the total number of protons  
and neutrons in an isotope of an element while the atomic  
number is the number of protons in the atoms of a  
specific element.(d) The isotopes of a specific element are determined by  
the atomic number. Every element is composed of at least  
one isotope.(e) Different isotopes of a specific element have the same  
number of protons but different numbers of neutrons or  
mass numbers.2-19. (a) Re: at. no. 75, at. wt. 186.2 (b) Co: at. no. 27, at.  
wt. 58.9332 (c) Br: at. no. 35, at. wt. 79.904

(d) Si: at. no. 14, at. wt. 28.086

2-20. copper (Cu)

2-22. O: at. no. 8, mass no. 16

N: at. no. 7, mass no. 14

Si: at. no. 14, mass no. 28

Ca: at. no. 20, mass no. 40

2-24.  $5.81 \times 12.00 = 69.7 \text{ amu}$ . The element is Ga.

2-26. 79.9 amu

2-27.  $^{28}\text{Si}$ :  $0.9221 \times 27.98 = 25.80$

$^{29}\text{Si}$ :  $0.0470 \times 28.98 = 1.362$

$^{30}\text{Si}$ :  $0.0309 \times 29.97 = \underline{0.926}$   
 $\underline{28.088} = \underline{28.09 \text{ amu}}$

2-29. Let  $x$  = decimal fraction of  $^{35}\text{Cl}$  and  $y$  = decimal fraction of  $^{37}\text{Cl}$ . Since there are two isotopes present,  $x + y = 1$ ,  $y = 1 - x$ .

$$(x \times 35) + (y \times 37) = 35.5$$

$$(x \times 35) + [(1 - x) \times 37] = 35.5$$

$$x = 0.75 \text{ (75\% } ^{35}\text{Cl)} \quad y = 0.25 \text{ (25\% } ^{37}\text{Cl)}$$

2-31. (a) They are both basic units of matter. Most elements are composed of individual atoms and many compounds are composed of individual molecules. Molecules are composed of atoms chemically bonded together.

(b) A compound is a pure form of matter. It is composed of individual units called molecules.

(c) They are both pure forms of matter. Compounds, however, are composed of two or more elements chemically combined.

(d) Most elements are composed of individual atoms. Some elements, however, are composed of molecules, which in most cases, contain two atoms.

2-32. (b)  $\text{Br}_2$  (d)  $\text{S}_8$  (f)  $\text{P}_4$

2-33. P, phosphorus O, oxygen Br, bromine F, fluorine S, sulfur Mg, magnesium

2-34. Hf is the symbol of the element hafnium. HF is the formula of a compound composed of one atom of hydrogen and one atom of fluorine.

2-36. (a)  $\text{N}_2$ , diatomic element (b) CO, diatomic compound

2-39. (a) six carbons, four hydrogens, two chlorines  
 (b) two carbons, six hydrogens, one oxygen  
 (c) one copper, one sulfur, 18 hydrogens, 13 oxygens  
 (d) nine carbons, eight hydrogens, four oxygens  
 (e) two aluminums, three sulfurs, 12 oxygens  
 (f) two nitrogens, eight hydrogens, one carbon, three oxygens

2-40. (a) 12 (b) 9 (c) 33 (d) 21 (e) 17 (f) 14

2-41. (a) 8 (b) 7 (c) 4 (d) 3

2-42. (a)  $\text{SO}_2$  (b)  $\text{CO}_2$  (c)  $\text{H}_2\text{SO}_4$  (d)  $\text{C}_2\text{H}_2$

2-44. (a) They are both basic forms of matter. Atoms are neutral but ions are atoms that have acquired an electrical charge. Positive and negative ions are always found together.

(b) They are both basic forms of matter containing more than one atom. Molecules are neutral but polyatomic ions have acquired an electrical charge.

(c) Both have an electrical charge. Cations have a positive charge and anions have a negative charge.

(d) Both are classified as compounds, which are composed of the atoms of two or more elements. The basic unit of a molecular compound is a neutral molecule but the basic units of ionic compounds are cations and anions.

(e) Both are the basic units of compounds. Molecules are the basic entities of molecular compounds, and an ionic formula unit represents the smallest whole number of cations and anions representing a net charge of zero.

2-46. (a)  $\text{Ca}(\text{ClO}_4)_2$  (b)  $(\text{NH}_4)_3\text{PO}_4$  (c)  $\text{FeSO}_4$

2-47. (a) one calcium, two chlorines, and eight oxygens

(b) three nitrogens, 12 hydrogens, one phosphorus, and four oxygens (c) one iron, one sulfur, and four oxygens

2-50. (c)  $\text{S}^{2-}$

2-52. (d)  $\text{Li}^+$

2-54. FeS,  $\text{Li}_2\text{SO}_3$

2-56.  $\text{SO}_3$  represents the formula of a compound. It could be a gas.  $\text{SO}_3^{2-}$  is an anion and does not exist independently. It is part of an ionic compound with the other part being a cation.

2-57. (a)  $\text{K}^+$ : 19 p, 18 e (b)  $\text{Br}^-$ : 35 p, 36 e

(c)  $\text{S}^{2-}$ : 16 p, 18 e (d)  $\text{NO}_2^-$ : 7 + 16 = 23 p, 24 e

(e)  $\text{Al}^{3+}$ : 13 p, 10 e (f)  $\text{NH}_4^+$ : 7 + 4 = 11 p, 10 e

2-59. (a)  $\text{Ca}^{2+}$  (b)  $\text{Te}^{2-}$  (c)  $\text{PO}_3^{3-}$  (d)  $\text{NO}_2^+$

2-61. This is the  $\text{Br}^-$  ion. It is part of an ionic compound.

2-64. (a)  $^{90}_{38}\text{Sr}^{2+}$  (b)  $^{52}_{24}\text{Cr}^{3+}$  (c)  $^{79}_{34}\text{Se}^{2-}$

(d)  $^{14}_7\text{N}^{3-}$  (e)  $^{139}_{57}\text{La}^{3+}$

2-66. (a) Na: 11 p, 12 n, and 11 e;  $\text{Na}^+$  has 10 electrons.

(b) Ca: 20 p, 20 n, and 20 e;  $\text{Ca}^{2+}$  has 18 electrons.

(c) F: 9 p, 10 n, and 9 e;  $\text{F}^-$  has 10 electrons.

(d) Sc: 21 p, 24 n, and 21 e;  $\text{Sc}^{3+}$  has 18 electrons.

2-68. Let  $x$  = mass no. of I and  $y$  = mass no. of Tl

Then (1)  $x + y = 340$  or  $x = 340 - y$

$$(2) x = \frac{2}{3}y - 10$$

Substituting for  $x$  from (1) and solving for  $y$

$y = 210 \text{ amu (Tl)}$  and  $x = 340 - 210 = 130 \text{ amu (I)}$

2-70. 121.8 (Sb)  $\text{Sb}^{3+}$  has  $51 - 3 = 48$  electrons.  $^{121}\text{Sb}$  has  $121 - 51 = 70$  neutrons.  $^{123}\text{Sb}$  has  $123 - 51 = 72$  neutrons.  $^{121}\text{Sb}$ , 57.9% due to neutrons;  $^{121}\text{Sb}$ , 58.5% due to neutrons

2-71. 118 neutrons and 78 protons [platinum (Pt)]

$78 - 2 = 76$  electrons for  $\text{Pt}^{2+}$

2-73. Mass of other atom = 16 (oxygen)

$\text{NO}^+ = (7 + 8) - 1 = 14$  electrons

2-75. (a) H:  $\frac{1.008}{12.00} \times 8.000 = 0.672$

(b) N:  $\frac{14.01}{12.00} \times 8.000 = 9.34$

(c) Na:  $\frac{22.99}{12.00} \times 8.000 = 15.3$

(d) Ca:  $\frac{40.08}{12.00} \times 8.000 = 26.72$

2-76.  $\frac{43.3}{10.0} = 4.33$  times as heavy as  $^{12}\text{C}$

$4.33 \times 12.0 \text{ amu} = 52.0 \text{ amu}$ . The element is Cr.



## CHAPTER 3

3-1. (c) It has a definite volume but not a definite shape.

3-2. The gaseous state is compressible because the basic particles are very far apart and thus the volume of a gas is mostly empty space.

3-4. (a) physical (b) chemical (c) physical  
(d) chemical (e) chemical (f) physical (g) physical  
(h) chemical (i) physical

3-6. (a) chemical (b) physical (c) physical  
(d) chemical (e) physical

3-9. Physical property: melts at 660°C. Physical change: melting. Chemical property: burns in oxygen. Chemical change: formation of aluminum oxide

3-10. Original substance: green, solid (physical); can be decomposed (chemical). Substance is a compound. Gas: gas, colorless (physical); can be decomposed (chemical). Substance is a compound since it can be decomposed. Solid: shiny, solid (physical); cannot be decomposed (chemical). Substance is an element since it cannot be decomposed.

3-12. 2.60 g/mL

3-14.  $1064 \text{ g}/657 \text{ mL} = \underline{1.62 \text{ g/mL}}$  (carbon tetrachloride)

3-17. 1450 g

3-18. 670 g

3-19. 5.6 lb

3-21. 625 mL

3-22. 1.74 g/mL (magnesium)

3-23. 0.476 g/mL; Yes, it floats.

3-24. 0.951 g/mL, 4790 mL

Pumice floats in water but sinks in alcohol.

3-27. 2080 g

3-28.  $111.0 \text{ g}/125 \text{ mL} = 0.888 \text{ g/mL}$

3-30. Water: 1000 g; Gasoline: 670 g

One liter of water has a greater mass.

3-31.  $160 \text{ g}/8.3 \text{ mL} = 19 \text{ g/mL}$ . It's gold.

3-34. One needs a conversion factor between mL ( $\text{cm}^3$ ) and  $\text{ft}^3$ .

$$\left(\frac{2.54 \text{ cm}}{\text{in.}}\right)^3 = \frac{16.4 \text{ cm}^3}{\text{in.}^3} = \frac{16.4 \text{ mL}}{\text{in.}^3} \left(\frac{12 \text{ in.}}{\text{ft}}\right)^3 = \frac{1728 \text{ in.}^3}{\text{ft}^3}$$

$$\frac{1.00 \cancel{\text{ g}}}{\cancel{\text{ mL}}} \times \frac{1 \text{ lb}}{453.6 \cancel{\text{ g}}} \times \frac{16.4 \cancel{\text{ mL}}}{\cancel{\text{ in.}^3}} \times \frac{1728 \cancel{\text{ in.}^3}}{\text{ft}^3} = \underline{62.5 \text{ lb/ft}^3}$$

3-35.  $2.0 \times 10^5 \text{ lb}$  (100 tons)

3-36. Carbon dioxide is a compound composed of carbon and oxygen. It can be prepared from a mixture of carbon and oxygen, but the compound is no longer a mixture of the two elements.

3-38. Ocean water is the least pure because it contains a large amount of dissolved compounds. That is why it is not drinkable and cannot be used for crop irrigation. Drinking

water also contains chlorine and some dissolved compounds but not nearly as much as ocean water. Rainwater is most pure but still contains some dissolved gases from the air.

3-40. (a) liquid only

3-41. (a) homogeneous (b) heterogeneous  
(c) heterogeneous (d) homogeneous  
(e) homogeneous (f) homogeneous solution  
(g) heterogeneous (h) homogeneous

3-43. (a) liquid (b) various solid phases (c) gas and liquid (d) liquid (e) solid (f) liquid (g) solid and liquid (h) liquid and gas (i) gas

3-45. A mixture of all three would have carbon tetrachloride on the bottom, water in the middle, and kerosene on top. Water and kerosene float on carbon tetrachloride; kerosene floats on water.

3-47. Ice is less dense than water. An ice-water mixture is pure but heterogeneous.

3-48. (a) solution (a solid dissolved in a liquid)  
(b) heterogeneous mixture (probably a solid suspended in a liquid such as dirty water) (c) element (d) compound  
(e) solution (two liquids)

3-50. Mass of mixture = 85 + 942 = 1027 kg

$$\frac{85 \text{ kg}}{1027 \text{ kg}} \times 100\% = \underline{8.3\% \text{ tin}}$$

3-52. 64 kg nickel

3-54.  $122 \text{ lb iron} \times \frac{100 \text{ lb duriron}}{86 \text{ lb iron}} = \underline{140 \text{ lb duriron}}$

3-56. (a) exothermic (b) endothermic (c) endothermic  
(d) exothermic (e) exothermic

3-57. Gasoline is converted into heat energy when it burns. The heat energy causes the pistons to move, which is mechanical energy. The mechanical energy turns the alternator, which generates electrical energy. The electrical energy is converted into chemical energy in the battery.

3-59. (a) potential (b) kinetic (c) potential  
(It is stored because of its composition.) (d) kinetic  
(e) kinetic

3-62. Kinetic energy is at a maximum nearest the ground when the swing is moving the fastest. Potential energy is at a maximum when the swing has momentarily stopped at the highest point. Assuming no gain or loss of energy, the total of the two energies is constant.

3-63.  $0.853 \text{ J}/(\text{g} \cdot ^\circ\text{C})$

3-64.  $\frac{56.6 \text{ cal}}{365 \text{ g} \cdot 5.0 ^\circ\text{C}} = 0.031 \text{ cal}/(\text{g} \cdot ^\circ\text{C})$  (gold)

3-66.

$$^\circ\text{C} = \frac{\text{cal}}{\text{sp. heat} \times \text{g}} = \frac{150 \text{ cal}}{0.092 \frac{\text{cal}}{\text{g} \cdot ^\circ\text{C}} \times 50.0 \text{ g}} = 33^\circ\text{C rise}$$

$T(^{\circ}\text{C}) = 25 + 33 = 58^{\circ}\text{C}$

This compares to a  $3.0^{\circ}\text{C}$  rise in temperature for 50.0 g of water.



3-68. 506 J

3-69.  $58 - 25 = 33^\circ\text{C}$  rise in temperature

$$g = \frac{\text{cal}}{\text{sp. heat} \cdot ^\circ\text{C}} = \frac{16.0 \text{ cal}}{0.106 \frac{\text{cal}}{\text{g} \cdot ^\circ\text{C}} \cdot 33^\circ\text{C}} = \underline{4.6 \text{ g}}$$

3-70. The copper skillet, because it has a lower specific heat. The same amount of applied heat will heat the copper skillet more than the iron.

3-72. Iron:  $9.38^\circ\text{C}$  rise Gold:  $32^\circ\text{C}$  rise Water:  $0.997^\circ\text{C}$  rise3-74.  $45^\circ\text{C}$ 

3-76. 2910 J

3-80. 860 g

3-81. heat lost by metal = heat gained by water

$$100.0 \text{ g} \times 68.7^\circ\text{C} \times \text{specific heat} = 100.0 \text{ g} \times$$

$$6.3^\circ\text{C} \times \frac{1.00 \text{ cal}}{\text{g} \cdot ^\circ\text{C}} \text{ specific heat} = \underline{0.092 \text{ cal/g} \cdot ^\circ\text{C}}$$

The metal is copper.

3-82. Density of A =  $0.86 \text{ g/mL}$ ; density of B =  $0.89 \text{ g/mL}$ 

Liquid A floats on liquid B.

3-84. 15 g of sugar

3-85.  $9.27 \text{ g/mL}$ 

3-87. 3.17% salt

$$3-89. 50.0 \text{ mL gold} \times \frac{19.3 \text{ g}}{\text{mL gold}} = 965 \text{ g gold}$$

$$50.0 \text{ mL alum.} \times \frac{2.70 \text{ g}}{\text{mL alum.}} = 135 \text{ g alum.}$$

$$\frac{965 \text{ g gold}}{(965 + 135) \text{ g alloy}} \times 100\% = \underline{87.7\% \text{ gold}}$$

$$3-91. \text{ specific heat} = 0.13 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} (\text{gold})$$

$$25.0 \text{ g gold} \times \frac{1 \text{ mL}}{19.3 \text{ g gold}} = \underline{1.30 \text{ mL}}$$

3-94. When a log burns, most of the compounds formed in the combustion are gases and dissipate into the atmosphere. Only some solid residue (ashes) is left. When zinc and sulfur (both solids) combine, the only product is a solid so there is no weight change. When iron burns, however, its only product is a solid. It weighs more than the original iron because the iron has combined with the oxygen gas from the air.

## CHAPTER 4

4-1. An active metal reacts with water and air. A noble metal is not affected by air, water, or most acids.

4-2. 32

4-3. (c)  $\text{I}_2$ , and (g)  $\text{Br}_2$ 

4-5. (a) Fe, and (d) La—transition elements

(b) Te, (f) H, and (g) In—representative elements (e) Xe—noble gas (c) Pm—inner transition element

4-7. (b) Ti, (e) Pd, and (g) Ag

4-8. The most common physical state is a solid, and metals are more common than nonmetals.

4-10. (a) Ne, (d) Cl, and (f) N

4-12. (a) Ru, (b) Sn, (c) Hf, and (h) W

4-13. (d) Te and (f) B

4-14. (a) Ar (b) Hg (c)  $\text{N}_2$  (d) Be (e) Po

4-16. Element 118 is in Group VIIIA (noble gas).

4-18. (a) lithium fluoride (b) barium telluride

(c) strontium nitride (d) barium hydride

(e) aluminum chloride

4-20. (a)  $\text{Rb}_2\text{Se}$  (b)  $\text{SrH}_2$  (c) RaO (d)  $\text{Al}_4\text{C}_3$ (e)  $\text{BeF}_2$ 

4-22. (a) bismuth(V) oxide (b) tin(II) sulfide

(c) tin(IV) sulfide (d) copper(I) telluride

(e) titanium(IV) carbide

4-24. (a)  $\text{Cu}_2\text{S}$  (b)  $\text{V}_2\text{O}_3$  (c) AuBr (d)  $\text{Ni}_2\text{C}$  (e)  $\text{CrO}_3$ 4-26. In 4-22: (a)  $\text{Bi}_2\text{O}_5$ , (c)  $\text{SnS}_2$ , and (e) TiC;in 4-24: (e)  $\text{CrO}_3$ 4-28. (c)  $\text{ClO}_3^-$ 4-30. ammonium,  $\text{NH}_4^+$ 4-31. (b) permanganate ( $\text{MnO}_4^-$ ), (c) perchlorate ( $\text{ClO}_4^-$ ),(e) phosphate ( $\text{PO}_4^{3-}$ ), and (f) oxalate ( $\text{C}_2\text{O}_4^{2-}$ )

4-32. (a) chromium(II) sulfate (b) aluminum sulfite

(c) iron(II) cyanide (d) rubidium hydrogen carbonate

(e) ammonium carbonate (f) ammonium nitrate

(g) bismuth(III) hydroxide

4-34. (a)  $\text{Mg}(\text{MnO}_4)_2$  (b)  $\text{Co}(\text{CN})_2$  (c)  $\text{Sr}(\text{OH})_2$ (d)  $\text{Tl}_2\text{SO}_3$  (e)  $\text{In}(\text{HSO}_4)_3$  (f)  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ (g)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (h)  $\text{Hg}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ 

4-36.

|                  | $\text{HSO}_3^-$                                       | $\text{Te}^{2-}$                                    | $\text{PO}_4^{3-}$                                      |
|------------------|--|---|---|
| $\text{NH}_4^+$  | $\text{NH}_4\text{HSO}_3$<br>ammonium<br>bisulfite     | $(\text{NH}_4)_2\text{Te}$<br>ammonium<br>telluride | $(\text{NH}_4)_3\text{PO}_4$<br>ammonium<br>phosphate   |
| $\text{Co}^{2+}$ | $\text{Co}(\text{HSO}_3)_2$<br>cobalt(II)<br>bisulfite | $\text{CoTe}$<br>cobalt(II)<br>telluride            | $\text{Co}_3(\text{PO}_4)_2$<br>cobalt(II)<br>phosphate |
| $\text{Al}^{3+}$ | $\text{Al}(\text{HSO}_3)_3$<br>aluminum<br>bisulfite   | $\text{Al}_2\text{Te}_3$<br>aluminum<br>telluride   | $\text{AlPO}_4$<br><i>aluminum</i><br><i>phosphate</i>  |

4-38. (a) sodium chloride (b) sodium hydrogen carbonate (c) calcium carbonate (d) sodium hydroxide

(e) sodium nitrate (f) ammonium chloride

(g) aluminum oxide (h) calcium hydroxide

(i) potassium hydroxide

4-39. (a)  $\text{Ca}_2\text{XeO}_6$  (b)  $\text{K}_4\text{XeO}_6$  (c)  $\text{Al}_4(\text{XeO}_6)_3$ 

4-40. (a) phosphonium fluoride (b) potassium hypobromite

(c) cobalt(III) iodate (d) calcium silicate (actual name

is calcium metasilicate) (e) aluminum phosphite

(f) chromium(II) molybdate

4-41. (a) Si (b) I (c) H (d) Kr (e) H (f) As

4-43. (a) carbon disulfide (b) boron trifluoride

(c) tetraphosphorus decoxide (d) dibromine trioxide

(e) sulfur trioxide (f) dichlorine oxide or dichlorine monoxide (g) phosphorus pentachloride (h) sulfur hexafluoride

4-45. (a)  $P_4O_6$  (b)  $CCl_4$  (c)  $IF_3$  (d)  $Cl_2O_7$  (e)  $SF_6$  (f)  $XeO_2$

4-47. (a) hydrochloric acid (b) nitric acid (c) hypochlorous acid (d) permanganic acid (e) periodic acid (f) hydrobromic acid

4-48. (a)  $HCN$  (b)  $H_2Se$  (c)  $HClO_2$  (d)  $H_2CO_3$  (e)  $HI$  (f)  $HC_2H_3O_2$

4-50. (a) hypobromous acid (b) iodic acid (c) phosphorous acid (d) molybdic acid (e) perxenic acid

4-52.  $ClO_2$  chlorine dioxide

4-53.  $A = F$   $X = Br$   $BrF_5$  (Br is more metallic.) bromine pentafluoride

4-55. Gas =  $N_2$ ; Al forms only +3. Thus the formula is  $AlN$  ( $N^{3-}$ ), for aluminum nitride.  $Ti_3N_2$ , titanium(II) nitride

4-57.  $Co^{2+}$  and  $Br^-$ :  $CoBr_2$  cobalt(II) bromide

4-58. Metal = Mg, nonmetal = S:  $MgH_2$ , magnesium hydride;  $H_2S$ , hydrogen sulfide or hydrosulfuric acid

4-60.  $NiI_2$ , nickel(II) iodide  $H_3PO_4$ , phosphoric acid  $Sr(ClO_3)_2$ , strontium chlorate  $H_2Te$ , hydrogen telluride or hydrotelluric acid  $As_2O_3$ , diarsenic trioxide  $Sb_2O_3$ , antimony(III) oxide  $SnC_2O_4$ , tin(II) oxalate

4-62. tin(II) hypochlorite,  $Sn(ClO)_2$  chromic acid,  $H_2CrO_4$  xenon hexafluoride,  $XeF_6$  barium nitride,  $Ba_3N_2$  hydrofluoric acid, HF iron(III) carbide,  $Fe_4C_3$ , lithium phosphate,  $Li_3PO_4$

4-63. (e)  $Rb_2C_2O_4$

4-65.  $Rb_2O_2$ ,  $MgO_2$ ,  $Al_2(O_2)_3$ ,  $Ti(O_2)_2$   $H_2O_2$ , hydrogen peroxide, hydroperoxic acid

4-67. (a)  $Na_2CO_3$  (b)  $CaCl_2$  (c)  $KClO_4$  (d)  $Al(NO_3)_3$  (e)  $Ca(OH)_2$  (f)  $NH_4Cl$

4-69.  $N^{3-}$ , nitride  $NO_2^-$ , nitrite  $NO_3^-$ , nitrate  $NH_4^+$ , ammonium  $CN^-$ , cyanide

4-71. (e) chromium(III) carbonate

4-73. (c) barium chlorite

## CHAPTER 5

5-1. (a)  $Cl_2(g)$  (b)  $C(s)$  (c)  $K_2SO_4(s)$  (d)  $H_2O(l)$  (e)  $P_4(s)$  (f)  $H_2(g)$  (g)  $Br_2(l)$  (h)  $NaBr(s)$  (i)  $S_8(s)$  (j)  $Na(s)$  (k)  $Hg(l)$  (l)  $CO_2(g)$

5-2. (a)  $CaCO_3 \rightarrow CaO + CO_2$   
 (b)  $4 Na + O_2 \rightarrow 2Na_2O$   
 (c)  $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$   
 (d)  $2H_2O_2 \rightarrow 2H_2O + O_2$

5-4. (a)  $2Al + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2$   
 (b)  $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$   
 (c)  $3Mg + N_2 \rightarrow Mg_3N_2$   
 (d)  $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

5-6. (a)  $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$   
 (b)  $2H_2S + O_2 \rightarrow 2S + 2H_2O$

(c)  $Si_2H_6 + 8H_2O \rightarrow 2Si(OH)_4 + 7H_2$   
 (d)  $C_2H_6 + 5Cl_2 \rightarrow C_2HCl_5 + 5HCl$

5-8. (a)  $2B_4H_{10} + 11O_2 \rightarrow 4B_2O_3 + 10H_2O$   
 (b)  $SF_6 + 2SO_3 \rightarrow 3O_2SF_2$   
 (c)  $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$   
 (d)  $2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$

5-10. (a)  $2Na(s) + 2H_2O(l) \rightarrow H_2(g) + 2NaOH(aq)$   
 (b)  $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$   
 (c)  $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$   
 (d)  $2H_3PO_4(aq) + 3Ca(OH)_2(aq) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l)$

5-12.  $Ni(s) + 2N_2O_4(l) \rightarrow Ni(NO_3)_2(s) + 2NO(g)$

5-14. In exercise 5-2, (a) and (d) are decomposition reactions and (b) is a combination and combustion reaction. In exercise 5-4, (c) is a combination reaction and (d) is a combustion reaction.

5-16. (a)  $2C_7H_{14}(l) + 21O_2(g) \rightarrow 14CO_2(g) + 14H_2O(l)$   
 (b)  $2LiCH_3(s) + 4O_2(g) \rightarrow Li_2O(s) + 2CO_2(g) + 3H_2O(l)$   
 (c)  $C_4H_{10}O(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$   
 (d)  $2C_2H_5SH(g) + 9O_2(g) \rightarrow 2SO_2(g) + 4CO_2(g) + 6H_2O(l)$

5-18. (a)  $Ba(s) + H_2(g) \rightarrow BaH_2(s)$   
 (b)  $8Ba(s) + S_8(s) \rightarrow 8BaS(s)$   
 (c)  $Ba(s) + Br_2(l) \rightarrow BaBr_2(s)$   
 (d)  $3Ba(s) + N_2(g) \rightarrow Ba_3N_2(s)$

5-20. (a)  $Ca(HCO_3)_2(s) \rightarrow CaO(s) + 2CO_2(g) + H_2O(l)$   
 (b)  $2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$   
 (c)  $N_2O_3(g) \rightarrow NO_2(g) + NO(g)$

5-22. (a)  $2K(s) + Cl_2(g) \rightarrow 2KCl(s)$   
 (b)  $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$   
 (c)  $2Au_2O_3(s) \rightarrow 4Au(s) + 3O_2(g)$   
 (d)  $2C_3H_8O(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$   
 (e)  $P_4(s) + 10F_2(g) \rightarrow 4PF_5(s)$

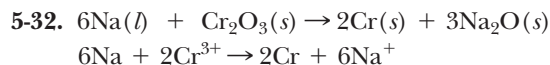
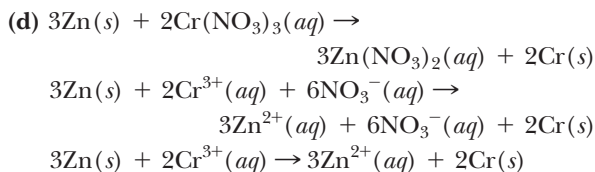
5-24. (a)  $Na_2S \rightarrow 2Na^+(aq) + S^{2-}(aq)$   
 (b)  $Li_2SO_4 \rightarrow 2Li^+(aq) + SO_4^{2-}(aq)$   
 (c)  $K_2Cr_2O_7 \rightarrow 2K^+(aq) + Cr_2O_7^{2-}(aq)$   
 (d)  $CaS \rightarrow Ca^{2+}(aq) + S^{2-}(aq)$   
 (e)  $2(NH_4)_2S \rightarrow 4NH_4^+(aq) + 2S^{2-}(aq)$   
 (f)  $4Ba(OH)_2 \rightarrow 4Ba^{2+}(aq) + 8OH^-(aq)$

5-26. (a)  $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$   
 (b)  $Sr(OH)_2(s) \rightarrow Sr^{2+}(aq) + 2OH^-(aq)$

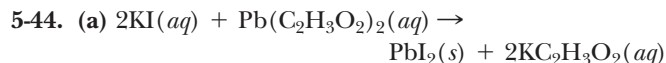
5-28. (a) no reaction  
 (b)  $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$   
 (c)  $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$   
 (d) no reaction

5-30. (a)  $CuCl_2(aq) + Fe(s) \rightarrow FeCl_2(aq) + Cu(s)$   
 $Cu^{2+}(aq) + 2Cl^-(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + 2Cl^-(aq) + Cu(s)$   
 $Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$

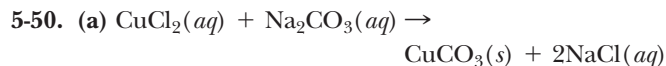
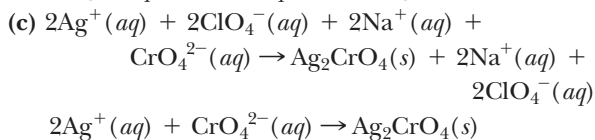
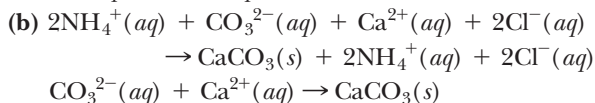
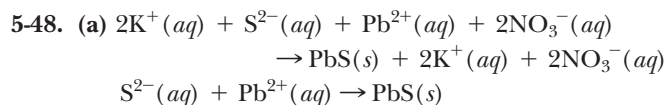
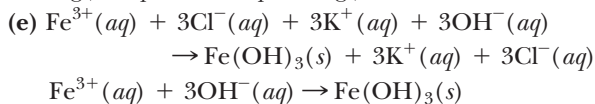
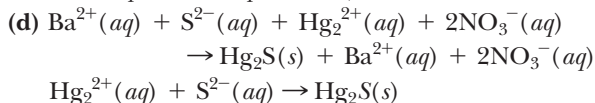
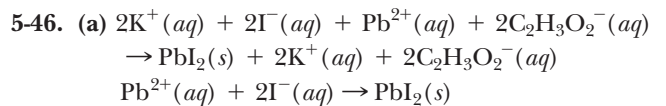
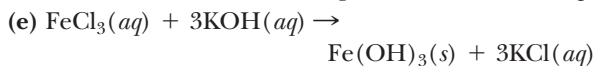
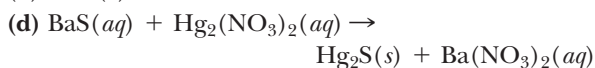
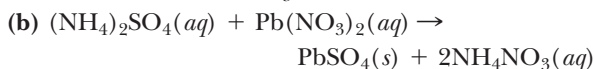
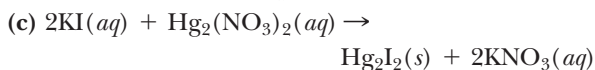
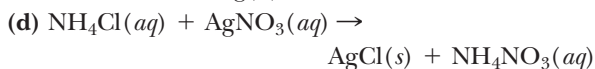
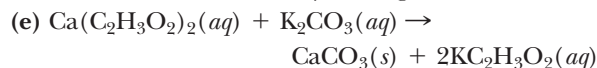
(b) and (c) no reaction



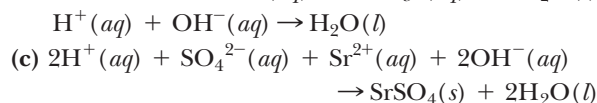
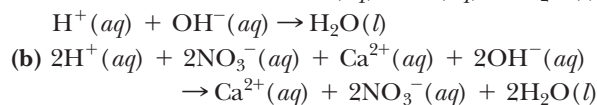
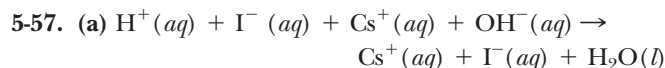
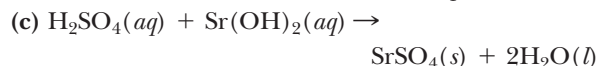
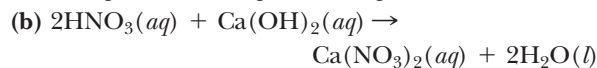
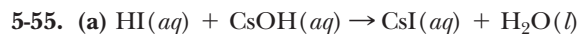
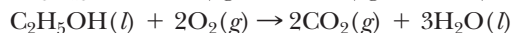
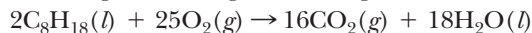
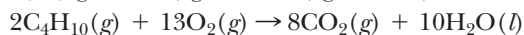
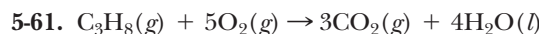
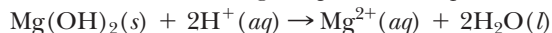
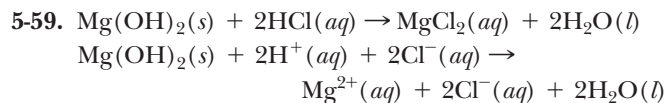
5-34. Insoluble compounds are (b)  $\text{PbSO}_4$ , and (d)  $\text{Ag}_2\text{S}$

5-36. (a)  $\text{AgBr}$  (b)  $\text{Ag}_2\text{CO}_3$  (c)  $\text{Ag}_3\text{PO}_4$ 5-38. (a)  $\text{CuCO}_3$  (b)  $\text{CdCO}_3$  (c)  $\text{Cr}_2(\text{CO}_3)_3$ 5-40.  $\text{Hg}_2\text{Cl}_2$ 5-42. (b)  $\text{Ca}_3(\text{PO}_4)_2$ 

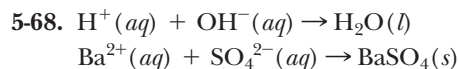
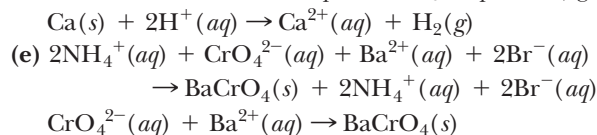
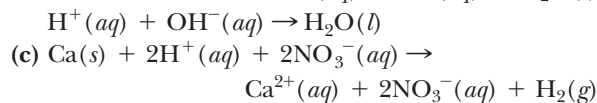
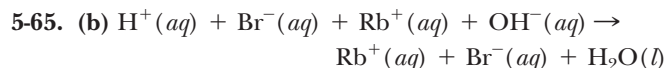
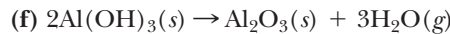
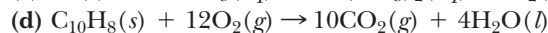
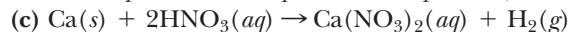
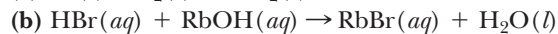
(b) and (c) no reaction occurs

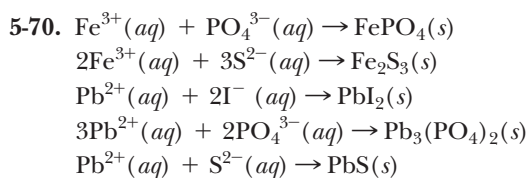
Filter the solid  $\text{CuCO}_3$ .Filter the solid  $\text{PbSO}_4$ .Filter the solid  $\text{Hg}_2\text{I}_2$ .Filter the solid  $\text{AgCl}$ ; the desired product remains after water is removed by boiling.Filter the solid  $\text{CaCO}_3$ ; the desired product remains after the water is removed by boiling.

5-51. (b) HF

5-53. (c)  $\text{Al}(\text{OH})_3$ Net ionic equation is the same as the total ionic equation since  $\text{SrSO}_4$  precipitates.

5-62. In both of these reactions, the reactants change from neutral atoms to cations and anions in the products. Ions are formed from neutral atoms from the loss or gain of electrons.





## CHAPTER 6

6-1. 0.609 lb of pennies

$$6-3. 145 \text{ g Au} \times \frac{108 \text{ g Ag}}{197.0 \text{ g Au}} = \underline{79.5 \text{ g Ag}}$$

6-4. 94.4 lb C

6-6. 71.5 g Cu

$$6-8. 25.0 \text{ g C} \times \frac{x \text{ g}}{12.01 \text{ g C}} = 33.3 \text{ g} \quad x = 16.0 \text{ g(O)}$$

The compound is CO.

6-10. 40.1 lb S

$$6-11. 6.022 \times 10^{23} \text{ units} \times \frac{1 \text{ sec}}{2 \text{ units}} \times \frac{1 \text{ min}}{60 \text{ sec}} \\ \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{1 \text{ year}}{365 \text{ day}} \\ = \underline{9.548 \times 10^{15} \text{ years (9.548 quadrillion)}}$$

$$\frac{9.5 \times 10^{15} \text{ years}}{5.5 \times 10^9} = 1.7 \times 10^6 \text{ years (1.7 million)}$$

6-13.  $6.022 \times 10^{26}$  (if mass in kg);  $6.022 \times 10^{20}$  (if mass in mg)

- 6-14. (a) 0.468 mol P,  $2.82 \times 10^{23}$  atoms P  
 (b) 150 g Rb,  $1.05 \times 10^{24}$  atoms  
 (c) Al: 27.0 g, 1.00 mol,  
 (d) 5.00 mol X element is Ge  
 (e)  $1.66 \times 10^{-24}$  mol,  $7.95 \times 10^{-23}$  g

6-16. (a) 63.5 g Cu (b) 16 g S (c) 40.1 g Ca

6-18. (a)  $1.93 \times 10^{25}$  atoms (b)  $6.03 \times 10^{23}$  atoms  
(c)  $1.20 \times 10^{24}$  atoms

$$6-20. 50.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 18.5 \text{ mol Al} \\ 50.0 \text{ g Fe} \times \frac{1 \text{ mol Ni}}{55.85 \text{ g Fe}} = 0.895 \text{ mol Fe}$$

There are more moles of atoms (more atoms) in 50.0 g of Al.

$$6-21. 20.0 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} = 0.341 \text{ mol Ni} \\ 2.85 \times 10^{23} \text{ atoms} \times \frac{1 \text{ mol Ni}}{6.022 \times 10^{23} \text{ atoms}} \\ = 0.473 \text{ mol Ni}$$

The  $2.85 \times 10^{23}$  atoms of Ni contain more atoms than 20.0 g.6-23.  $1.40 \times 10^{21}$  atoms =  $2.32 \times 10^{-3}$  mol  
 $0.251 \text{ g} / (2.32 \times 10^{-3} \text{ mol}) = 108 \text{ g/mol (silver)}$ 6-25. (a) 106.6 amu (b) 80.07 amu (c) 108.0 amu  
(d) 98.09 amu (e) 106.0 amu (f) 60.05 amu  
(g) 459.7 amu

$$6-27. \text{Cr}_2(\text{SO}_4)_3 (2 \times 52.00) + (3 \times 32.07) + (12 \times 16.00) \\ = \underline{392.2 \text{ amu}}$$

6-29. (a) 189 g H<sub>2</sub>O,  $6.32 \times 10^{24}$  molecules  
(b)  $5.00 \times 10^{-3}$  mol BF<sub>3</sub>, 0.339 g BF<sub>3</sub>  
(c) 0.219 mol SO<sub>2</sub>,  $1.32 \times 10^{23}$  molecules  
(d) 0.209 g K<sub>2</sub>SO<sub>4</sub>,  $7.23 \times 10^{19}$  formula units  
(e) 7.47 mol SO<sub>3</sub>, 598 g SO<sub>3</sub>  
(f)  $7.61 \times 10^{-3}$  mol,  $4.58 \times 10^{21}$  molecules

$$6-31. 21.5 \text{ g} / 0.0684 \text{ mol} = \underline{314 \text{ g/mol}}$$

6-33. 161 g/mol

6-35. 5.10 mol C, 15.3 mol H, 2.55 mol O:  
Total = 23.0 mol of atoms 61.3 g C, 15.4 g H,  
40.8 g O: Total mass = 117.5 g6-36. 0.135 mol Ca(ClO<sub>3</sub>)<sub>2</sub>, 0.135 mol Ca, 0.270 mol Cl,  
0.810 mol O Total = 1.215 mol of atoms

$$6-38. 1.50 \text{ mol H}_2\text{SO}_4 \times \frac{2 \text{ mol H}}{\text{mol H}_2\text{SO}_4} \times \frac{1.008 \text{ g H}}{\text{mol H}} \\ = \underline{3.02 \text{ g H}} \\ 48.1 \text{ g S, } 72.0 \text{ g O}$$

$$6-40. 1.20 \times 10^{22} \text{ molecules} \times \frac{1 \text{ mol O}_2}{6.022 \times 10^{23} \text{ molecules}} \\ = \underline{0.0199 \text{ mol O}_2} \\ 0.0199 \text{ mol O}_2 \times \frac{2 \text{ mol O atoms}}{\text{mol O}_2} \\ = 0.0398 \text{ mol O atoms} \\ 0.0199 \text{ mol O}_2 \times \frac{32.00 \text{ g O}_2}{\text{mol O}_2} \\ = 0.637 \text{ g O}_2 \text{ The mass is the same.}$$

6-42. Total mass of compound = 1.375 + 3.935 = 5.310 g,  
25.89% N, 74.11% O

6-43. 46.7% Si, 53.3% O

6-45. (a) C<sub>2</sub>H<sub>6</sub>O 52.14% C, 13.13% H, 34.73% O(b) C<sub>3</sub>H<sub>6</sub> 85.62% C, 14.38% H(c) C<sub>9</sub>H<sub>18</sub> 85.66% C, 14.34% H

(b) and (c) are actually the same. The difference comes from rounding off.

(d) Na<sub>2</sub>SO<sub>4</sub> 32.36% Na, 22.57% S, 45.07% O(e) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 29.16% N, 8.392% H, 12.50% C,  
49.95% O

6-47. 12.06% Na, 11.34% B, 71.31% O, 5.286% H

6-49. C<sub>7</sub>H<sub>5</sub>NO<sub>3</sub>. Formula weight = (7 × 12.01) + (5 ×  
1.008) + 32.07 + 14.01 + (3 × 16.00) = 183.2 amu

$$\text{C: } \frac{84.07 \text{ amu}}{183.2 \text{ amu}} \times 100\% = \underline{45.89\% \text{ C}}$$

$$\text{H: } \frac{5.040 \text{ amu}}{183.2 \text{ amu}} \times 100\% = \underline{2.751\% \text{ H}}$$

$$\text{S: } \frac{32.07 \text{ amu}}{183.2 \text{ amu}} \times 100\% = \underline{17.51\% \text{ S}}$$

$$\text{N: } \frac{14.01 \text{ amu}}{183.2 \text{ amu}} \times 100\% = \underline{7.647\% \text{ C}}$$

$$\text{O: } 100\% - (45.89 + 2.751 + 17.51 + 7.647) \\ = \underline{26.20\% \text{ O}}$$

**6-51.**  $\text{Na}_2\text{C}_2\text{O}_4$  Formula weight =  $(2 \times 22.99) + (2 \times 12.01) + (4 \times 16.00) = 134.0 \text{ amu}$

There is 24.02 g  $(2 \times 12.01)$  of C in 134.0 g of compound.

$$125 \text{ g } \text{Na}_2\text{C}_2\text{O}_4 \times \frac{24.02 \text{ g C}}{134.0 \text{ g } \text{Na}_2\text{C}_2\text{O}_4} = \underline{22.4 \text{ g C}}$$

**6-52.** 4.72 lb P

**6-54.**  $1.40 \times 10^3$  lb Fe

**6-55.** (a)  $\text{N}_2\text{O}_4$  and (d)  $\text{H}_2\text{C}_2\text{O}_4$

**6-56.** (a) FeS (b)  $\text{SrI}_2$  (c)  $\text{KClO}_3$  (d)  $\text{I}_2\text{O}_5$

(e)  $\text{Fe}_2\text{O}_{2.66} = \text{Fe}_3\text{O}_4$  (f)  $\text{C}_3\text{H}_5\text{Cl}_3$

**6-58.**  $\text{N}_2\text{O}_3$

**6-60.**  $\text{KO}_2$

**6-62.**  $\text{MgC}_2\text{O}_4$

**6-63.**  $\text{CH}_2\text{Cl}$

**6-65.**  $\text{N}_2\text{H}_8\text{SO}_3$

**6-66.**  $\text{C}_{8/3}\text{H}_{8/3}\text{O} = \text{C}_8\text{H}_8\text{O}_3$

**6-68.**  $\text{C}_3\text{H}_4\text{Cl}_4$  (empirical formula)  $\text{C}_9\text{H}_{12}\text{Cl}_{12}$  (molecular formula)

**6-70.**  $\text{B}_2\text{C}_2\text{H}_6\text{O}_4$  (molecular formula)

**6-71.** Empirical formula =  $\text{KC}_2\text{NH}_3\text{O}_2$  Empirical mass = 112.2 g/emp. unit

$$\frac{224 \text{ g/mol}}{112.2 \text{ g/emp. unit}} = 2 \text{ emp. units/mol}$$

$\text{K}_2\text{C}_4\text{N}_2\text{H}_6\text{O}_4$  (molecular formula)

**6-73.**  $\text{I}_6\text{C}_6$

**6-75.**  $7.5 \times 10^{-10}$  mol pennies

**6-76.**  $0.443 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.0316 \text{ mol N}$

Thus 1.420 g of M also equals 0.0316 mol M since M and N are present in equimolar amounts.

$$1.420 \text{ g} / 0.0316 \text{ mol} = \underline{44.9 \text{ g/mol [scandium (Sc)]}}$$

**6-79.**  $2.78 \times 10^{-3}$  mol  $\text{P}_4$

$$2.78 \times 10^{-3} \frac{\text{mol P}_4}{\text{mol P}_4} \times \frac{4 \text{ mol P}}{\text{mol P}_4} \\ \times \frac{6.022 \times 10^{23} \text{ atoms P}}{\text{mol P}} = \underline{6.70 \times 10^{21} \text{ atoms P}}$$

**6-80.** 100 mol  $\text{H}_2 = 202 \text{ g H}_2$  therefore  
100 H atoms < 100  $\text{H}_2$  molecules < 100 g  $\text{H}_2$   
< 100 mol  $\text{H}_2$

**6-82.** 120 g/mol of compound 120 - 55.8 = 64 g of S

$$\frac{64 \text{ g S}}{32.07 \text{ g S/mol}} = 2 \text{ mol S}$$

Formula =  $\text{FeS}_2$

**6-83.** (a)  $2\text{Na}^+$  and  $\text{S}_4\text{O}_6^{2-}$  (b) 27.9 g S (c)  $\text{Na}_2\text{S}_2\text{O}_3$   
(d) 270.3 g/mol (e) 0.0925 mol  $\text{Na}_2\text{S}_4\text{O}_6$ ,  $5.57 \times 10^{22}$   
formula units (f) 35.5% oxygen

**6-85.**  $\frac{2\text{N}}{2\text{N} + x\text{O}} = 0.368$   $\frac{28.02}{28.02 + 16.00x} = 0.368$   
 $x = 3 \text{ N}_2\text{O}_3$  dinitrogen trioxide

**6-87.**  $\text{C}_{12}\text{H}_4\text{Cl}_4\text{O}_2$  (molecular formula)

**6-89.** Empirical formula  $\text{CrCl}_3\text{O}_{12}$  Actual formula =  $\text{Cr}(\text{ClO}_4)_3$  chromium(III) perchlorate

**6-90.** Assume exactly 100 g of compound. There is then 51.1 g  $\text{H}_2\text{O}$  and 48.9 g  $\text{MgSO}_4$ .

$$\text{MgSO}_4: 48.9 \text{ g } \text{MgSO}_4 \times \frac{1 \text{ mol}}{120.4 \text{ g } \text{MgSO}_4} \\ = 0.406 \text{ mol } \text{MgSO}_4$$

$$2.94 \text{ mol } \text{H}_2\text{O} / 0.406 \text{ mol } \text{MgSO}_4 \\ = 7.0 \text{ mol } \text{H}_2\text{O} / \text{mol } \text{MgSO}_4$$

The formula is  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

**6-93.**  $1.20 \text{ g } \text{CO}_2 \times \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \times \frac{1 \text{ mol C}}{\text{mol } \text{CO}_2} \\ = 0.0273 \text{ mol C}$

$$0.489 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} \times \frac{2 \text{ mol H}}{\text{mol } \text{H}_2\text{O}} \\ = 0.0543 \text{ mol H}$$

C:  $\frac{0.0273}{0.0273} = 1.0$  H:  $\frac{0.0543}{0.0273} = 2.0$   $\text{CH}_2$

## CHAPTER 7

**7-1.** (a)  $\frac{1 \text{ mol } \text{H}_2}{1 \text{ mol } \text{Mg}}$  (b)  $\frac{2 \text{ mol } \text{HCl}}{1 \text{ mol } \text{Mg}}$  (c)  $\frac{1 \text{ mol } \text{H}_2}{2 \text{ mol } \text{HCl}}$   
(d)  $\frac{2 \text{ mol } \text{HCl}}{1 \text{ mol } \text{MgCl}_2}$

**7-2.** (a)  $\frac{2 \text{ mol } \text{C}_4\text{H}_{10}}{8 \text{ mol } \text{CO}_2}$  (b)  $\frac{2 \text{ mol } \text{C}_4\text{H}_{10}}{13 \text{ mol } \text{O}_2}$   
(c)  $\frac{13 \text{ mol } \text{O}_2}{8 \text{ mol } \text{CO}_2}$  (d)  $\frac{10 \text{ mol } \text{H}_2\text{O}}{13 \text{ mol } \text{O}_2}$

**7-4.** (a) 3.33 mol  $\text{Al}_2\text{O}_3$ , 3.33 mol  $\text{AlCl}_3$ , 10.0 mol NO, 20.0 mol  $\text{H}_2\text{O}$  (b) 1.00 mol  $\text{Al}_2\text{O}_3$ , 1.00 mol  $\text{AlCl}_3$ , 3.00 mol NO, 6.00 mol  $\text{H}_2\text{O}$

**7-6.** (a) 15.0 mol  $\text{O}_2$  and 10.0 mol  $\text{CH}_4$  react  
(b) 6.67 mol HCN and 20.0 mol  $\text{H}_2\text{O}$  produced

**7-8.** (a) 126 g  $\text{SiF}_4$  and (b) 43.8 g  $\text{H}_2\text{O}$  produced  
(b) 73.0 g  $\text{SiO}_2$  reacts

**7-9.** (a)  $\text{mol } \text{H}_2\text{O} \rightarrow \text{mol } \text{H}_2$

$$0.400 \frac{\text{mol } \text{H}_2\text{O}}{\text{mol } \text{H}_2\text{O}} \times \frac{2 \text{ mol } \text{H}_2}{2 \text{ mol } \text{H}_2\text{O}} = \underline{0.400 \text{ mol } \text{H}_2}$$

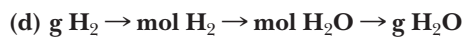
(b)  $\text{g } \text{O}_2 \rightarrow \text{mol } \text{O}_2 \rightarrow \text{mol } \text{H}_2\text{O}$

$$0.640 \text{ g } \text{O}_2 \times \frac{1 \text{ mol } \text{O}_2}{32.00 \text{ g } \text{O}_2} \times \frac{2 \text{ mol } \text{H}_2\text{O}}{1 \text{ mol } \text{O}_2} \\ = \underline{0.0400 \text{ mol } \text{H}_2\text{O}}$$

(c)  $\text{g } \text{O}_2 \rightarrow \text{mol } \text{O}_2 \rightarrow \text{mol } \text{H}_2$

$$0.032 \text{ g } \text{O}_2 \times \frac{1 \text{ mol } \text{O}_2}{32.00 \text{ g } \text{O}_2} \times \frac{2 \text{ mol } \text{H}_2}{1 \text{ mol } \text{O}_2} \\ = \underline{0.0020 \text{ mol } \text{H}_2}$$





$$0.400 \overline{\text{g H}_2} \times \frac{1 \overline{\text{mol H}_2}}{2.016 \overline{\text{g H}_2}} \times \frac{2 \overline{\text{mol H}_2\text{O}}}{2 \overline{\text{mol H}_2}} \times \frac{18.02 \overline{\text{g H}_2\text{O}}}{\overline{\text{mol H}_2\text{O}}} = \underline{\underline{3.58 \text{ g H}_2\text{O}}}$$

7-10. (a) 1.35 mol CO<sub>2</sub>, 1.80 mol H<sub>2</sub>O, 2.25 mol O<sub>2</sub>(b) 4.81 g H<sub>2</sub>O (c) 1.10 g C<sub>3</sub>H<sub>8</sub> (d) 44.1 g C<sub>3</sub>H<sub>8</sub>(e) 5.27 g CO<sub>2</sub> (f) 0.0996 mol H<sub>2</sub>O7-12. 47.2 g N<sub>2</sub>

7-14. 0.728 g HCl



$$0.520 \overline{\text{mol FeS}_2} \times \frac{1 \overline{\text{mol H}_2\text{S}}}{1 \overline{\text{mol FeS}_2}} \times \frac{6.022 \times 10^{23} \overline{\text{molecules}}}{\overline{\text{mol H}_2\text{S}}} = \underline{\underline{3.13 \times 10^{23} \text{ molecules}}}$$

7-17. 16,900 g (16.9 kg) HNO<sub>3</sub>7-19.  $2.30 \times 10^3 \text{ g}$  (2.30 kg) C<sub>2</sub>H<sub>5</sub>OH

7-20. 8140 g (8.14 kg) CO

7-21. (a) CuO limiting reactant producing 1.00 mol N<sub>2</sub>(b) stoichiometric mixture producing 1.00 mol N<sub>2</sub>(c) NH<sub>3</sub> limiting reactant producing 0.500 mol N<sub>2</sub>(d) CuO limiting reactant producing 0.209 mol N<sub>2</sub>(e) NH<sub>3</sub> limiting reactant producing 1.75 mol N<sub>2</sub>

$$7-22. \text{(a)} \quad 3.00 \overline{\text{mol CuO}} \times \frac{2 \overline{\text{mol NH}_3}}{3 \overline{\text{mol CuO}}} = 2.00 \text{ mol NH}_3 \text{ used}$$

3.00 - 2.00 = 1.00 mol NH<sub>3</sub> in excess

(c) 1.50 mol CuO in excess

7-25. H<sub>2</sub>SO<sub>4</sub> is the limiting reactant and the yield of H<sub>2</sub> is 1.00 mole.

$$1.00 \overline{\text{mol H}_2\text{SO}_4} \times \frac{2 \overline{\text{mol Al}}}{3 \overline{\text{mol H}_2\text{SO}_4}} = 0.667 \text{ mol of Al used}$$

0.800 - 0.667 = 0.133 mol Al remaining

$$7-26. \quad 3.44 \overline{\text{mol C}_5\text{H}_6} \times \frac{10 \overline{\text{mol CO}_2}}{2 \overline{\text{mol C}_5\text{H}_6}} = 17.2 \text{ mol CO}_2$$

$$20.6 \overline{\text{mol O}_2} \times \frac{10 \overline{\text{mol CO}_2}}{13 \overline{\text{mol O}_2}} = 15.8 \text{ mol CO}_2$$

Since O<sub>2</sub> is the limiting reactant:

$$15.8 \overline{\text{mol CO}_2} \times \frac{44.01 \overline{\text{g CO}_2}}{\overline{\text{mol CO}_2}} = \underline{\underline{695 \text{ g CO}_2}}$$

7-28. Since NH<sub>3</sub> produces the least N<sub>2</sub>, it is the limiting reactant and the yield of N<sub>2</sub> is 0.750 mol.

$$7-29. \quad 20.0 \overline{\text{g AgNO}_3} \times \frac{1 \overline{\text{mol AgNO}_3}}{169.9 \overline{\text{g AgNO}_3}} \times \frac{2 \overline{\text{mol AgCl}}}{2 \overline{\text{mol AgNO}_3}} = 0.118 \text{ mol AgCl}$$

$$10.0 \overline{\text{g CaCl}_2} \times \frac{1 \overline{\text{mol CaCl}_2}}{111.0 \overline{\text{g CaCl}_2}} \times \frac{2 \overline{\text{mol AgCl}}}{1 \overline{\text{mol CaCl}_2}} = 0.180 \text{ mol AgCl}$$

Since AgNO<sub>3</sub> produces the least AgCl, it is the limiting reactant.

$$0.118 \overline{\text{mol AgCl}} \times \frac{143.4 \overline{\text{g AgCl}}}{\overline{\text{mol AgCl}}} = \underline{\underline{16.9 \text{ g AgCl}}}$$

Convert moles of AgCl (the limiting reactant) to grams of CaCl<sub>2</sub> used.

$$0.118 \overline{\text{mol AgCl}} \times \frac{1 \overline{\text{mol CaCl}_2}}{2 \overline{\text{mol AgCl}}} \times \frac{111.0 \overline{\text{g CaCl}_2}}{\overline{\text{mol CaCl}_2}} = \underline{\underline{6.55 \text{ g CaCl}_2 \text{ used}}}$$

$$10.0 \text{ g} - 6.55 \text{ g} = \underline{\underline{3.5 \text{ g CaCl}_2 \text{ remaining}}}$$

7-31. Products: 3.53 g H<sub>2</sub>O, 4.71 g S, 2.94 g NOReactants remaining: 3.8 g HNO<sub>3</sub> remaining7-32. 30.0 g SO<sub>3</sub> (theoretical yield) and 70.7% yield7-35. 86.4%

7-36. If 86.4% is converted to CO<sub>2</sub>, the remainder (13.6%) is converted to CO. Thus,  $0.136 \times 57.0 \text{ g} = 7.75 \text{ g}$  of C<sub>8</sub>H<sub>18</sub> is converted to CO. Notice that 1 mole of C<sub>8</sub>H<sub>18</sub> forms 8 moles of CO (because of the eight carbons in C<sub>8</sub>H<sub>18</sub>). Thus

$$7.75 \overline{\text{g C}_8\text{H}_{18}} \times \frac{1 \overline{\text{mol C}_8\text{H}_{18}}}{114.2 \overline{\text{g C}_8\text{H}_{18}}} \times \frac{8 \overline{\text{mol CO}}}{1 \overline{\text{mol C}_8\text{H}_{18}}} \times \frac{28.01 \overline{\text{g CO}}}{\overline{\text{mol CO}}} = \underline{\underline{15.2 \text{ g CO}}}$$

7-37. Theoretical yield  $\times 0.700 = 250 \text{ g}$  (actual yield)Theoretical yield =  $250 \text{ g} / 0.700 = 357 \text{ g N}_2$ 

$$357 \overline{\text{g Na}_2} \times \frac{1 \overline{\text{mol N}_2}}{28.02 \overline{\text{g N}_2}} \times \frac{4 \overline{\text{mol H}_2}}{1 \overline{\text{mol N}_2}} \times \frac{2.016 \overline{\text{g H}_2}}{\overline{\text{mol H}_2}} = \underline{\underline{103 \text{ g H}_2}}$$

7-40.  $2\text{Mg}(s) + \text{O}_2 \rightarrow 2\text{MgO}(s) + 1204 \text{ kJ}$ 7-42.  $\text{CaCO}_3(s) + 176 \text{ kJ} \rightarrow \text{CaO}(s) + \text{CO}_2(g)$ 

$$7-43. \quad 1.00 \overline{\text{g C}_8\text{H}_{18}} \times \frac{1 \overline{\text{mol C}_8\text{H}_{18}}}{114.2 \overline{\text{g C}_8\text{H}_{18}}} \times \frac{5840 \overline{\text{kJ}}}{\overline{\text{mol C}_8\text{H}_{18}}} = \underline{\underline{48.0 \text{ kJ}}}$$

$$1.00 \overline{\text{g CH}_4} \times \frac{1 \overline{\text{mol CH}_4}}{16.04 \overline{\text{g CH}_4}} \times \frac{890 \overline{\text{kJ}}}{\overline{\text{mol CH}_4}} = \underline{\underline{55.6 \text{ kJ}}}$$

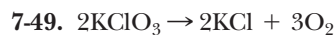
7-45.  $\text{kJ} \rightarrow \text{mol Al} \rightarrow \text{g Al}$ 

$$35.8 \overline{\text{kJ}} \times \frac{2 \overline{\text{mol Al}}}{850 \overline{\text{kJ}}} \times \frac{26.99 \overline{\text{g Al}}}{\overline{\text{mol Al}}} = \underline{\underline{2.27 \text{ g Al}}}$$

7-46. 69.7 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>

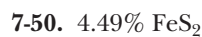
$$7-48. \quad 125 \overline{\text{g Fe}_2\text{O}_3} \times \frac{1 \overline{\text{mol Fe}_2\text{O}_3}}{159.7 \overline{\text{g Fe}_2\text{O}_3}} \times \frac{2 \overline{\text{mol Fe}_3\text{O}_4}}{3 \overline{\text{mol Fe}_2\text{O}_3}} \times \frac{3 \overline{\text{mol FeO}}}{1 \overline{\text{mol Fe}_3\text{O}_4}} \times \frac{1 \overline{\text{mol Fe}}}{1 \overline{\text{mol FeO}}} \times \frac{55.85 \overline{\text{g Fe}}}{\overline{\text{mol Fe}}} = \underline{\underline{87.4 \text{ g Fe}}}$$





Find the mass of  $\text{KClO}_3$  needed to produce 12.0 g  $\text{O}_2$ .

$$\begin{aligned} \text{g O}_2 &\rightarrow \text{mol O}_2 \rightarrow \text{mol KClO}_3 \rightarrow \text{g KClO}_3 \\ 12.0 \text{ g O}_2 &\times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \\ &\times \frac{122.6 \text{ g KClO}_3}{\text{mol KClO}_3} = 30.7 \text{ g KClO}_3 \\ \text{percent purity} &= \frac{30.7 \text{ g}}{50.0 \text{ g}} \times 100\% = \underline{61.4\%} \end{aligned}$$

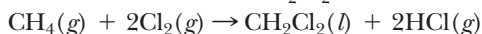


7-52. (1)  $\text{NH}_3$  is the limiting reactant.

(2) 141 g  $\text{NO}$  (theoretical yield),  $\underline{28.4\%}$  yield

7-54.  $\text{H}_2\text{O}$  is the limiting reactant producing 11.0 g  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

7-55. Molecular formula =  $\text{CH}_2\text{Cl}_2$



$\text{Cl}_2$  is the limiting reactant producing

9.00 g  $\text{CH}_2\text{Cl}_2$

### CHAPTER 8

8-1. Ultraviolet light has shorter wavelengths but higher energy than visible light. Because of this high energy, ultraviolet light can damage living cells in tissues, thus causing a burn.

8-2. Since these two shells are close in energy, transitions of electrons from these two levels to the  $n = 1$  shell have similar energy. Thus, the wavelengths of light from the two transitions are very close together.

8-3. Since these two shells are comparatively far apart in energy, transitions from these two levels to the  $n = 1$  shell have comparatively different energies. Thus, the wavelengths of light from the two transitions are quite different. (The  $n = 3$  to  $n = 1$  transition has a shorter wavelength than the  $n = 2$  to the  $n = 1$  transition.)

8-5.  $1p$  and  $3f$

8-8. A  $4p$  orbital is shaped roughly like a two-sided baseball bat with two "lobes" lying along one of the three axes. This shape represents the region of highest probability of finding the  $4p$  electrons.

8-9. The  $3s$  orbital is spherical in shape. There is an equal probability of finding the electron regardless of the orientation from the nucleus. (In fact, the probability lies in three concentric spheres with the highest probability in the sphere farthest from the nucleus.) The highest probability of finding the electron lies farther from the nucleus in the  $3s$  than in the  $2s$ .

8-11. One  $3s$ , three  $3p$ , and five  $3d$ , for a total of nine.

8-13. (a)  $3p$ , three (b)  $4d$ , five (c)  $6s$ , one

8-15.  $2n^2$ :  $2(3)^2 = 18$  and  $2(2)^2 = 8$

8-18.  $2(5)^2 = 50$

8-19. The first four subshells in the fifth shell ( $s$ ,  $p$ ,  $d$ , and  $f$ ) hold 32 electrons. The  $g$  subshell holds  $50 - 32 = 18$  electrons.

8-20. Since each orbital holds two electrons, there are nine orbitals in this subshell.

8-21. The  $1s$  subshell always fills first.

8-24. (a)  $6s$  (b)  $5p$  (c)  $4p$  (d)  $4d$

8-26.  $4s$ ,  $4p$ ,  $5s$ ,  $4d$ ,  $5p$ ,  $6s$ ,  $4f$

8-27. (a)  $\text{Mg}$ :  $1s^2 2s^2 2p^6 3s^2$

(b)  $\text{Ge}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

(c)  $\text{Pd}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^8$

(d)  $\text{Si}$ :  $1s^2 2s^2 2p^6 3s^2 3p^2$

8-29.  $1s^2 2s^2 2p^6 3s^2 3p^6$

8-31. (a)  $\text{S}$ :  $[\text{Ne}] 3s^2 3p^4$  (b)  $\text{Zn}$ :  $[\text{Ar}] 4s^2 3d^{10}$

(c)  $\text{Pu}$ :  $[\text{Rn}] 7s^2 6d^1 5f^5$  (d)  $\text{I}$ :  $[\text{Kr}] 5s^2 4d^{10} 5p^5$

8-33. (a)  $\text{In}$  (b)  $\text{Y}$  (c)  $\text{Ce}$  (d)  $\text{Ar}$

8-35. (a)  $3p$  (b)  $5p$  (c)  $5d$  (d)  $5s$

8-37. Both have three valence electrons. The outer electron in IIIA is in a  $p$  subshell; in IIIB it is in a  $d$  subshell.

8-39. (a)  $\text{F}$  (b)  $\text{Ga}$  (c)  $\text{Ba}$  (d)  $\text{Gd}$  (e)  $\text{Cu}$

8-41. (a) VIIA (b) IIIA (c) IIA (e) IB

8-42. VA:  $[\text{NG}] ns^2 np^3$  VB:  $[\text{NG}] ns^2 (n-1)d^3$

8-44. (b) and (e) belong to Group IVA

8-46. (a) IVA (b) VIIIA (c) IB (d)  $\text{Pr}$  and  $\text{Pa}$

8-47. (a)  $[\text{NG}] ns^2$  (b)  $[\text{NG}] ns^2 (n-1)d^{10}$

(c)  $[\text{NG}] ns^2 np^4$  or  $[\text{NG}] ns^2 (n-1)d^{10} np^4$

(d)  $[\text{NG}] ns^2 (n-1)d^2$

8-48. Helium does not have a filled  $p$  subshell. (There is no  $1p$  subshell.)

8-50.  $[\text{Ne}] 3s^2 3p^6$

8-52. The theoretical order of filling is  $6d$ ,  $7p$ ,  $8s$ ,  $5g$ . The  $6d$  is completed at element number 112. The  $7p$  and  $8s$  fill at element number 120. Thus element number 121 would theoretically begin the filling of the  $5g$  subshell. This assumes the normal order of filling.

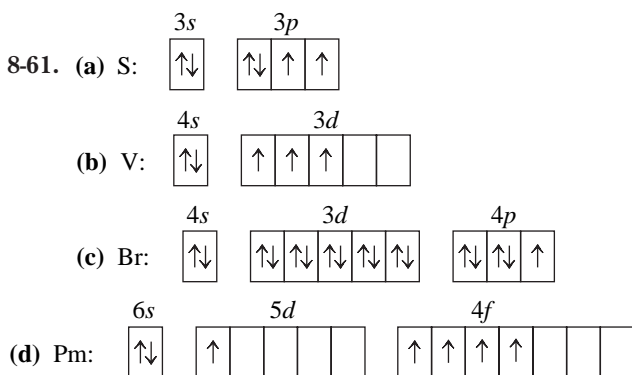
8-54.  $7s^2 6d^{10} 5f^4 7p^6$  Total 32

8-55.  $8s^2 5g^{18} 7d^{10} 6f^4 8p^6$  Total 50

8-56. (a) transition (b) representative (c) noble gas (d) inner transition

8-58. element number 118 (under  $\text{Rn}$ )

8-60. (a) This is excluded by Hund's rule since electrons are not shown in separate orbitals of the same subshell with parallel spins. (b) This is correct. (c) This is excluded by the Aufbau principle because the  $2s$  subshell fills before the  $2p$ . (d) This is excluded by the Pauli exclusion principle since the two electrons in the  $2s$  orbital cannot have the same spin.



8-63. IIB, none; VB, three; VIA, two; VIIA, one;  
 $[ns^1(n-1)d^5]$ , six; Pm, five

8-65. IVA and VIA

8-67. (a) As (b) Ru (c) Ba (d) I

8-69. Cr, 117 pm Nb, 134 pm

8-71. (a) V (b) Cl (c) Mg (d) Fe (e) B

8-72. In, 558 kJ/mol Ge, 762 kJ/mol

8-73. Te, 869 kJ/mol Br, 1140 kJ/mol

8-75. (a)  $\text{Cs}^+$  easiest, (b)  $\text{Rb}^{2+}$  hardest

8-77. (d) I

8-79. (a) Rb

8-81. (a)  $\text{Mg}^{2+}$  (b)  $\text{K}^+$  (c) S (d) Mg (e)  $\text{S}^{2-}$  (f)  $\text{Se}^{2-}$

8-83. The outer electron in Hf is in a shell higher in energy than that in Zr. This alone would make Hf a larger atom. However, in between Zr and Hf lie several subshells including the long  $4f$  subshell (Ce through Lu). The filling of these subshells, especially the  $4f$ , causes a gradual contraction that offsets the higher shell for Hf.

8-84.  $\text{C}^+$  (1086 kJ/mol),  $\text{C}^{2+}$  (3439 kJ/mol),  $\text{C}^{3+}$  (8059 kJ/mol),  $\text{C}^{4+}$  (14,282 kJ/mol),  $\text{C}^{5+}$  (52,112 kJ/mol).

Notice that the energy required to form  $\text{C}^+$  (1086 kJ) is about twice the energy required to form  $\text{Ga}^+$  (579 kJ), which is a metal. Thus it is apparent that metal cations form more easily than nonmetal cations.

8-85. (a) B (b) Ar (c) K, Cr, and Cu (d) Ga (e) Hf

8-87. (a) B (b) Br (c) Sb (d) Si

8-89. (a) Sr, metal, representative element, IIA

(b) Pt, metal, transition metal, VIIIB

(c) Br, nonmetal, representative element, VIIA

8-91. P

8-93. Z = Sn, X = Zr

8-97. (a) Ca (b)  $\text{Br}^-$  (c) S (d)  $\text{S}^{2-}$  (e)  $\text{Na}^+$

8-99.

| $s^1$ |    | $s^2$ |       |       |       |       |       |       |       |    |    | $p^1$ |    |  | $p^2$ |  |  | $p^3$ |  |   | $p^4$ |  |
|-------|----|-------|-------|-------|-------|-------|-------|-------|-------|----|----|-------|----|--|-------|--|--|-------|--|---|-------|--|
| 1     |    |       |       |       |       |       |       |       |       |    |    |       |    |  |       |  |  |       |  | 2 |       |  |
| 3     | 4  |       |       |       |       |       |       |       |       | 5  | 6  | 7     | 8  |  |       |  |  |       |  |   |       |  |
| 9     | 10 | $d^1$ | $d^2$ | $d^3$ | $d^4$ | $d^5$ | $d^6$ | $d^7$ | $d^8$ | 11 | 12 | 13    | 14 |  |       |  |  |       |  |   |       |  |
| 15    | 16 | 17    | 18    | 19    | 20    | 21    | 22    | 23    | 24    | 25 | 26 | 27    | 28 |  |       |  |  |       |  |   |       |  |
| 29    | 30 | 31    | 32    | 33    | 34    | 35    | 36    | 37    | 38    | 39 | 40 | 41    | 42 |  |       |  |  |       |  |   |       |  |
| 43    | 44 | 45*   |       |       |       |       |       |       |       |    |    |       |    |  |       |  |  |       |  |   |       |  |

\*46–50 would be in a  $4f$  subshell

- (a) six in second period, 14 in fourth  
 (b) third period, #14; fourth period, #28  
 (c) first inner transition element is #46 (assuming an order of filling like that on Earth)  
 (d) Elements #11 and #17 are most likely to be metals.  
 (e) Element #12 would have the larger radius in both cases.  
 (f) Element #7 would have the higher ionization energy in all three cases.  
 (g) The ions that would be reasonable are  $16^{2+}$  (metal cation),  $13^-$  (nonmetal anion),  $15^+$  (metal cation), and  $1^-$  (nonmetal anion). The  $9^{2+}$  ion is not likely because the second electron would come from a filled inner subshell. The  $7^+$  ion is not likely because it would be a nonmetal cation. The  $17^{4+}$  ion is not likely because #17 has only three electrons in the outer shell.

## CHAPTER 9

9-1. (a)  $\cdot\text{Ca}\cdot$  (b)  $\cdot\text{Sb}\cdot$  (c)  $\cdot\text{Sn}\cdot$  (d)  $\cdot\text{I}\cdot$

(e)  $:\ddot{\text{Ne}}:$  (f)  $\cdot\ddot{\text{Bi}}\cdot$  (g)  $\cdot\text{VI}A:$

9-2. (a) Group IIIA (b) Group VA (c) Group IIA

9-4. The electrons from filled inner subshells are not involved in bonding.

9-6. (b) Sr and S (c) H and K (d) Al and F

9-8. (b)  $\text{S}^-$  (c)  $\text{Cr}^{2+}$  (e)  $\text{In}^+$  (f)  $\text{Pb}^{2+}$  (h)  $\text{Tl}^{3+}$

9-10. They have the noble gas configuration of He, which requires only two electrons.

9-11. (a)  $\text{K}^+$  (b)  $\cdot\ddot{\text{O}}:\cdot$  (c)  $:\ddot{\text{I}}:\cdot$  (d)  $:\ddot{\text{P}}:\cdot$  (e)  $\text{Ba}^+$

(f)  $\cdot\ddot{\text{Xe}}:\cdot$  (g)  $\text{Sc}^{3+}$

9-13. (b)  $\text{O}^-$  (e)  $\text{Ba}^+$  (f)  $\text{Xe}^+$

9-14. (a)  $\text{Mg}^{2+}$  (b)  $\text{Ga}^{3+}$  (pseudo-noble gas configuration.) (c)  $\text{Br}^-$  (d)  $\text{S}^{2-}$  (e)  $\text{P}^{3-}$

9-17.  $\text{Se}^{2-}$ ,  $\text{Br}^-$ ,  $\text{Rb}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Y}^{3+}$

9-18.  $\text{Tl}^{3+}$  has a full  $5d$  subshell. This is a pseudo-noble gas configuration.

9-19.  $\text{Cs}_2\text{S}$ ,  $\text{Cs}_3\text{N}$ ,  $\text{BaBr}_2$ ,  $\text{BaS}$ ,  $\text{Ba}_3\text{N}_2$ ,  $\text{InBr}_3$ ,  $\text{In}_2\text{S}_3$ ,  $\text{InN}$

9-21. (a)  $\text{CaI}_2$  (b)  $\text{CaO}$  (c)  $\text{Ca}_3\text{N}_2$  (d)  $\text{CaTe}$   
 (e)  $\text{CaF}_2$

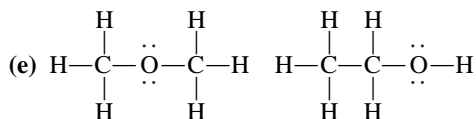
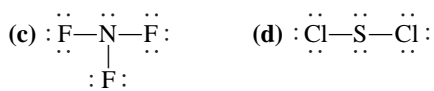
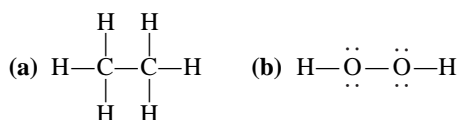
9-23. (a)  $\text{Cr}^{3+}$  (b)  $\text{Fe}^{3+}$  (c)  $\text{Mn}^{2+}$  (d)  $\text{Co}^{2+}$   
 (e)  $\text{Ni}^{2+}$  (f)  $\text{V}^{3+}$

9-26. (a)  $\text{H}_2\text{S}$  (b)  $\text{GeH}_4$  (c)  $\text{ClF}$  (d)  $\text{Cl}_2\text{O}$  (e)  $\text{NCl}_3$   
 (f)  $\text{CBr}_4$

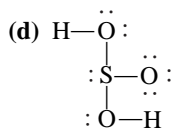
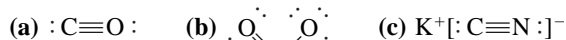
9-28. (b)  $\text{Cl}_3$  (d)  $\text{NBr}_4$  (e)  $\text{H}_3\text{O}$

9-30. (a)  $\text{SO}_4^{2-}$  (b)  $\text{IO}_3^-$  (c)  $\text{SeO}_4^{2-}$  (d)  $\text{H}_2\text{PO}_4^-$   
 (e)  $\text{C}_2^{2-}$

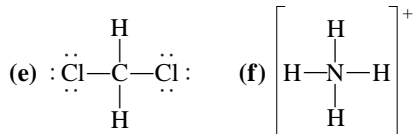
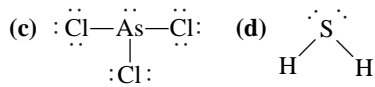
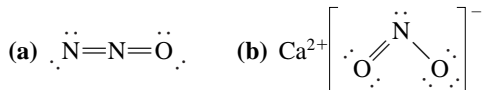
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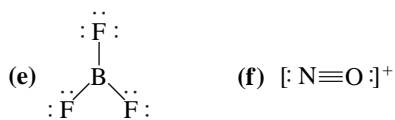
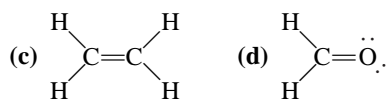
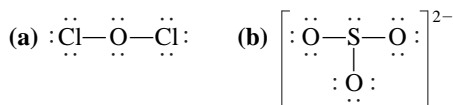
9-34.



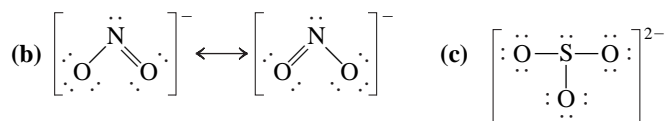
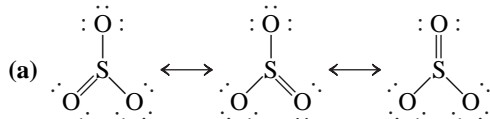
9-36.



9-37.

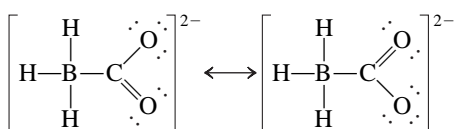


9-40.



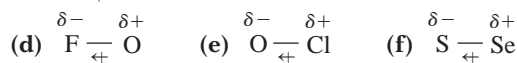
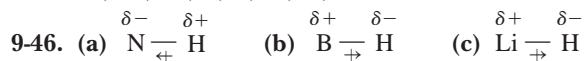
(only one structure)

9-42.



9-43. A resonance hybrid is the actual structure of a molecule or ion that is implied by the various resonance structures. Each resonance structure contributes a portion of the actual structure. For example, the two structures shown in problem 9-42 imply that both carbon-oxygen bonds have properties that are halfway between those of a single and a double bond.

9-45. Cs, Ba, Be, B, C, Cl, O, F

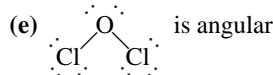
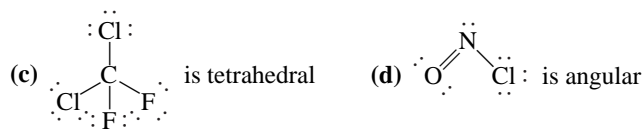


(i) C—S (very low polarity)

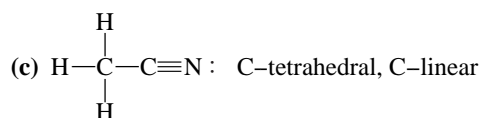
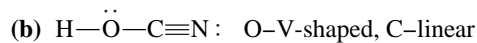
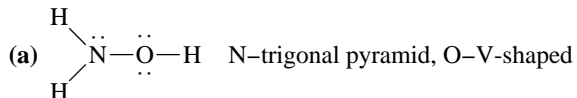
9-47. (i) nonpolar, (b) = (f), (d) = (e) = (g), (a), (c), (h)

9-48. Only (d) Al—F is predicted to be ionic on this basis since the electronegativity difference is 2.5.

9-51. (b) I—I (nonpolar), (c) C—H (nearly nonpolar)


 9-55. (a) No angle between two points      (b)  $180^\circ$   
 (c)  $120^\circ$ 

9-57.

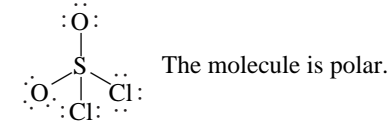


(d) See problem 9-42. B— tetrahedral, C— trigonal planar

9-59. If the molecule has a symmetrical geometry and all bonds are the same, the bond dipoles cancel and the molecule is nonpolar.

 9-60. (a) polar      (b) nonpolar      (c) polar      (d) polar  
 (e) polar

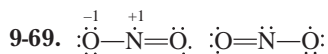
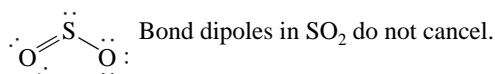
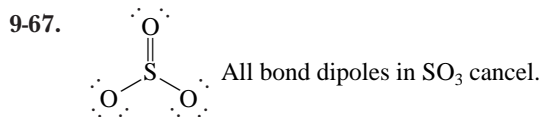
9-62.



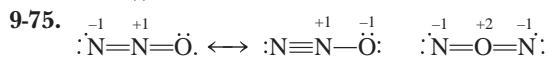
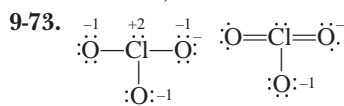
9-63. Since the H—S bond is much less polar than the H—O bond, the resultant molecular dipole is

much less. The  $\text{H}_2\text{S}$  molecule is less polar than the  $\text{H}_2\text{O}$  molecule.

**9-65.** The  $\text{CHF}_3$  molecule is more polar than the  $\text{CHCl}_3$  molecule. The  $\text{C}-\text{F}$  bond is more polar than the  $\text{C}-\text{Cl}$  bond, which means that the resultant molecular dipole is larger for  $\text{CHF}_3$ .

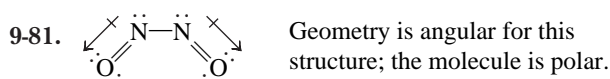
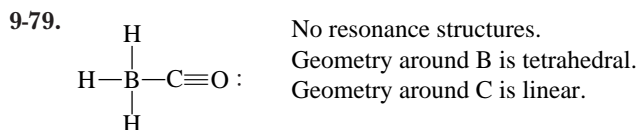
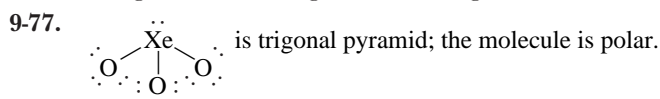


**9-71.** (a) C, -1, O, +1 (b) 5, +2, single bonded O's, -1  
(c) C, -1, N, O (b) H's, O, S, +1, O in  $\text{H}-\text{O}-\text{S}$ , 0, other O, -1



Both resonance structures for  $\text{NNO}$  have much less formal charge than the  $\text{NON}$  structure.

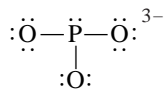
**9-76.** (a) e.g.,  $\text{RbCl}$  (b) e.g.,  $\text{SrO}$  (c) e.g.,  $\text{AlN}$



Other resonance structures:

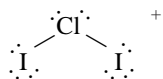


**9-84.** Valence electrons for neutral  $\text{PO}_3 = 5(\text{P}) + (3 \times 6)$  (O's) = 23. Since the species has 26 electrons it must be an anion with a  $-3$  charge (i.e.,  $\text{PO}_3^{3-}$ ).



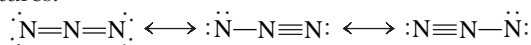
The geometry of the anion is trigonal pyramid with a  $\text{O}-\text{P}-\text{O}$  angle of about  $109^\circ$ .

**9-85.** Valence electrons for neutral  $\text{ClI}_2 = 3 \times 7 = 21$ . Since the species has 20 valence electrons it must be a cation with a  $+1$  charge (i.e.,  $\text{ClI}_2^+$ ).

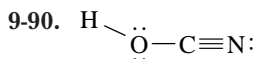


The geometry of the cation is V-shaped with an angle of about  $109^\circ$ .

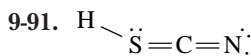
**9-87.**  $\text{K}_3\text{N}$ , potassium nitride  $\text{KN}_3 = \text{K}^+\text{N}_3^-$  Resonance structures:



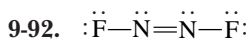
In all resonance structures, the geometry around N is linear.



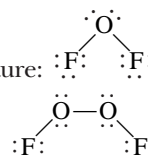
The angle of  $105^\circ$  indicates that the  $\text{H}-\text{O}-\text{C}$  angle is V-shaped with an angle of about  $109^\circ$ . This would involve two bonds and two pairs of electrons on the O. The geometry around the C is linear.



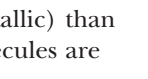
The angle of  $116^\circ$  indicates that the  $\text{H}-\text{S}-\text{C}$  angle is V-shaped with an angle of about  $120^\circ$ . This would involve three bonds and one pair of electrons on the S. The geometry around the C is linear.



**9-94.** Oxygen difluoride,  $\text{OF}_2$ . Lewis structure:

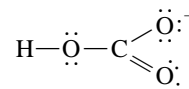


Dioxygen difluoride,  $\text{O}_2\text{F}_2$ . Lewis structure:



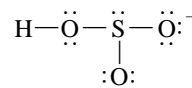
Oxygen is less electronegative (more metallic) than fluorine and so is named first. Both molecules are angular; thus they are polar.

**9-96.** Formula =  $\text{NaHCO}_3 = \text{Na}^+\text{HCO}_3^-$



The geometry around the C is trigonal planar with the approximate  $\text{H}-\text{O}-\text{C}$  angle of  $120^\circ$ .

**9-98.** Formula =  $\text{CaH}_2\text{S}_2\text{O}_6 = \text{Ca}(\text{HSO}_3)_2$  calcium bisulfite or calcium hydrogen sulfite



The geometry around the S is trigonal pyramid. The  $\text{H}-\text{O}-\text{S}$  angle is about  $109^\circ$ .

**9-99.** (1) (a) 17 (b) 31 (c)  $51_3$  (d) 97 (e)  $7(13)$   
(f)  $10(13)_2$  (g)  $67_2$  (h)  $3_26$

(2) On Zerk, six electrons fill the outer  $s$  and  $p$  orbitals to make a noble gas configuration.

Therefore, we have a "sextet" rule on Zerk.

(a)  $1-7:$  (b)  $3^+1:$  (ionic) (c)  $1-5-1$   
|  
1

(d)  $9^+ :7^-$  (ionic) (e)  $:7-13:$  (f)  $10^{2+}(:13^-)_2$  (ionic)

(g)  $:7-6-7:$  (h)  $(3^+)_2:6:^{2-}$  (ionic)

## CHAPTER 10

**10-1.** The molecules of water are closely packed together and thus offer much more resistance. The molecules in a gas are dispersed into what is mostly empty space.

**10-3.** Since a gas is mostly empty space, more molecules can be added. In a liquid, the space is mostly occupied by the molecules so no more can be added.

**10-5.** Gas molecules are in rapid but random motion. When gas molecules collide with a light dust particle suspended in the air, they impart a random motion to the particle.

**10-6.** 1260 mi/hr

**10-7.** The molecule with the largest formula weight travels the slowest.  $\text{SF}_6(146.1 \text{ amu}) < \text{SO}_2(64.07 \text{ amu})$

$< \text{N}_2\text{O}(44.02 \text{ amu}) < \text{CO}_2(44.01 \text{ amu})$

$< \text{N}_2(28.02 \text{ amu}) < \text{H}_2(2.016 \text{ amu})$

**10-9.** When the pressure is high, the gas molecules are forced close together. In a highly compressed gas the molecules can occupy an appreciable part of the total volume. When the temperature is low, molecules have a lower average velocity. If there is some attraction, they can momentarily stick together when moving slowly.

**10-10.** (a) 2.17 atm (b) 0.0266 torr (c) 9560 torr  
(d) 0.0558 atm (e) 3.68 lb/in.<sup>2</sup> (f) 11 kPa

**10-11.** (a) 768 torr (b)  $2.54 \times 10^4 \text{ atm}$  (c) 8.40 lb/in.<sup>2</sup>  
(d) 19 torr

**10-13.** 0.0102 atm

**10-15.** Assume a column of Hg has a cross-section of  $1 \text{ cm}^2$  and is 76.0 cm high. Weight of Hg =  $76.0 \text{ cm} \times 1 \text{ cm}^2 \times 13.6 \text{ g/cm}^3 = 1030 \text{ g}$ . If water is substituted,

1030 g of water in the column is required. Height  $\times 1 \text{ cm}^2 \times 1.00 \text{ g/cm}^3 = 1030 \text{ g}$  height = 1030 cm

$$1030 \text{ cm} \times \frac{1 \text{ in.}}{2.54 \text{ cm}} \times \frac{1 \text{ ft}}{12 \text{ in.}} = \underline{\underline{33.8 \text{ ft}}}$$

If a well is 40 ft deep, the water cannot be raised in one stage by suction since 33.8 ft is the theoretical maximum height that is supported by the atmosphere.

**10-16.** 10.2 L

**10-18.** 978 mL

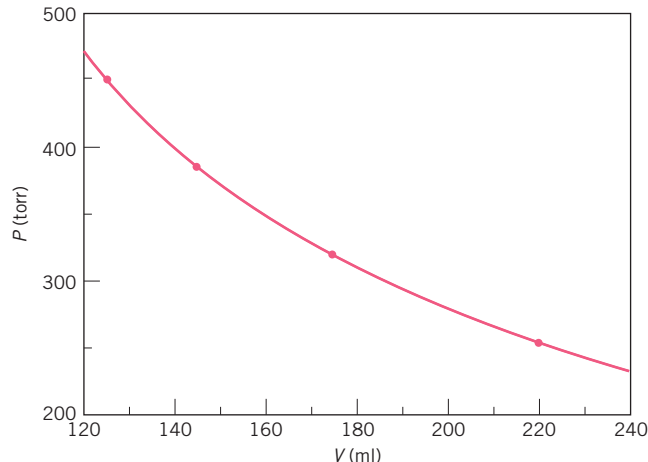
**10-19.** 67.9 torr

$$\mathbf{10-22.} \quad V_{\text{final}} (V_f) = 15 V_{\text{initial}} (V_i) \frac{V_f}{V_i} = \frac{P_i}{P_f}$$

$$\frac{15 V_i}{V_i} = \frac{0.950 \text{ atm}}{P_f}$$

$$P_f = 0.950 \text{ atm} \times 15 = 14.3 \text{ atm}$$

**10-23.**



**10-24.** 1.94 L

**10-26.** 77°C

**10-28.**  $2.60 \times 10^4 \text{ L}$

**10-29.** 341 K (68°C)

**10-31.** 2.94 atm

**10-32.**  $191 \text{ K} - 273 = -82^\circ\text{C}$

**10-34.** 596 K (323°C)

**10-35.** 30.2 lb/in.<sup>2</sup>

**10-38.** (a) and (d)

**10-40.** Exp. 1,  $T$  increases; Exp. 2,  $V$  decreases; Exp. 3,  $P$  increases; Exp. 4,  $T$  increases

**10-42.** 1.24 atm

**10-43.** 76.8 L

**10-45.** 88.5 K =  $-185^\circ\text{C}$

**10-48.** 258 K ( $-15^\circ\text{C}$ )

**10-49.** 409 mL

**10-50.** 1.70 L

**10-51.** Let  $x$  = total moles needed in the expanded balloon.

$$188 \text{ L} \times \frac{x}{8.40 \text{ mol}} = 275 \text{ L} \quad x = 12.3 \text{ mol}$$

$$12.3 - 8.4 = \underline{\underline{3.9 \text{ mol must be added.}}}$$

**10-53.**  $n_2 = 2.50 \times 10^{-3} \text{ mol} \times \frac{164 \text{ mL}}{75.0 \text{ mL}} = 5.47 \times 10^{-3} \text{ mol}$

$$(5.47 \times 10^{-3}) - (2.50 \times 10^{-3}) = 2.97 \times 10^{-3} \text{ mol}$$

$$2.97 \times 10^{-3} \text{ mol N}_2 \times \frac{28.02 \text{ g N}_2}{\text{mol N}_2} = \underline{\underline{0.0832 \text{ g N}_2}}$$

**10-55.** 98°C

**10-57.** 13.0 g

**10-58.** 589 torr

**10-60.** 3.35 g

**10-62.**  $n = 1.0 \times 10^6 \text{ mol}$  of gas in the balloon. 8800 lb He or 64,000 lb air

$$\text{Lifting power with He} = 64,000 - 8800 = \underline{\underline{55,000 \text{ lb}}}$$

$$\text{Lifting power with H}_2 = 64,000 - 4000 = \underline{\underline{60,000 \text{ lb}}}$$

Helium is a noncombustible gas whereas hydrogen forms an explosive mixture with  $\text{O}_2$ .

**10-64.** 762 torr

**10-66.** 6.8 torr

**10-69.**  $P_{\text{N}_2} = 756 \text{ torr}$ ;  $P_{\text{O}_2} = 84.0 \text{ torr}$ ;  $P_{\text{SO}_2} = 210 \text{ torr}$

**10-70.** 730 torr

**10-72.**  $P_{\text{N}_2} = 300 \text{ torr}$ ;  $P_{\text{O}_2} = 85 \text{ torr} \times \frac{4.00 \text{ L}}{2.00 \text{ L}} = 170 \text{ torr}$ ;

$$P_{\text{CO}_2} = 225 \text{ torr}; \quad P_{\text{tot}} = 695 \text{ torr};$$

**10-73.**  $P_A = 0.550 \text{ atm}$ ;  $P_B = 0.300 \text{ atm}$ ;

**10-75.** 7.63 L

**10-77.** 112 L

**10-79.**  $1.39 \times 10^{-3} \text{ g}$

**10-80.** 1.24 g/L

**10-82.** 34.0 g/mol

**10-84.**  $1.00 \text{ L} \times \frac{273 \text{ K}}{298 \text{ K}} \times \frac{1.20 \text{ atm}}{1.00 \text{ atm}} = 1.10 \text{ L (STP)}$

$$\frac{3.60 \text{ g}}{1.10 \text{ L}} = \underline{\underline{3.27 \text{ g/L (STP)}}}$$



**10-85.** Find moles of  $N_2$  in 1 L at 500 torr and  $22^\circ\text{C}$  using the ideal gas law.  $n = 0.272 \text{ mol } N_2$  mass =  $0.762 \text{ g } N_2$   
Density =  $0.762 \text{ g/L}$  (500 torr and  $22^\circ\text{C}$ )

**10-87.** 25.8 L  $\text{CO}_2$  (STP)

**10-88.** Vol.  $\text{O}_2 \rightarrow \text{mol } \text{O}_2 \rightarrow \text{mol } \text{Mg} \rightarrow \text{g } \text{Mg}$

$$5.80 \text{ L } \text{O}_2 \times \frac{1 \text{ mol } \text{O}_2}{22.4 \text{ L } \text{O}_2} \times \frac{2 \text{ mol } \text{Mg}}{1 \text{ mol } \text{O}_2} \times \frac{24.31 \text{ g } \text{Mg}}{\text{mol } \text{Mg}}$$

$$= 12.6 \text{ g } \text{Mg}$$

**10-90.** 3.47 L

**10-92.** (a)  $\text{g } \text{C}_4\text{H}_{10} \rightarrow \text{mol } \text{C}_4\text{H}_{10} \rightarrow \text{mol } \text{CO}_2 \rightarrow \text{Vol } \text{CO}_2$

$$85.0 \text{ g } \text{C}_4\text{H}_{10} \times \frac{1 \text{ mol } \text{C}_4\text{H}_{10}}{58.12 \text{ g } \text{C}_4\text{H}_{10}} \times \frac{8 \text{ mol } \text{CO}_2}{2 \text{ mol } \text{C}_4\text{H}_{10}} \times \frac{22.4 \text{ L}}{\text{mol } \text{CO}_2} = 131 \text{ L}$$

(b) 96.1 L  $\text{O}_2$  (c) 124 L  $\text{CO}_2$

**10-93.** 2080 kg Zr (2.29 tons)

**10-95.**  $n_{\text{O}_2} = 1.46 \text{ mol } \text{O}_2$   $1.46 \text{ mol } \text{O}_2 \times \frac{1 \text{ mol } \text{CO}_2}{2 \text{ mol } \text{O}_2} = 0.730 \text{ mol } \text{CO}_2$   $V = 12.0 \text{ L } \text{CO}_2$

**10-96.** Force =  $12.0 \text{ cm}^2 \times 15.0 \text{ cm} \times \frac{13.6 \text{ g}}{\text{cm}^3} = 2450 \text{ g}$

$$P = \frac{2450 \text{ g}}{12.0 \text{ cm}^2} = 204 \text{ g/cm}^2$$

$$1 \text{ atm} = 76.0 \text{ cm} \times \frac{13.6 \text{ g}}{\text{cm}^3} = 1030 \text{ g/cm}^2$$

$$204 \text{ g/cm}^2 \times \frac{1 \text{ atm}}{1030 \text{ g/cm}^2} = 0.198 \text{ atm}$$

**10-98.**  $n = 0.0573 \text{ mol} \frac{8.37 \text{ g}}{0.0573 \text{ mol}} = 146 \text{ g/mol}$

**10-99.** Empirical formula =  $\text{CH}_2$  molar mass = 41.9 g/mol molecular formula =  $\text{C}_3\text{H}_6$

**10-101.**  $n_{\text{tot}} = 0.265 \text{ mol } \text{O}_2 + 0.353 \text{ mol } \text{N}_2 + 0.160 \text{ mol } \text{CO}_2 = 0.778 \text{ mol of gas}$

$$V = 6.92 \text{ L}$$

$$P_{\text{O}_2} = \frac{0.265}{0.778} \times 2.86 \text{ atm} = 0.974 \text{ atm}$$

$$P_{\text{N}_2} = 1.30 \text{ atm} \quad P_{\text{CO}_2} = 0.59 \text{ atm}$$

**10-102.**  $n = 5 \times 10^{-20} \text{ mol}$   $P = 4 \times 10^{-17} \text{ atm}$

**10-103.** 19.6 L/mol density of  $\text{CO}_2 = 2.25 \text{ g/L}$

**10-104.** Density =  $\frac{\text{mass}}{V} = \frac{P \times MM}{RT} = 0.525 \text{ g/L}$  (hot air)

density at STP = 1.29 g/L

$0.525/1.29 = 0.41$  (Hot air is less than half as dense as air at STP.)

**10-106.** 0.0103 mol of  $\text{H}_3\text{BCO}$  produces 0.0412 mol of gaseous products;  $V = 1.12 \text{ L}$  (products at  $25^\circ\text{C}$  and 0.900 atm)

**10-108.**  $2\text{Al}(s) + 3\text{F}_2(g) \rightarrow 2\text{AlF}_3(s)$

$$\text{original } \text{F}_2 = 0.310 \text{ mol } \text{F}_2$$

leftover  $\text{F}_2 = 0.0921 \text{ mol}$

$$0.310 - 0.092 = 0.218 \text{ mol } \text{F}_2 \text{ reacts forming}$$

12.2 g  $\text{AlF}_3$

**10-110.** 135 L

**10-112.** 0.763 mol  $\text{H}_2\text{O}$  in the ice.  $V$  (of vapor) = 645 L

**10-113.**  $9.81 \times 10^{-4} \text{ mol } \text{NH}_3$  produces 11.0 mL  $\text{N}_2\text{H}_4$

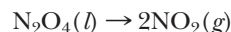
**10-115.** Empirical formula =  $\text{NO}_2$

(2) Find molar mass of product compound.

$$n = \frac{PV}{RT} = \frac{715 \text{ torr} \times 1.05 \text{ L}}{760 \text{ torr/atm} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 273 \text{ K}}$$

$$\text{Molar mass} = \frac{2.03 \text{ g}}{0.0441 \text{ mol}} = 46.0 \text{ g/mol}$$

(3) Since one compound decomposes to one other compound, the reactant compound must have the same empirical formula as the product compound. Since the empirical mass of  $\text{NO}_2 = 46.01 \text{ g/emp unit}$ , then the product must be  $\text{NO}_2$  (MM = 46.0 g/mol). Since 0.0220 mol of reactant form 0.0441 mol of product (1:2 ratio), the reaction must be



**10-117.**  $6\text{Li}(s) + \text{N}_2(g) \rightarrow 2\text{Li}_3\text{N}(s)$   $3\text{Mg}(s) + \text{N}_2(g) \rightarrow \text{Mg}_3\text{N}_2(s)$

10.8 mol  $\text{N}_2$  reacts with 450 g Li or 788 g Mg

## CHAPTER 11

**11-1.** Since gas molecules are far apart, they travel a comparatively large distance between collisions. Liquid molecules, on the other hand, are close together so do not travel far between collisions. The farther molecules travel, the faster they mix.

**11-3.** Both the liquid molecules and food coloring molecules are in motion. Through constant motion and collisions the food coloring molecules eventually become dispersed.

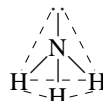
**11-5.** Generally, solids have greater densities than liquids. (Ice and water are notable exceptions.) Since the molecules of a solid are held in fixed positions, more of them usually fit into the same volume compared to the liquid state. This is similar to being able to get more people into a room if they are standing still than if they are moving around.

**11-6.**  $\text{CH}_4 < \text{CCl}_4 < \text{GeCl}_4$

**11-8.** All are nonpolar molecules with only London forces between molecules. The higher the molar mass, the greater the London forces and the more likely that the compound is a solid.  $\text{I}_2$  is the heaviest and is a solid;  $\text{Cl}_2$  is the lightest and is a gas.

**11-10.** If  $\text{H}_2\text{O}$  were linear, the two equal bond dipoles would be exactly opposite and would therefore cancel. Hydrogen bonding can occur only when the molecule is polar.

**11-12.**



$\text{NH}_3$  molecules interact by hydrogen bonding.



11-14. (a) HBr (b) SO<sub>2</sub> (f) CO

11-17. (a) HF (c) H<sub>2</sub>NCl (d) H<sub>2</sub>O (f) HCOOH

11-19. (a) ion-ion (b) hydrogen bonding plus London  
(c) dipole-dipole plus London (d) London only

11-20. F<sub>2</sub> < HCl < HF < KF

11-23. CO<sub>2</sub> is a nonpolar molecular compound.  
SiO<sub>2</sub> is a network solid.

11-25. PbCl<sub>2</sub> is most likely ionic (Pb<sup>2+</sup>, 2Cl<sup>-</sup>),  
while the melting point of PbCl<sub>4</sub> indicates that  
it is a molecular compound.

11-26. Motor oil is composed of large molecules  
that increase viscosity. Motor oil also has a higher  
surface tension.

11-28. Water evaporates quickly on a hot day and  
thus lowers the air temperature.

11-30. The comparatively low boiling point of ethyl  
chloride indicates that it has a high vapor pressure at  
room temperature (25°C). In fact, it boils rapidly,  
cooling the skin to below the freezing point of water.

11-32. The liquid other than water. The higher the vapor  
pressure, the faster the liquid evaporates and the liquid  
cools.

11-33. Equilibrium refers to a state where opposing forces  
are balanced. In the case of a liquid in equilibrium with its  
vapor, it means that a molecule escaping to the vapor is  
replaced by one condensing to the liquid.

11-35. The substance is a gas at 1 atm and 75°C. It would  
boil at a temperature below 75°C.

11-38. Ethyl alcohol boils at about 52°C at that altitude. At  
10°C ethyl ether is a gas at that altitude.

11-39. Death Valley is below sea level. The atmospheric  
pressure is more than 1 atm so water boils above its  
normal boiling point.

11-41. Both exist as atoms with only London forces, but  
the higher atomic mass of argon accounts for its higher  
boiling point.

11-43. Figure 11-15 is not very precise; at 10°C the  
actual vapor pressure of water is 9.2 torr. Liquid water  
could theoretically exist but it would rapidly evaporate  
and be changed to ice by the cooling effect.

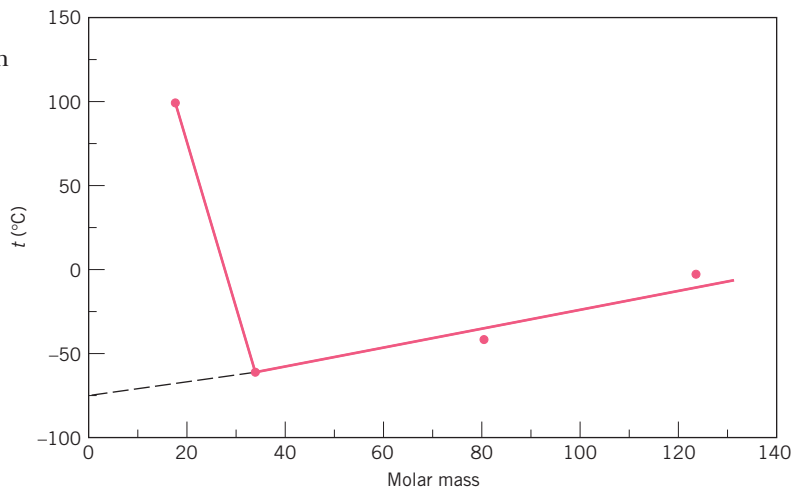
11-44. The liquid with the higher vapor pressure (420  
torr) has the lower boiling point. It also probably has the  
lower heat of vaporization.

11-46. Molecular O<sub>2</sub> is heavier than Ne atoms and so has  
higher intermolecular forces (London). CH<sub>3</sub>OH has  
hydrogen bonding, which would indicate a much higher  
heat of vaporization than the other two.

11-47. This is a comparatively high heat of fusion, so the  
melting point is probably also comparatively high.

11-49. This is a comparatively high boiling point, so the  
compound probably also has a high melting point.

11-50.



The boiling point of H<sub>2</sub>O would be about -75°C  
without hydrogen bonding.

11-53.  $7.07 \times 10^3$  J

11-55. 2.54 g H<sub>2</sub>O, 1.64 g NaCl, 6.69 g benzene

11-57. 555 cal (ether), 2000 cal (H<sub>2</sub>O)

Water would be more effective.  $1.30 \times 10^4$  J (13.0 kJ)

11-59. NH<sub>3</sub>:  $6.12 \times 10^5$  J Freon:  $7.25 \times 10^4$  J

On the basis of mass, ammonia is the more effective  
refrigerant.

11-61. Condensation:  $62.2 \times 10^4$  J Cooling:  $8.6 \times 10^4$  J  
Total =  $7.08 \times 10^5$  J (708 kJ)

11-63.  $2.83 \times 10^4$  cal

11-65. heat ice:  $132 \text{ g} \times 20^\circ\text{C} \times \frac{0.492 \text{ cal}}{\text{g} \cdot ^\circ\text{C}} = 1300 \text{ cal}$

melt ice:  $132 \text{ g} \times \frac{79.8 \text{ cal}}{\text{g}} = 10,500 \text{ cal}$

heat H<sub>2</sub>O:  $132 \text{ g} \times 100^\circ\text{C} \times \frac{1.00 \text{ cal}}{\text{g} \cdot ^\circ\text{C}} = 13,200 \text{ cal}$

vap. H<sub>2</sub>O:  $132 \text{ g} \times \frac{540 \text{ cal}}{\text{g}} = 71,300 \text{ cal}$

Total = 96,300 cal (96.3 kcal)

11-67. Let Y = the mass of the sample in grams. Then  
 $\left(\frac{2260 \text{ J}}{\text{g}} \times Y\right) + \left(25.0^\circ\text{C} \times Y \times \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ\text{C}}\right) = 28,400 \text{ J}$

$Y = \underline{12.0 \text{ g}}$

11-69. 18°C

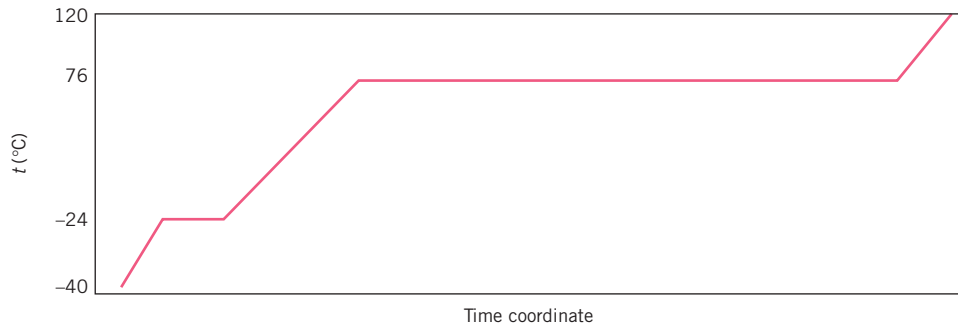
11-70. (b) melting (c) boiling

11-71. The average kinetic energy of all molecules of water  
at the same temperature is the same regardless of the  
physical state.

11-73. Because H<sub>2</sub>O molecules have an attraction  
for each other, moving them apart increases the potential  
energy. Since the molecules in a gas at 100°C are farther  
apart than in a liquid at the same temperature, the  
potential energy of the gas molecules is greater.

11-74. The water does not become hotter, but it will boil faster.

11-76.



The time of boiling is over ten times longer than the time of melting

11-78.  $C_2H_5NH_2$ :  $17^\circ C$ , hydrogen bonding

$CH_3OCH_3$ :  $-25^\circ C$ , dipole-dipole (polar)

$CO_2$ :  $-78^\circ C$ , London forces only (nonpolar)

11-79.  $SF_6$  is a molecular compound and  $SnO$  is an ionic compound (i.e.,  $Sn^{2+}$ ,  $O^{2-}$ ). All ionic compounds are found as solids at room temperature because of the strong ion-ion forces.

11-81. There is hydrogen bonding in  $CH_3OH$ . Hydrogen bonding is a considerably stronger attraction than ordinary dipole-dipole forces. The stronger the attractions the higher the boiling point.

11-83.  $SiH_4$  is nonpolar.  $PH_3$  and  $H_2S$  are both polar but  $H_2S$  is more polar with more and stronger dipole-dipole attractions.

11-85. Carbon monoxide is polar, whereas nitrogen is not. The added dipole-dipole attraction in  $CO$  may account for the slightly higher boiling point.

$$11-87. 2000 \text{ W} \times \frac{453.6 \text{ g}}{\text{W}} \times \frac{266 \text{ J}}{\text{g}} = 2.41 \times 10^8 \text{ J}$$

Heating 1 g of  $H_2O$  from  $25.0^\circ C$  to  $100.0^\circ C$  and the vaporizing the water requires

$$(75.0^\circ C \times 4.184 \text{ J}/^\circ C) + 2260 \text{ J} = 2.57 \times 10^3 \text{ J/g } H_2O$$

$$\frac{2.41 \times 10^8 \text{ J}}{2.57 \times 10^3 \text{ J/g } H_2O} = 9.38 \times 10^4 \text{ g } H_2O = \underline{\underline{93.8 \text{ kg } H_2O}}$$

11-88.  $V = 100 \text{ L}$ ,  $T = 34 + 273 = 307 \text{ K}$ ,

$$P(H_2O) = 0.700 \times 39.0 \text{ torr} = 27.3 \text{ torr}$$

Use the ideal gas law to find moles of water.

$$n = \frac{PV}{RT} = \frac{27.3 \text{ torr}}{760 \text{ torr/atm}} \times 100 \text{ L} \\ = \frac{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 307 \text{ K}}{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 307 \text{ K}} = 0.143 \text{ mol}$$

$$0.143 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{\text{mol } H_2O} = \underline{\underline{2.58 \text{ g } H_2O}}$$

11-90. Calculate the heat required first to heat the water from  $25^\circ C$  to  $100^\circ C$  then to vaporize the water.

$3.10 \times 10^5 \text{ J}$  (to heat water),  $2.260 \times 10^6 \text{ J}$  (to vaporize water) = 2570 kJ total

$$\text{Cr: } \frac{2570 \text{ kJ}}{21.0 \text{ kJ/mol}} \times \frac{52.00 \text{ g Cr}}{\text{mol Cr}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = \underline{\underline{6.36 \text{ kg Cr}}}$$

8.81 kg Mo, 13.5 kg W

11-91. The element must be mercury (Hg) since it is a liquid at room temperature and must be a metal since it forms a +2 ion.

The 15.0 kJ represents the heat required to melt  $X \text{ g}$  of Hg, heat  $X \text{ g}$  from  $-39^\circ C$  to  $357^\circ C$  (i.e.,  $396^\circ C$ ), and vaporize  $X \text{ g}$  of Hg.

$$(11.5 \text{ J/g} \times X) + \left[ 396^\circ C \times 0.139 \frac{\text{J}}{\text{g}^\circ C} \times X \right] \\ + (29.5 \text{ J/g} \times X) = 15.00 \text{ kJ} \times \frac{10^3 \text{ J}}{\text{kJ}}$$

$$11.5 \text{ J/g } X + 55.0 \text{ J/g } X + 29.5 \text{ J/g } X = 15,000 \text{ J}$$

$$X = \underline{\underline{156 \text{ g Hg}}}$$

11-93. Calculate the mass of water in the vapor state in the room at  $-5^\circ C$  (268 K) using the ideal gas law. 2.99 mol  $H_2O$  (in vapor) = 53.9 g  $H_2O$  (capacity of the room) Eventually, all of the 50.0 g should sublime since it is less than the room could contain.

## CHAPTER 12

12-1. The ion-ion forces in the crystal hold the crystal together and resist the ion-dipole forces between water and the ions in the crystal. The ion-dipole forces remove the ions from the crystal.

12-3. Calcium bromide is soluble, lead(II) bromide is insoluble, benzene and water are immiscible, and alcohol and water are miscible.

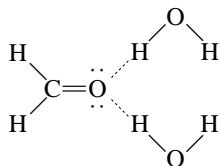
12-4. (a)  $LiF \rightarrow Li^+(aq) + F^-(aq)$

(b)  $(NH_4)_3PO_4 \rightarrow 3NH_4^+(aq) + PO_4^{3-}(aq)$

(c)  $Na_2CO_3 \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$

(d)  $Ca(C_2H_3O_2)_2 \rightarrow Ca^{2+}(aq) + 2C_2H_3O_2^-(aq)$

12-6.



There is hydrogen bonding between solute and solvent.

12-8. At 10°C,  $\text{Li}_2\text{SO}_4$  is the most soluble; at 70°C, KCl is the most soluble.

12-10. (a) unsaturated (b) supersaturated  
(c) saturated (d) unsaturated

12-12. A specific amount of  $\text{Li}_2\text{SO}_4$  will precipitate unless the solution becomes supersaturated.

$$\left[ 500 \text{ g-H}_2\text{O} \times \frac{35 \text{ g}}{100 \text{ g-H}_2\text{O}} \right] - \left( 500 \text{ g-H}_2\text{O} \times \frac{28 \text{ g}}{100 \text{ g-H}_2\text{O}} \right) = \underline{\underline{35 \text{ g Li}_2\text{SO}_4 \text{ (precipitate)}}$$

12-13. 1.49%

12-15. 0.375 mol NaOH

12-17. 30 g  $\text{KNO}_3$ 

12-18. 8.81% NaOH

12-19. 100 ppm

12-21.  $8.3 \times 10^7$  L

12-23. 0.542 M

12-24. (a) 0.873 M (b) 1.40 M (c) 12.4 L (d) 41.4 g  
(e) 0.294 M (f) 0.024 mol (g) 307 mL  
(h) 49.1 g (i) 2.00 mL

12-28.  $1.17 \times 10^{-3}$  M12-29.  $\text{Ba}^{2+}$ : 0.166 M  $\text{OH}^-$ : 0.332 M

12-31. 1.84 M

12-33. 1.32 g/mL

12-34. 0.833 L

12-36. Slowly add 313 mL of the 0.800 M NaOH to about 500 mL of water in a 1-L volumetric flask. Dilute to the 1-L mark with water.

12-38. 0.140 M

12-39. 720 mL

12-41. 2.86 mL

12-42. Find the total moles and the total volume.

$$n = V \times M = 0.150 \text{ L} \times 0.250 \text{ mol/L} = 0.0375 \text{ mol (solution 1)}$$

$$n = V \times M = 0.450 \text{ L} \times 0.375 \text{ mol/L} = 0.169 \text{ mol (solution 2)}$$

$$n_{\text{tot}} = 0.206 \text{ mol} \quad V_{\text{tot}} = 0.600 \text{ L}$$

$$\frac{n}{V} = \frac{0.206 \text{ mol}}{0.600 \text{ L}} = \underline{\underline{0.343 \text{ M}}}$$

$$12-43. 0.500 \text{ L} \times \frac{0.250 \text{ mol KOH}}{\text{L}} \times \frac{1 \text{ mol Cr(OH)}_3}{3 \text{ mol KOH}} \times \frac{103.0 \text{ g Cr(OH)}_3}{\text{mol Cr(OH)}_3} = \underline{\underline{4.29 \text{ g Cr(OH)}_3}}$$

12-45. 146 g  $\text{BaSO}_4$ 

12-46. 4.08 L

12-48. 0.653 L

12-50. 0.864 M

12-52. 0.994 M

12-54. NaOH is the limiting reactant, producing 1.75 g of  $\text{Mg(OH)}_2$ .

12-56. An aqueous solution of AB is a good conductor of electricity. AB is dissociated into ions such as  $\text{A}^+$  and  $\text{B}^-$ . A solution of AC is a weak conductor of electricity, which means that AC is only partially dissociated into ions: i.e.,  $\text{AC} \rightleftharpoons \text{A}^+ + \text{C}^-$ . A solution of AD is a nonconductor of electricity because it is present as undissociated molecules in solution.

12-58. 1 mole of NaBr has a mass of 102.9 g, 1 molar NaBr is a solution containing 102.9 g of NaBr per liter of solution, and 1 molal NaBr is a solution containing 102.9 g of NaBr per kilogram of solvent.

12-59. 2.50 *m* (The molality is the same in both solvents since the mass of solvent is the same.)

12-61. 15.8 g NaOH

12-63.  $-0.37^\circ\text{C}$ 

12-65. The salty water removes water from the cells of the skin by osmosis. After a prolonged period, a person would dehydrate and become thirsty.

12-68. We can concentrate a dilute solution by boiling away some solvent if the solute is not volatile. Reverse osmosis can also be used to concentrate a solution if pressure greater than the osmotic pressure is applied on a concentrated solution separated from the solvent by a semipermeable membrane. As the solution becomes more concentrated, the osmotic pressure becomes greater, and the corresponding pressure that is applied must be increased.

12-69. 1.00 *m*

12-71. 807 g glycol

12-72.  $101.4^\circ\text{C}$ 12-74. 2.9 *m*12-77.  $-14.5^\circ\text{C}$ 

12-79. HCl is a strong electrolyte that produces two particles (ions) for each mole of HCl that dissolves. HF is a weak electrolyte that is essentially present as nonionized molecules in solution.

12-82. (a)  $-5.8^\circ\text{C}$  (b)  $-6.4^\circ\text{C}$  (c)  $-5.0^\circ\text{C}$ 

12-83. Dissolve the mixture in 100 g of  $\text{H}_2\text{O}$  and heat to over  $45^\circ\text{C}$ . Cool to  $0^\circ\text{C}$  where the solution is saturated with about 10 g of  $\text{KNO}_3$  and about 25 g of KCl.  $50 - 25 = 25$  g of KCl precipitates.

12-85. 90.9%  $\text{H}_2\text{O}$ ; 3.03% salt; 6.06% sugar

12-87. 0.10 mol of  $\text{Ag}^+$  reacts with 0.10 mol of  $\text{Cl}^-$ , leaving 0.05 mol of  $\text{Cl}^-$  in 1.0 L of solution.  $[\text{Cl}^-] = 0.05 \text{ M}$

$$12-89. 0.225 \cancel{L} \times \frac{0.196 \cancel{mol} HCl}{\cancel{L}} \times \frac{1 \text{ mol M}}{2 \cancel{mol} HCl} = 0.0221 \text{ mol M}$$

$$\frac{1.44 \text{ g}}{0.0221 \text{ mol}} = \underline{\underline{65.2 \text{ g/mol (Zn)}}}$$

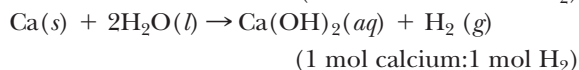
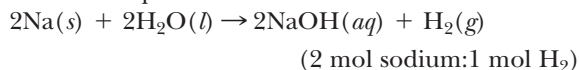
12-91. molality = 0.426 *m* molar mass = 60.1 g/mol  
empirical formula = CH<sub>4</sub>N molecular formula = C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>

12-93. 0.30 *m* sugar < 0.12 *m* KCl (0.24 *m* ions) < 0.05 *m* CrCl<sub>3</sub> (0.20 *m* ions) < 0.05 *m* K<sub>2</sub>CO<sub>3</sub> (0.15 *m* ions) < pure water.

12-95. *n*(hydroxide) = 0.0584 mol  
*n*(H<sub>2</sub>) = 0.0292 mol H<sub>2</sub>

$$\frac{0.0584}{0.0292} = 2(2 \text{ mol hydroxide:1 mol H}_2)$$

Balanced Equations:

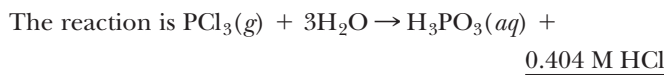


The answer is sodium since it produces the correct ratio of hydrogen.

12-96. 2.91 L

12-98. 8.60 L

12-100. The formula must be PCl<sub>3</sub>. The structure is trigonal pyramidal.



$$12-102. (2\text{Na}^+\text{S}^{2-}) 10.0 \text{ g-Na}_2\text{S} \times \frac{1 \text{ mol Na}_2\text{S}}{78.05 \text{ g-Na}_2\text{S}} = 0.128 \text{ mol Na}_2\text{S}$$

$$\Delta T = 1.86 \times \frac{0.128 \text{ mol}}{100 \text{ g}} \times 3 \text{ mol ions/mol Na}_2\text{S} \times \frac{1000 \text{ g/kg}}{1000 \text{ g/kg}} = 7.14^\circ\text{C change}$$

The answer is Na<sub>2</sub>S since it would have a freezing point of -7.14°C.

$$12-104. \Delta T = K_{fm} \quad 1.15^\circ\text{C} = 1.86 \times \frac{0.806}{1.00 + X}$$

Solving for X, X = 0.30 kg 0.30 kg = 300 g =  
300 mL of water added.

## CHAPTER 13

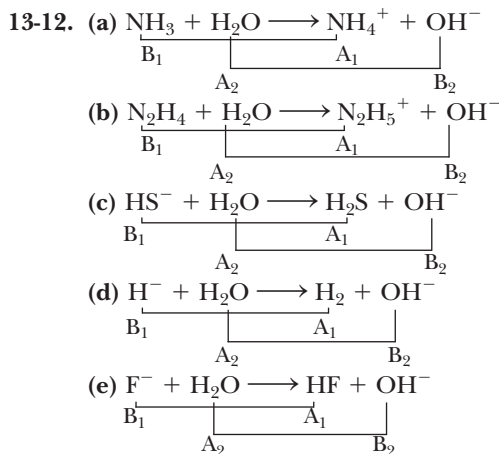
13-1. (a) HNO<sub>3</sub>, nitric acid (b) HNO<sub>2</sub>, nitrous acid  
(c) HClO<sub>3</sub>, chloric acid (d) H<sub>2</sub>SO<sub>3</sub>, sulfurous acid

13-3. (a) CsOH, cesium hydroxide (b) Sr(OH)<sub>2</sub>, strontium hydroxide (c) Al(OH)<sub>3</sub>, aluminum hydroxide (d) Mn(OH)<sub>3</sub>, manganese(III) hydroxide

13-5. (a)  $\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$   
(b)  $\text{CsOH} \rightarrow \text{Cs}^+ + \text{OH}^-$   
(c)  $\text{Ba(OH)}_2 \rightarrow \text{Ba}^{2+} + 2\text{OH}^-$   
(d)  $\text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^-$

13-7. Acid Conjugate Acid Conjugate  
base base base  
(a) HNO<sub>3</sub> NO<sub>3</sub><sup>-</sup> (d) CH<sub>4</sub> CH<sub>3</sub><sup>-</sup>  
(b) H<sub>2</sub>SO<sub>4</sub> HSO<sub>4</sub><sup>-</sup> (e) H<sub>2</sub>O OH<sup>-</sup>  
(c) HPO<sub>4</sub><sup>2-</sup> PO<sub>4</sub><sup>3-</sup> (f) NH<sub>3</sub> NH<sub>2</sub><sup>-</sup>

13-9. (a) HClO<sub>4</sub>, ClO<sub>4</sub><sup>-</sup> and H<sub>2</sub>O, OH<sup>-</sup>  
(b) HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HClO and ClO<sup>-</sup>  
(c) H<sub>2</sub>O, OH<sup>-</sup> and NH<sub>3</sub>, NH<sub>2</sub><sup>-</sup>  
(d) NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub> and H<sub>3</sub>O<sup>+</sup>, H<sub>2</sub>O



13-13. base:  $\text{HS}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{O}$   
acid:  $\text{HS}^- + \text{OH}^- \rightleftharpoons \text{S}^{2-} + \text{H}_2\text{O}$

13-16. The information indicates that HBr is a strong acid. The Br<sup>-</sup> ion, however, would be a very weak base in water.

13-18. (a)  $\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$   
(b)  $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$   
(c)  $\text{HClO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_3^-$   
(d)  $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_3^-$

13-20.  $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$

13-22. HX is a weak acid. The concentration of H<sub>3</sub>O<sup>+</sup> must equal the concentration of the HX that ionized.

$$\frac{0.010}{0.100} \times 100\% = \underline{\underline{10\% \text{ ionized}}}$$

13-24. [H<sub>3</sub>O<sup>+</sup>] = 0.55 M

13-25. [H<sub>3</sub>O<sup>+</sup>] = 0.030 × 0.55 = 0.017 M

13-27. From the first ionization: [H<sub>3</sub>O<sup>+</sup>] = 0.354 M

Of that, 25% undergoes further ionization.

$$0.25 \times 0.354 = 0.089 \text{ M [H}_3\text{O}^+]$$

from the second ionization.

The total [H<sub>3</sub>O<sup>+</sup>] = 0.354 + 0.089 = 0.443 M

13-28.  $\frac{0.050}{1.0} \times 100\% = \underline{\underline{5.0\% \text{ ionized}}}$

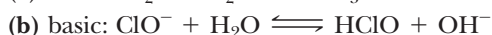
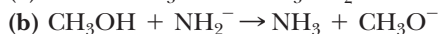
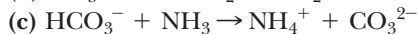
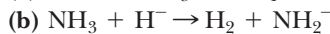
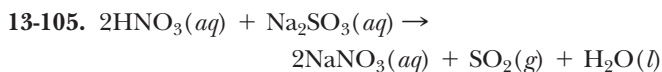
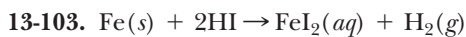
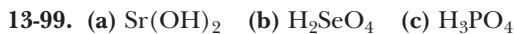
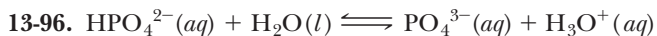
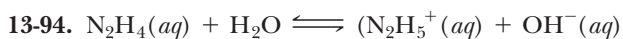
13-30. The conjugate acid of HSO<sub>4</sub><sup>-</sup> is H<sub>2</sub>SO<sub>4</sub>. This is a strong acid so it completely ionizes in water. Thus it cannot exist in the molecular form in water.

13-31. (a) acid (b) normal salt (c) acid  
(d) acid salt (e) normal salt (f) base

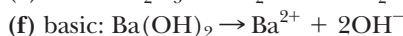
13-33. (a)  $\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$   
(b)  $2\text{HI} + \text{Ca(OH)}_2 \rightarrow \text{CaI}_2 + 2\text{H}_2\text{O}$   
(c)  $\text{HClO}_2 + \text{KOH} \rightarrow \text{KClO}_2 + \text{H}_2\text{O}$

- 13-35. (a)  $\text{H}^+(aq) + \text{NO}_3^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \rightarrow \text{Na}^+(aq) + \text{NO}_3^-(aq) + \text{H}_2\text{O}(l)$   
 $\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$  (net ionic)  
 (b)  $2\text{H}^+(aq) + 2\text{I}^-(aq) + \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Ca}^{2+}(aq) + 2\text{I}^-(aq) + 2\text{H}_2\text{O}(l)$   
 $\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$  (net ionic)  
 (c)  $\text{HClO}_2(aq) + \text{K}^+(aq) + \text{OH}^-(aq) \rightarrow \text{K}^+(aq) + \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l)$   
 $\text{HClO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l)$  (net ionic)
- 13-37.  $\text{H}_2\text{C}_2\text{O}_4(aq) + 2\text{NH}_3(aq) \rightarrow (\text{NH}_4)_2\text{C}_2\text{O}_4(aq)$   
 $\text{H}_2\text{C}_2\text{O}_4(aq) + 2\text{NH}_3(aq) \rightarrow 2\text{NH}_4^+(aq) + \text{C}_2\text{O}_4^{2-}(aq)$   
 Net ionic equation is the same as the total ionic equation.
- 13-39. (a) KOH and  $\text{HClO}_3$  (b)  $\text{Al}(\text{OH})_3$  and  $\text{H}_2\text{SO}_3$   
 (c)  $\text{Ba}(\text{OH})_2$  and  $\text{HNO}_2$  (d)  $\text{NH}_3$  and  $\text{HNO}_3$
- 13-41. (a)  $2\text{HBr} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaBr}_2 + 2\text{H}_2\text{O}$   
 (b)  $2\text{HClO}_2 + \text{Sr}(\text{OH})_2 \rightarrow \text{Sr}(\text{ClO}_2)_2 + 2\text{H}_2\text{O}$   
 (c)  $2\text{H}_2\text{S} + \text{Ba}(\text{OH})_2 \rightarrow \text{Ba}(\text{HS})_2 + 2\text{H}_2\text{O}$   
 (d)  $\text{H}_2\text{S} + 2\text{LiOH} \rightarrow \text{Li}_2\text{S} + 2\text{H}_2\text{O}$
- 13-43.  $\text{LiOH} + \text{H}_2\text{S} \rightarrow \text{LiHS} + \text{H}_2\text{O}$   
 $\text{LiOH} + \text{LiHS} \rightarrow \text{Li}_2\text{S} + \text{H}_2\text{O}$
- 13-44.  $\text{H}_2\text{S}(aq) + \text{OH}^-(aq) \rightarrow \text{HS}^-(aq) + \text{H}_2\text{O}(l)$   
 $\text{HS}^-(aq) + \text{OH}^-(aq) \rightarrow \text{S}^{2-}(aq) + \text{H}_2\text{O}(l)$
- 13-47.  $\text{H}_2\text{S} + \text{NaOH} \rightarrow \text{NaHS} + \text{H}_2\text{O}$
- 13-50. The system would not be at equilibrium if  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-2}$  M. Therefore,  $\text{H}_3\text{O}^+$  reacts with  $\text{OH}^-$  until the concentration of each is reduced to  $10^{-7}$  M. This is a neutralization reaction, i.e.,  $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$
- 13-51. (a)  $[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$  M  
 (b)  $[\text{H}_3\text{O}^+] = 10^{-15}$  M  
 (c)  $[\text{OH}^-] = 5.0 \times 10^{-10}$  M
- 13-53.  $[\text{H}_3\text{O}^+] = 0.0250$  M  $[\text{OH}^-] = 4.00 \times 10^{-13}$  M
- 13-55. (a) acidic (b) basic (c) acidic
- 13-57. (a) acidic (b) basic (c) acidic (d) basic
- 13-59. (a) 6.00 (b) 9.00 (c) 12.00 (d) 9.40 (e) 10.19
- 13-61. (a) pH = 4.0, pOH = 10.0 (b) pOH = 5.0, pH = 9.0  
 (c) pH = 1.70, pOH = 12.30 (d) pOH = 3.495, pH = 10.505
- 13-63. (a)  $1.0 \times 10^{-3}$  M (b)  $2.9 \times 10^{-4}$  M  
 (c)  $1.0 \times 10^{-6}$  M (d)  $2.4 \times 10^{-8}$  M  
 (e)  $2.0 \times 10^{-13}$  M
- 13-65. For exercise 13-59: (a) acidic (b) basic (c) basic (d) basic (e) basic  
 For exercise 13-63: (a) acidic (b) acidic (c) acidic (d) basic (e) basic
- 13-67. pH = 5.0 (less acidic), pH = 2.0 (more acidic)
- 13-69. pH = 1.12
- 13-71. pH = 12.56
- 13-72.  $[\text{H}_3\text{O}^+] = 0.100 \times 0.10 = 0.010 = 1.0 \times 10^{-2}$  M  
 pH = 2.00
- 13-74. (a) strongly acidic (b) strongly acidic  
 (c) weakly acidic (d) strongly basic (e) neutral  
 (f) weakly basic (g) weakly acidic (h) strongly acidic
- 13-75. Ammonia (pH = 11.4), eggs (pH = 7.8), rainwater ( $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-6}$  M, pH = 5.70), grape juice ( $[\text{OH}^-] = 1.0 \times 10^{-10}$  M, pH = 4.0), vinegar ( $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-3}$  M, pH = 2.60), sulfuric acid (pOH = 13.6, pH = 0.4)
- 13-78. (b)  $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$   
 (c)  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- 13-80. (a)  $\text{K}^+$  The cation of the strong base KOH.  
 (d)  $\text{NO}_3^-$  The conjugate base of the strong acid  $\text{HNO}_3$ .  
 (e)  $\text{O}_2$  dissolves in water without formation of ions.
- 13-81. (a)  $\text{HS}^-$  (b)  $\text{H}_3\text{O}^+$  (c)  $\text{OH}^-$  (d)  $(\text{CH}_3)_2\text{NH}$
- 13-83. (a)  $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$   
 (b)  $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$   
 (c)  $(\text{CH}_3)_2\text{NH}_2^+ + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH} + \text{H}_3\text{O}^+$   
 (d)  $\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{OH}^-$   
 (e)  $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$   
 (f) no hydrolysis (cation of a strong base)
- 13-85.  $\text{Ca}(\text{ClO})_2 \rightarrow \text{Ca}^{2+}(aq) + 2\text{ClO}^-(aq)$   
 $\text{ClO}^-(aq) + \text{H}_2\text{O} \rightleftharpoons \text{HClO}(aq) + \text{OH}^-(aq)$
- 13-87. (a) neutral (neither ion hydrolyzes)  
 (b) acidic (cation hydrolysis)  
 (c) basic (anion hydrolysis)  
 (d) neutral (neither ion hydrolyzes)  
 (e) acidic (cation hydrolysis)  
 (f) basic (anion hydrolysis)
- 13-89.  $\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{C}_2\text{H}_2(g) + \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$
- 13-90. cation:  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$   
 anion:  $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$   
 Since the solution is basic, the anion hydrolysis reaction must take place to a greater extent than the cation hydrolysis.
- 13-92. (a), (b), (e), (h), and (i) are buffer solutions.
- 13-93. There is no equilibrium when HCl dissolves in water. A reservoir of nonionized acid must be present to react with any strong base that is added. Likewise, the  $\text{Cl}^-$  ion does not exhibit base behavior in water, so it cannot react with any  $\text{H}_3\text{O}^+$  added to the solution.

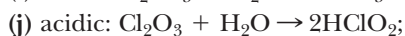




(c) neutral

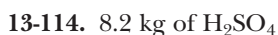


(g) neutral



13-112.  $\text{LiOH}$ , strongly basic,  $\text{pH} = 13.0$ ;  $\text{SrBr}_2$ , neutral,  $\text{pH} = 7.0$ ;  $\text{KClO}$ , weakly basic,  $\text{pH} = 10.2$ ;  $\text{NH}_4\text{Cl}$ , weakly acidic,  $\text{pH} = 5.2$ ;  $\text{HI}$ , strongly acidic,  $\text{pH} = 1.0$

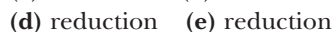
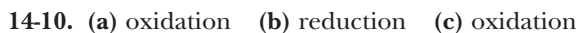
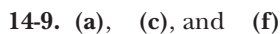
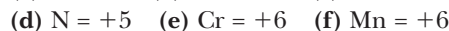
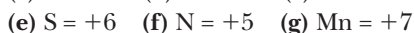
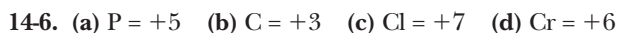
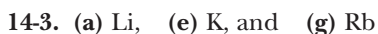
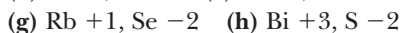
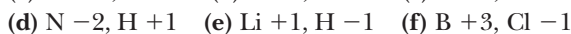
When  $\text{pH} = 1.0$ ,  $[\text{H}_3\text{O}^+] = 0.10 \text{ M}$ . If  $\text{HI}$  is completely ionized, its initial concentration must be  $0.10 \text{ M}$ .



$$[\text{OH}^-] = 0.025 \frac{\text{mol Ca}(\text{OH})_2}{\text{mol Ca}(\text{OH})_2} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ca}(\text{OH})_2}$$

$$= 0.050 \text{ mol/L} \quad \text{pOH} = 1.30 \quad \text{pH} = 12.70$$

## CHAPTER 14



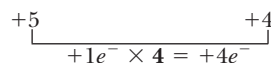
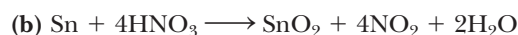
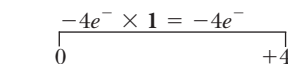
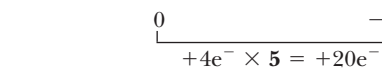
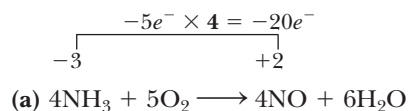
14-12.

| Reactant Oxidized | Product of Oxidation | Reactant Reduced | Product of Reduction              | Oxidizing Agent  | Reducing Agent   |
|-------------------|----------------------|------------------|-----------------------------------|------------------|------------------|
| $\text{Br}^-$     | $\text{Br}_2$        | $\text{MnO}_2$   | $\text{Mn}^{2+}$                  | $\text{MnO}_2$   | $\text{Br}^-$    |
| $\text{CH}_4$     | $\text{CO}_2$        | $\text{O}_2$     | $\text{CO}_2, \text{H}_2\text{O}$ | $\text{O}_2$     | $\text{CH}_4$    |
| $\text{Fe}^{2+}$  | $\text{Fe}^{3+}$     | $\text{MnO}_4^-$ | $\text{Mn}^{2+}$                  | $\text{MnO}_4^-$ | $\text{Fe}^{2+}$ |

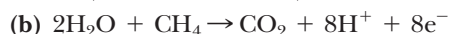
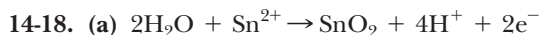
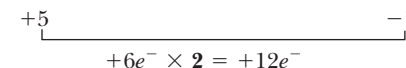
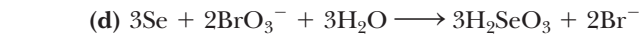
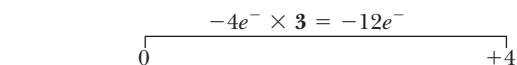
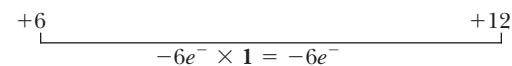
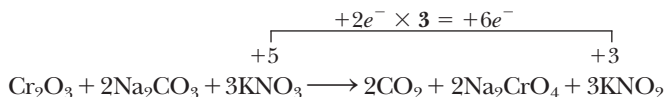
14-13.

| Reactant Oxidized | Product of Oxidation | Reactant Reduced             | Product of Reduction | Oxidizing Agent              | Reducing Agent   |
|-------------------|----------------------|------------------------------|----------------------|------------------------------|------------------|
| $\text{Al}$       | $\text{AlO}_2^-$     | $\text{H}_2\text{O}$         | $\text{H}_2$         | $\text{H}_2\text{O}$         | $\text{Al}$      |
| $\text{Mn}^{2+}$  | $\text{MnO}_4^-$     | $\text{Cr}_2\text{O}_7^{2-}$ | $\text{Cr}^{3+}$     | $\text{Cr}_2\text{O}_7^{2-}$ | $\text{Mn}^{2+}$ |

14-16.



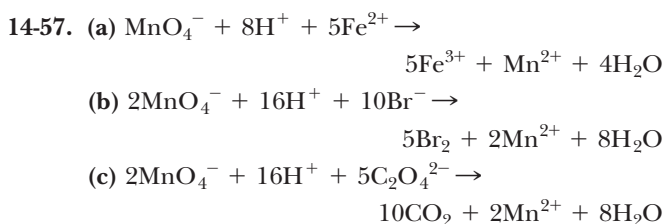
(c) Before the number of electrons lost is calculated, notice that a temporary coefficient of "2" is needed for the  $\text{Na}_2\text{CrO}_4$  in the products since there are 2 Cr's in  $\text{Cr}_2\text{O}_3$  in the reactants.





- 14-20.** (a) 
$$\begin{array}{r} \text{S}^{2-} \rightarrow \text{S} + 2\text{e}^- \quad \times 3 \\ 3\text{e}^- + 4\text{H}^+ + \text{NO}_3^- \rightarrow \text{NO} + 2\text{H}_2\text{O} \quad \times 2 \\ \hline 3\text{S}^{2-} + 8\text{H}^+ + 2\text{NO}_3^- \rightarrow 3\text{S} + 2\text{NO} + 4\text{H}_2\text{O} \end{array}$$
- (b)  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$
- (c) 
$$\begin{array}{r} \text{H}_2\text{O} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^- \quad \times 3 \\ 6\text{e}^- + 6\text{H}^+ + \text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \quad \times 1 \\ \hline 3\text{SO}_3^{2-} + 2\text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{SO}_4^{2-} \end{array}$$
- (d)  $2\text{H}^+ + 2\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$
- (e)  $\text{AsO}_4^{3-} + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_2 + \text{AsO}_3^{3-} + \text{H}_2\text{O}$
- (f)  $4\text{Zn} + \text{NO}_3^- + 10\text{H}^+ \rightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$
- 14-22.** (a)  $2\text{OH}^- + \text{SnO}_2^{2-} \rightarrow \text{SnO}_3^{2-} + \text{H}_2\text{O} + 2\text{e}^-$
- (b)  $6\text{e}^- + 4\text{H}_2\text{O} + 2\text{ClO}_2^- \rightarrow \text{Cl}_2 + 8\text{OH}^-$
- (c)  $6\text{OH}^- + \text{Si} \rightarrow \text{SiO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^-$
- (d)  $8\text{e}^- + 6\text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{NH}_3 + 9\text{OH}^-$
- 14-24.** (a) In acid solution:  
 $4\text{H}_2\text{O} + \text{S}^{2-} + 4\text{I}_2 \rightarrow \text{SO}_4^{2-} + 8\text{I}^- + 8\text{H}^+$   
 Add  $8\text{OH}^-$  to both sides and simplify.  
 $8\text{OH}^- + \text{S}^{2-} + 4\text{I}_2 \rightarrow \text{SO}_4^{2-} + 8\text{I}^- + 4\text{H}_2\text{O}$
- (b)  $8\text{OH}^- + \text{I}^- + 8\text{MnO}_4^- \rightarrow 8\text{MnO}_4^{2-} + \text{IO}_4^- + 4\text{H}_2\text{O}$
- (c)  $2\text{H}_2\text{O} + \text{SnO}_2^{2-} + \text{BiO}_3^- \rightarrow \text{SnO}_3^{2-} + \text{Bi}(\text{OH})_3 + \text{OH}^-$
- (d)  $32\text{OH}^- + \text{CrI}_3 \rightarrow \text{CrO}_4^{2-} + 3\text{IO}_4^- + 16\text{H}_2\text{O} + 27\text{e}^- \quad \times 2$   
 $2\text{e}^- + \text{Cl}_2 \rightarrow 2\text{Cl}^- \quad \times 27$   
 $2\text{CrI}_3 + 64\text{OH}^- + 27\text{Cl}_2 \rightarrow 2\text{CrO}_4^{2-} + 6\text{IO}_4^- + 32\text{H}_2\text{O} + 54\text{Cl}^-$
- 14-26.** (a)  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
- (b) 
$$\begin{array}{r} \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \\ 2\text{e}^- + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} \\ \hline 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \\ 2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \\ 2\text{e}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^- \\ \hline 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \end{array}$$
- 14-27.** Reactions (a), (c), (e), and (f) are predicted to be favorable.
- 14-29.** (a) no reaction  
 (b)  $\text{Br}_2(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{SnBr}_2(\text{aq})$   
 (c) no reaction  
 (d)  $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{Br}^-(\text{aq}) \rightarrow 2\text{Br}_2(\text{l}) + 2\text{H}_2\text{O}(\text{l})$   
 (e)  $3\text{Br}_2(\text{l}) + 2\text{Al}(\text{s}) \rightarrow 2\text{AlBr}_3(\text{s})$
- 14-31.** (c)  $2\text{F}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HF}(\text{aq}) + \text{O}_2(\text{g})$   
 (e)  $\text{Mg}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{s}) + \text{H}_2(\text{g})$
- 14-33.** From Table 14-1:  
 $\text{Fe} + 2\text{H}_2\text{O} \rightarrow$  no reaction  
 $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$
- Acid rain has a higher  $\text{H}^+(\text{aq})$  concentration, thus making the second reaction more likely.
- 14-36.**  $\text{Zn}(\text{s})$  reacts at the anode and  $\text{MnO}_2(\text{s})$  reacts at the cathode. The total reaction is  

$$\text{Zn}(\text{s}) + 2\text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Zn}(\text{OH})_2(\text{s}) + 2\text{MnO}(\text{OH})(\text{s})$$
- 14-38.** anode:  $\text{Cd}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cd}(\text{OH})_2(\text{s}) + 2\text{e}^-$   
 cathode:  $\text{NiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq})$
- 14-40.** The spontaneous reaction is  
 $\text{Pb}(\text{NO}_3)_2(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Fe}(\text{NO}_3)_2(\text{aq}) + \text{Pb}(\text{s})$   
 anode:  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$   
 cathode:  $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$
- 14-41.** The Daniell cell is more powerful. The greater the separation between oxidizing and reducing agents as shown in Table 14-1, the more powerful is the cell.
- 14-43.**  $3\text{Fe}(\text{s}) + 2\text{Cr}^{3+}(\text{aq}) \rightarrow 3\text{Fe}^{2+}(\text{aq}) + 2\text{Cr}(\text{s})$   
 Zinc would spontaneously form a chromium coating as illustrated by the equation:  
 $3\text{Zn}(\text{s}) + 2\text{Cr}^{3+}(\text{aq}) \rightarrow 3\text{Zn}^{2+}(\text{aq}) + 2\text{Cr}(\text{s})$
- 14-44.** Sodium reacts spontaneously with water since it is an active metal. The actual cathode reaction is  
 $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$   
 Elemental sodium is produced by electrolysis of the molten salt, NaCl.
- 14-47.** The strongest oxidizing agent is reduced the easiest. Thus the reduction of  $\text{Ag}^+$  to  $\text{Ag}$  occurs first. This procedure can be used to purify silver.
- 14-48.**  $\text{K}_3\text{N}$  (-3),  $\text{N}_2\text{H}_4$  (-2),  $\text{NH}_2\text{OH}$ , (-1),  $\text{N}_2$  (0),  $\text{N}_2\text{O}$  (+1),  $\text{NO}$  (+2),  $\text{N}_2\text{O}_3$  (+3),  $\text{N}_2\text{O}_4$  (+4),  $\text{Ca}(\text{NO}_3)_2$  (+5)
- 14-49.**  $\text{Cd}(\text{s}) + \text{NiCl}_2(\text{aq}) \rightarrow \text{Ni}(\text{s}) + \text{CdCl}_2(\text{aq})$   
 $\text{Zn}(\text{s}) + \text{CdCl}_2(\text{aq}) \rightarrow \text{Cd}(\text{s}) + \text{ZnCl}_2(\text{aq})$   
 These reactions indicate that  $\text{Cd}^{2+}$  is a stronger oxidizing agent than  $\text{Zn}^{2+}$  but weaker than  $\text{Ni}^{2+}$ . It appears about the same as  $\text{Fe}^{2+}$ .
- 14-51.** The reactions that occur are  
 $4\text{Au}^{3+} + 6\text{H}_2\text{O} \rightarrow 4\text{Au} + 12\text{H}^+ + 3\text{O}_2$   
 $2\text{Au} + 3\text{F}_2 \rightarrow 2\text{AuF}_3$   
 These reactions and the fact that Au does not react with  $\text{Cl}_2$  rank  $\text{Au}^{3+}$  above  $\text{H}^+$  and  $\text{Cl}_2$  but below  $\text{F}_2$ .
- 14-52.**  $12\text{H}^+(\text{aq}) + 5\text{Zn}(\text{s}) + 2\text{NO}_3^-(\text{aq}) \rightarrow 5\text{Zn}^{2+}(\text{aq}) + \text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$   
 0.658 g  $\text{N}_2$  requires 7.68 g Zn.
- 14-54.**  $14\text{H}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 3\text{Cu}_2\text{O}(\text{s}) \rightarrow 6\text{Cu}^{2+}(\text{aq}) + 2\text{NO}(\text{g}) + 7\text{H}_2\text{O}(\text{l})$   
 10.0 g of  $\text{Cu}_2\text{O}$  produces 1.04 L of NO measured at STP.
- 14-56.**  $7\text{OH}^-(\text{aq}) + 4\text{Zn}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + 4\text{Zn}(\text{OH})_4^{2-}(\text{aq})$   
 6.54 g of Zn produces 0.493 L of  $\text{NH}_3$  at  $27.0^\circ\text{C}$  and 1.25 atm pressure.



14-58. 179 mL

14-59. 306 mL

## CHAPTER 15

15-1. Colliding molecules must have the proper orientation relative to each other at the time of the collision, and the colliding molecules must have the minimum kinetic energy for the particular reaction.

15-3. (a) As the temperature increases, the frequency of collisions between molecules increases, as does the average energy of the collisions. Both contribute to the increased rate of reaction.

(b) The cooking of eggs initiates a chemical reaction that occurs more slowly at lower temperatures.

(c) The average energy of colliding molecules at room temperature is not sufficient to initiate a reaction between  $\text{H}_2$  and  $\text{O}_2$ .

(d) A higher concentration of oxygen increases the rate of combustion.

(e) When a solid is finely divided, a greater surface area is available for collisions with oxygen molecules. Thus it burns faster.

(f) The souring of milk is a chemical reaction that slows as the temperature drops. It takes several days in a refrigerator.

(g) The platinum is a catalyst. Since the activation energy in the presence of a catalyst is lower, the reaction can occur at a lower temperature.

15-6. The rate of the forward reaction was at a maximum at the beginning of the reaction; the rate of the reverse reaction was at a maximum at the point of equilibrium.

15-7. In many cases, reactions do not proceed directly to the right because other products are formed between the same reactants. For example, combustion may produce carbon monoxide as well as carbon dioxide.

15-8. Products are easier to form because the activation energy for the forward reaction is less than for the reverse reaction. This is true of all exothermic reactions. The system should come to equilibrium faster starting with pure reactants.

15-10. (a) right (b) left (c) left (d) right  
 (e) right (f) has no effect (g) yield decreases  
 (h) yield increases but rate of formation decreases

15-12. (a) increase (b) increase (c) decrease  
 (d) decrease (e) decrease (f) no effect

15-14. (a) Since there are the same number of moles of gas on both sides of the equation, pressure (or volume) has no effect on the point of equilibrium.

(b) decrease the amount of NO

(c) decrease the amount of NO

15-15. (a)  $K_{\text{eq}} = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$  (b)  $K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{O}]^2}$

(c)  $K_{\text{eq}} = \frac{[\text{Cl}_2]^2[\text{H}_2\text{O}]^2}{[\text{HCl}]^4[\text{O}_2]}$  (d)  $K_{\text{eq}} = \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]}$

15-17. products

15-19. There will be an appreciable concentration of both reactants and products at equilibrium.

15-20.  $K_{\text{eq}} = 0.34$ 15-21.  $K_{\text{eq}} = 49.2$ 

15-23.  $K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{O}]^2} = \frac{(2.20/30.0)(4.00/30.0)^4}{(6.20/30.0)(3.00/30.0)^2} = 0.0112$

15-25. (a)  $[\text{H}_2] = [\text{I}_2] = 0.30 \text{ mol/L}$ (b)  $[\text{H}_2] = 0.30 \text{ mol/L}; [\text{I}_2] = 0.50 \text{ mol/L}$ (c)  $[\text{HI}] = 0.40 \text{ mol/L}; [\text{I}_2] = [\text{H}_2] = 0.10 \text{ mol/L}$ (d)  $K_{\text{eq}} = 0.063$  (e)  $K_{\text{r}} = 16$ .

This is a smaller value than that used in Table 15-1. This indicates that the equilibrium in this problem was established at a different temperature than that of Table 15-1.

15-27. (a)  $[\text{N}_2]_{\text{reacts}} = 0.50 - 0.40 = 0.10 \text{ mol/L}$ 

$$0.10 \frac{\text{mol N}_2}{\text{mol N}_2} \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} = 0.30 \text{ mol/L H}_2 \text{ (reacts)}$$

$$[\text{H}_2]_{\text{eq}} = 0.50 - 0.30 = \underline{0.20 \text{ mol/L}}$$

$$0.10 \frac{\text{mol N}_2}{\text{mol N}_2} \times \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} = 0.20 \text{ mol/L NH}_3 \text{ formed}$$

$$[\text{NH}_3]_{\text{eq}} = 0.50 + 0.20 = \underline{0.70 \text{ mol/L}}$$

$$(b) K_{\text{eq}} = \frac{(0.70)^2}{(0.20)^3(0.40)} = 150$$

15-28. (a) The concentration of  $\text{O}_2$  that reacts is

$$0.25 \frac{\text{mol NH}_3}{\text{mol NH}_3} \times \frac{5 \text{ mol O}_2}{4 \text{ mol NH}_3} = 0.31 \text{ mol/L O}_2$$

(b)  $[\text{NH}_3] = 0.75 \text{ mol/L}; [\text{O}_2] = 0.69 \text{ mol/L O}_2$ ; $[\text{NO}] = 0.25 \text{ mol/L NO (formed)}$  $[\text{H}_2\text{O}] = 0.38 \text{ mol/L H}_2\text{O}$ 

$$(c) K_{\text{eq}} = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^5} = \frac{(0.25)^4(0.38)^6}{(0.75)^4(0.69)^5}$$

15-30.  $[\text{PCl}_5] = 0.28 \text{ mol/L}$ 15-32.  $[\text{H}_2\text{O}] = 0.26 \text{ mol/L}$ 15-33. Let  $x = [\text{HCl}] = [\text{CH}_3\text{Cl}]$ 

$$K_{\text{eq}} = \frac{[\text{HCl}][\text{CH}_3\text{Cl}]}{[\text{CH}_4][\text{Cl}_2]} = \frac{x^2}{(0.20)(0.40)} = 56$$

$$x^2 = 4.5 \quad x = \underline{2.1 \text{ mol/L}}$$

15-35. (a)  $K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{BrO}^-]}{[\text{HBrO}]}$

(b)  $K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$  (c)  $K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$

$$(d) K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} \quad (e) K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$(f) K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

15-37. The acid HB is weaker because it produces a smaller hydronium ion concentration (higher pH) at the same initial concentration of acid. The stronger acid HX has the larger value of  $K_a$ .

$$15-39. (a) [\text{HOCN}]_{\text{eq}} = 0.20 - 0.0062 = 0.19$$

$$(b) K_a = \frac{[\text{H}_3\text{O}^+][\text{OCN}^-]}{[\text{HOCN}]} = \frac{(6.2 \times 10^{-3})(6.2 \times 10^{-3})}{0.19} = 2.0 \times 10^{-4}$$

$$(c) \text{pH} = 2.21$$

$$15-40. (a) \text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^- \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]}$$

$$(b) \text{From the equation } [\text{H}_3\text{O}^+] = [\text{X}^-] =$$

$$0.100 \times 0.58, [\text{HX}] = 0.58 - 0.058 = 0.52$$

$$(c) K_a = 6.5 \times 10^{-3} \quad (d) \text{pH} = 1.24$$

$$15-43. \text{Nv} + \text{H}_2\text{O} \rightleftharpoons \text{NvH}^+ + \text{OH}^- \quad K_b = 6.6 \times 10^{-6}$$

$$15-44. [\text{H}_3\text{O}^+] = 0.300 - 0.277 = 0.023$$

$$\text{pH} = 1.64 \quad K_a = 1.9 \times 10^{-3}$$

$$15-45. \text{pH} = 4.43$$

$$15-47. [\text{OH}^-] = 3.2 \times 10^{-3}$$

$$15-49. \text{pH} = 12.43$$

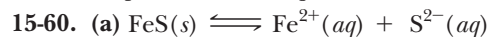
$$15-51. \text{pH} = 9.40$$

$$15-53. \text{p}K_a = 8.68 \quad \text{pH} = 8.68 + \log \frac{0.20/0.850}{0.60/0.850} = 8.68 - 0.48 = \underline{8.20}$$

$$15-56. \text{p}K_b = 6.01 \quad \text{pOH} = 6.01 + \log \frac{0.0288 \text{ mol acid}}{0.0469 \text{ mol base}}$$

$$\text{pOH} = 6.01 - 0.21 = 5.80 \quad \text{pH} = \underline{8.20}$$

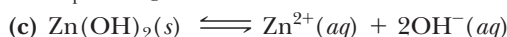
15-58. When the concentrations of acid and base species are equal,  $\text{pH} = \text{p}K_a$  and  $\text{pOH} = \text{p}K_b$ . If a buffer of  $\text{pH} = 7.50$  is required, then we look for an acid with  $K_a = [\text{H}_3\text{O}^+] = 3.2 \times 10^{-8}$  or a base with  $K_b = [\text{OH}^-] = 3.2 \times 10^{-7}$ . Since  $K_a = 3.2 \times 10^{-8}$  for HClO, an equimolar mixture of HClO and KClO produces the required buffer.



$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{S}^{2-}]$$

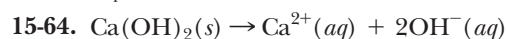


$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{S}^{2-}]$$



$$K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

$$15-62. K_{\text{sp}} = 4.8 \times 10^{-12}$$

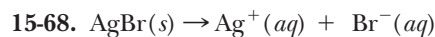


$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$\text{At equilibrium } [\text{Ca}^{2+}] = 1.3 \times 10^{-2} \text{ mol/L } [\text{OH}^-] = 2 \times (1.3 \times 10^{-2}) \text{ mol/L} = 2.6 \times 10^{-2} \text{ mol/L}$$

$$K_{\text{sp}} = [1.3 \times 10^{-2}][2.6 \times 10^{-2}]^2 = 8.8 \times 10^{-6}$$

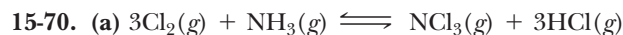
$$15-66. 9.1 \times 10^{-9} \text{ mol/L}$$



$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = 7.7 \times 10^{-13}$$

$$[7 \times 10^{-6}][8 \times 10^{-7}] = 6 \times 10^{-12}$$

This is a larger number than  $K_{\text{sp}}$ , so a precipitate of AgBr does form.

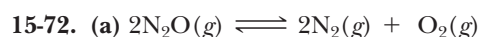


$$(b) K_{\text{eq}} = \frac{[\text{NCl}_3][\text{HCl}]^3}{[\text{NH}_3][\text{Cl}_2]^3}$$

(c) no effect

(d) decreases  $[\text{NH}_3]$  (e) reactants

$$(f) [\text{NH}_3] = 0.083 \text{ mol/L}$$



$$(b) K_{\text{eq}} = \frac{[\text{N}_2]^2[\text{O}_2]}{[\text{N}_2\text{O}]^2}$$

(c) decreases  $[\text{N}_2]$

(d) decreases  $[\text{N}_2\text{O}]$

$$(e) [\text{N}_2\text{O}]_{\text{eq}} = 0.10 - (0.015 \times 0.10) = 0.10 \text{ mol/L;}$$

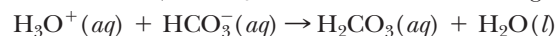
$$[\text{N}_2] = 0.015 \times 0.10 = 1.5 \times 10^{-3} \text{ mol/L;}$$

$$[\text{O}_2] = \frac{1.5 \times 10^{-3}}{2} = 7.5 \times 10^{-4} \text{ mol/L}$$

$$K_{\text{eq}} = \underline{1.7 \times 10^{-7}}$$

15-74. (a) A solution of  $\text{NaHCO}_3$  is slightly basic because the hydrolysis reaction occurs to a greater extent than the acid ionization reaction. That is,  $K_b$  is larger than  $K_a$ .

(b) It is used as an antacid to counteract excess stomach acidity.



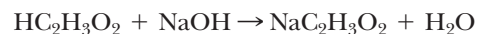
(d) No. The  $\text{HSO}_4^-$  does not react with  $\text{H}_3\text{O}^+$  because it would form  $\text{H}_2\text{SO}_4$ , which is a strong acid. The molecular form of a strong acid does not exist in water.

$$15-76. 0.265 \text{ L} \times 0.22 \text{ mol/L} = 0.058 \text{ mol HC}_2\text{H}_3\text{O}_2$$

$$0.375 \text{ L} \times \frac{0.12 \text{ mol Ba}(\text{C}_2\text{H}_3\text{O}_2)_2}{\text{L}} \times$$

$$\frac{2 \text{ mol C}_2\text{H}_3\text{O}_2^-}{\text{mol Ba}(\text{C}_2\text{H}_3\text{O}_2)_2} = 0.090 \text{ mol C}_2\text{H}_3\text{O}_2^- \quad \underline{\underline{\text{pH} = 4.93}}$$

15-77. The addition of the NaOH neutralizes part of the acetic acid to produce sodium acetate.



$1.00 - 0.20 = 0.80 \text{ mol}$  of  $\text{HC}_2\text{H}_3\text{O}_2$  remains, and  $0.20 \text{ mol}$  of  $\text{C}_2\text{H}_3\text{O}_2^-$  is formed after  $0.20 \text{ mol}$  of  $\text{OH}^-$  is added.

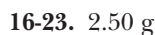
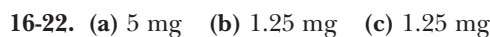
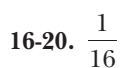
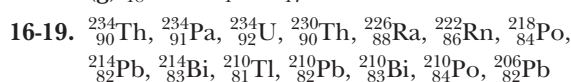
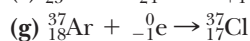
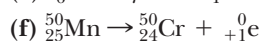
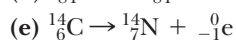
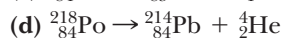
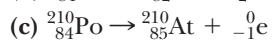
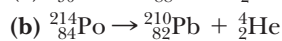
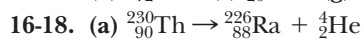
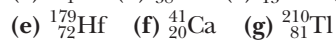
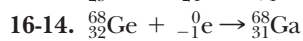
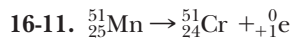
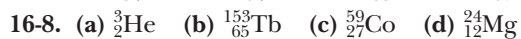
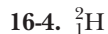
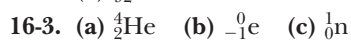
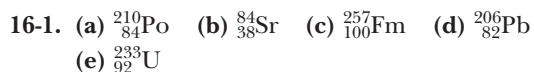
$$\underline{\underline{\text{pH} = 4.14}}$$

$$15-78. [\text{OH}^-] = 3.2 \times 10^{-4} \quad [\text{Mg}^{2+}] = [\text{OH}^-]/2 = 1.6 \times 10^{-4}$$

$$\times 10^{-4} K_{\text{sp}} = [1.6 \times 10^{-4}][3.2 \times 10^{-4}]^2 = 1.6 \times 10^{-11}$$

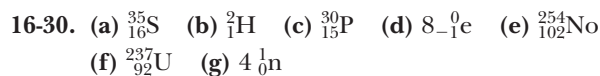
$$15-80. 1.0 \times 10^{-5} \text{ mol/L, } 0.023 \text{ g BaSO}_4/\text{L}$$

## CHAPTER 16

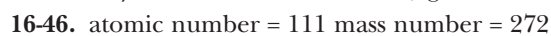
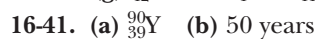
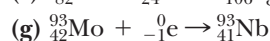
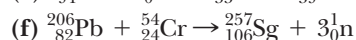
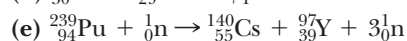
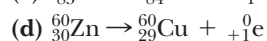
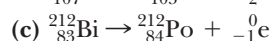
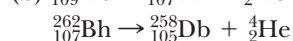
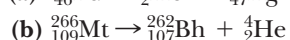
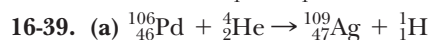
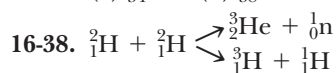
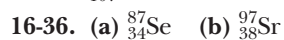
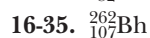
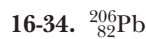


16-27. The energy from the radiation causes an electron in an atom or a molecule to be expelled, leaving behind a positive ion. When a molecule in a cell is ionized, it is damaged and may die or mutate.

16-29. Radiation entering a chamber causes ionization. The electrons formed migrate to the central electrode (positive) and cause a burst of current that can be detected and amplified. In a scintillation counter, the radiation is detected by phosphors that glow when radiation is absorbed.



16-32. one neutron



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Program (NURP); NOAA. Page 148: Charles D. Winters/Photo  
Researchers. Page 150 (top): Michael Watson. Page 150 (bottom):  
Michael Watson. Page 151: Andy Washnik. Page 155 (top left):  
Andy Washnik. Page 155 (top center): Andy Washnik. Page 155  
(top right): Andy Washnik. Page 155 (bottom left): Andy Washnik.  
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Andy Washnik. Page 158: MIR Science VU/Betz/Visuals  
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## CHAPTER 10

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Andy Washnik. Page 296 (top left): OPC, Inc. Page 296 (top right):  
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Researchers. *Page 304*: Michael Dalton/Fundamental Photographs. *Page 314*: Andrew Lambert Photography/Photo Researchers, Inc. *Page 319*: MIR Janis Miglavs/Danita Delimont.

#### CHAPTER 11

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#### CHAPTER 17

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#### CHAPTER 18

*Page W-42*: Dr. Tim Evans/SPL/Photo Researchers. *Page W-48*: PhotoDisc, Inc./Getty Images. *Page W-64*: MIR Chris Butler/Photo Researchers.

#### APPENDIX A

Opener: Vision/Photo Researchers.



# INDEX

- A**
- Absolute zero, 302, 304
- Accuracy, 17, 17
- Acetate ion ( $C_2H_3O_2^-$ ), 122*t*, 128*t*, 153*t*
- Acetic acid ( $HC_2H_3O_2$ ), 128*t*, 207, 398, 406–407, 492*t*
- Acetic anhydride, W28
- Acetaminophen, W27
- Acetone, W23
- Acetylene ( $C_2H_2$ ), 187, 212, W16–W17
- Acetylsalicylic acid, W27, W28
- Acids, 397, 398–410, 416–428
- in aqueous solutions, 365–366
  - binary, 127, 128
  - Brønsted-Lowry, 400–403
  - and buffers, 423–426
  - defined, 127
  - diluting, 375
  - diprotic, 409
  - and equilibrium, 489–496
  - monoprotic, 409
  - naming, 127–129
  - in neutralization reactions, 408–410
  - oxides as, 426–428
  - oxyacids, 128–129
  - pH of, 416–419
  - $pK_a$  of, 492, 492*t*
  - polyprotic, 409–410
  - properties of, 398, 398
  - strong, 148–149, 159–161
  - triprotic, 409
  - in water, 399
  - weak molecular, 404–406
- Acid anhydrides, 426–427
- Acid-base reactions, 400–410
- conjugate acids/bases, 401–403
  - neutralization reactions, 408–410
  - and strength of acids/bases, 404–407
- Acid ionization constant ( $K_a$ ), 490–496
- Acidosis, 425
- Acid rain, 397, 426, 428, 455, 530
- Acid salts, 409
- Acrilan™, W15*t*
- Acrylonitrile ( $C_3H_3N$ ), W15*t*, W17
- Actinides, 114, 237
- Actinium (Ac), 237
- Activated complex, 474
- Activation energy ( $E_a$ ), 473–476, 474, 476
- Active metals, 111, 455
- Active site (enzyme), W59
- Activity (radioactivity), 522
- Activity series, 151, 151*t*, 454
- Actual yield, 208–211
- Addition:
- rules for, 19–20, A2–A3
  - in scientific notation, A20–A21
- Addition polymers, W27
- Adenine, W60, W60, W62, W62
- Advil™, W27, W28
- Aging, 71
- AIDS, 13
- Air, 318*t*
- Alamogordo Flats, New Mexico, 530
- Alanine, W54
- Albrecht, H. O., 443
- Alchemists, 10, 397, 511
- Alcohol(s), 207, W20–W22. *See also* Ethyl alcohol; Methyl alcohol
- allyl, W7*t*
  - isopropyl, 144, 360, W21
  - naming, W20–W21
  - in organic chemistry, W20–W22
- Alcohol content, 372, W21
- Alcoholic beverages, W21
- Aldehydes, W22–W24, W49
- Aldopentose, W50
- Aldose, W49
- Algebraic Operating System (AOS), A31–A35
- Algebra, A10–A18
- Alkali metals, 113, 117, 154, 236, 440
- Alkaline batteries, 460
- Alkaline earth metals, 113, 117, 236, 440
- Alkaline solutions, *see* Bases
- Alkalosis, 425
- Alkanes, W8–W13, W9*t*
- Alkenes, W13–W16
- Alkylation, of crude-oil, W13
- Alkyl groups, W9, W9*t*
- Alkynes, W16–W17
- Alleve™, W28
- Allotropes, 269
- Alloy, 91, 91–92
- Allyl alcohol, W7*t*
- $\alpha$  helix structure, W56, W56
- $\alpha$  particles, 58, 59, 512, 520
- $\alpha$  radiation, 512, 512, 514, 519
- Aluminum (Al), 117
- activity of, 151*t*
  - atomic radius, 243
  - in binary ionic compounds, 256, 257
  - in combustion reactions, 143
  - density of, 84*t*
  - electron affinity, 244*t*
  - electron configuration, 234
  - in fuel cells, 463
  - ionization energy, 243*t*, 244
  - Lewis Dot symbols, 254*t*
  - in redox reactions, 454, 454*t*
- Aluminum oxide ( $Al_2O_3$ ), 257
- Alvin (submarine), 146
- Alzheimer's disease, 528, W28
- American Chemical Society, 190, 411
- Americium-241 (isotope), 520
- Amides, W25–W28, W53
- Amide bonds, W53
- Amines, W24–W25
- Amino acids, 263, W53–W55, W54, W64
- Aminobenzene, W18
- Amino groups, W53
- Ammonia ( $NH_3$ ), 65, 117, 399–401, 404, 407, 421, 496, W24–W25
- in binary ionic compounds, 262
  - boiling point, 347, 347*t*
  - composition of, 184–185
  - in early universe, 9
  - in equilibrium, 480–482, 490, 493*t*
  - in fertilizers, 169, 263
  - formation of, 141
  - hydrogen bonding in, 337
  - production of, 198–201, 198*t*
  - and VSEPR theory, 276
- Ammonium cation ( $NH_4^+$ ), 69, 122, 122*t*, 407, 421, 425, 460, 490, W24
- Ammonium cyanate ( $NH_4CNO$ ), W4
- Ammonium nitrate ( $NH_4NO_3$ ), 95, 169
- Amorphous solids, 338
- Amphetamine, W25
- Amphiprotic ions, 401
- amu, *see* Atomic mass unit
- Analgesics, W25, W27
- Anaestrazole, 11
- Anemia, 71
- Anesthetics, W22
- Angina pectoris, W22
- Anhydrides:
- acid, 426–427
  - base, 427
- Animal testing, 13
- Anions:
- defined, 67
  - from nonmetals, 117
  - oxyanions, 122
- Anion hydrolysis, 420–421
- Anode, 458, 459
- Antacids, 421
- Antarctica, 62
- Antifreeze, 386
- Antigravity, 100
- Antihistamines, 124, W25
- Antilogs, A25, A35
- Antimatter, 513
- Antimony (Sb), 55*t*
- Antipyretics, W27, W28
- Antitussive agents, W25
- AOS, *see* Algebraic Operating System
- Aquamarine, 339

- Aqueous (term), 156  
 Aqueous solutions, 363–390  
   boiling point, 385–386  
   colligative properties, 384–389  
   diluting, 375–377  
   electrolytes in, 382–383, 388–389  
   equilibrium for weak acids in, 490–492  
   equilibrium for weak bases in, 490  
   freezing point, 386–387  
   of gases, 369–370  
   of ionic compounds, 364–365  
   molarity, 373–377  
   of molecular compounds, 365–366  
   osmotic pressure, 387–388  
   percent by mass concentration, 370–373  
   solubility and temperature/pressure, 367–370  
   stoichiometry, 377–380  
   strength of oxidizing/reducing agents in, 454  
   titrations, 379–380  
   vapor pressure, 384  
 Arginine, W54  
 Argon (Ar), 234, 254*t*, 313, 521  
 Aromatic compounds, W17–W18  
 Arrhenius, Svante, 399  
 Arrhenius acids, 399, 401, 414  
 Arrhenius bases, 399, 401, 414  
 Arsenic (As), 111, 243, 254*t*, 527  
 Arthritis, 12, W28  
 Asbestos, 341  
 Asparagine, W54  
 Aspartic acid, W54  
 Asphyxiation, 483  
 Aspirin (C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>), 12, 65, W27, W28  
 Astatine-218 (isotope), 516*t*  
 Asymptotically (term), A30  
 -ate (suffix), 122, 128  
 Atmosphere (atm), 298, 298*t*  
 Atmosphere, Earth's, 66, 293, 296, W64  
 Atom(s), 5  
   and chemical bonds, 8–9  
   composition of, 58, 59, 59, 60*t*  
   defined, 56–57  
   hetero, W7  
   nuclear model of, 58, 59, 59  
   Atomic bomb, 520  
   Atomic mass, 62, 63, 174  
     and alpha radiation, 512–513  
     and beta radiation, 513  
     and periodic table, 111, 112  
   Atomic mass unit (amu), 59, 62, 170  
   Atomic number, 6, 61, 513  
   Atomic radii, 242–243, 243  
   Atomic theory, modern, *see* Modern atomic theory  
 Aufbau principle, 233  
 Auric ion (Au<sup>3+</sup>), 120*t*  
 Aurous ion (Au<sup>+</sup>), 120*t*  
 Autoionization, 413  
 Automobiles, 461, 478  
 Avogadro, Amedeo, 173  
 Avogadro's law, 307, 307–308  
 Avogadro's number, 173–174
- B**  
 Babylon, ancient, W48  
 Background radiation, 522  
 Baekeland, L. H., W16  
 Bakelite™, W16, W23  
 Balanced equations, 139–142, 198, 201  
   nuclear, 512  
   for redox reactions, 444–451  
   rules for balancing equations, 140  
   thermochemical equations, 211–213  
 Ball-and-stick models, W6  
 Bars (unit), 298  
 Barium (Ba), 221  
 Barium-139 (isotope), 529  
 Barium hydroxide (Ba(OH)<sub>2</sub>), 160, 400  
 Barium perchlorate (Ba(ClO<sub>4</sub>)<sub>2</sub>), 69, 69  
 Barometers, 297, 297  
 Bases, 398–404, 407–410, 416–427  
   Arrhenius, 399, 401, 414  
   Brønsted-Lowry, 400–403  
   and buffers, 423–425  
   conjugate, 401–403, 420–421, 423  
   and equilibrium, 489–496  
   in hydrolysis, 421–422  
   oxides as, 427  
   and pH, 416–419  
   p*K*<sub>b</sub>, 492, 493*t*  
   properties of, 398  
   strengths of, 404, 407  
   strong, 159–161, 399–400, 408–410  
   in water, 399–400  
   weak, 489–496  
   weak molecular, 407  
 Bases (DNA), W60, W61  
 Base anhydrides, 427  
 Base ionization constant (*K*<sub>b</sub>), 490, 492–495  
 Batteries, 459, 459–461  
 Battery acid, 91  
 Bayer & Co., W28  
 Becquerel (Bq), 522  
 Becquerel, Henri, 511, 512, 521  
 Beer, 427  
 Bell, Alexander Graham, 437  
 Bends, the, 369  
 Bent geometry, 276  
 Benzamide, W27  
 Benzedrine, W25  
 Benzene (C<sub>6</sub>H<sub>6</sub>), 187, 350*t*, 351*t*, W17–W18  
 Benzoic acid, W18, W26  
 Beryllium (Be), 236, 240, 243*t*, 244, 244*t*, 254*t*  
 β particles, 513  
 β-pleated sheet structure, W56, W56  
 β radiation, 513, 513, 514, 519  
 Bethe, Hans, 532  
 Beverages, carbonated, 369, 370  
 Bicarbonate ion (HCO<sub>3</sub><sup>-</sup>), 122*t*  
 “Big bang,” 4, 534  
 Binary acids, 127, 128  
 Binary ionic compounds, 256–258  
 Biochemistry, W43–W66  
   amino acids, W53–W55  
   carbohydrates, W49–W52  
   enzymes, W58–W59  
   genetics, W61–W64  
   lipids, W44–W49  
   nucleic acids, W60–W61  
   proteins, W55–W57  
   steroids, W47–W48  
 Bioluminescence, 443  
 Bipolar disorder, 124  
 Bismuth (Bi), 514, 516  
 Bismuth-210 (isotope), 517  
 Bismuth-214 (isotope), 517  
 Bisulfate ion (HSO<sub>4</sub><sup>-</sup>), 122*t*  
 Bisulfite ion (HSO<sub>3</sub><sup>-</sup>), 122*t*  
 Bleach (NaClO), 424, 469, 496  
 Blood, 363, 369, 388, 425  
 Blood alcohol concentration, 207  
 Blood cells, 31, 388  
 Body fat, 86  
 Body Solutions Evening Weight Loss Formula™, 99  
 Bohr, Niels, 5, 221, 224–226, 228  
 Bohr model (of hydrogen atom), 224–227, 225  
 Boiling, energy for, 350–351  
 Boiling point(s), 347–348, 347*t*, 351*t*  
   of alkanes, W12  
   of aqueous solutions, 385–386  
   defined, 82  
   normal, 347  
 Boiling-point elevation, 385, 386  
 Bonds. *See also* Bonding  
   amide, W53  
   covalent, 8, 65, 261  
   disulfide, W56–W57  
   double, 263, 264  
   ionic, 9, 68, 258  
   nonpolar, 273  
   peptide, W53, W55–W56  
   triple, 263, 264  
 Bond angle, maximum, 278  
 Bond energies, 475  
 Bonding, 8–9, 254–285  
   covalent, 260–264  
   electronegativity and polarity of, 272–274  
   and formal charge, 280–283  
   ionic, 255–259  
   Lewis structures, 264–270  
   and molecular geometry, 275–278  
   octet rule of, 254  
   with organic compounds, W4–W7  
   and polarity of molecules, 278–280  
   resonance structures in, 269–270  
 Bone cancer, 519  
 Borazine (B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>), 189  
 Boric acid (H<sub>3</sub>BO<sub>3</sub>), 71  
 Boron (B), 71, 141–142, 234, 236, 240, 243, 243*t*, 244*t*, 254*t*  
 Boyle, Robert, 299  
 Boyle's law, 297–301, 299, 301, 482  
 Brachytherapy, 528  
 Branched compounds, W9  
 Breakeven point, 533  
 Breast cancer, 11, 12  
 Breathalyzer testing, 207

- Breathing, 299  
 Bridge method (of balancing), 444–446  
 Brine solutions, 388  
 Bromide ion ( $\text{Br}^-$ ), 153*t*  
 Bromine (Br), 115, 243, 254*t*, 257, 454*t*, W14  
 Bromobenzene ( $\text{C}_6\text{H}_5\text{Br}$ ), 88  
 Bromoform ( $\text{CHBr}_3$ ), 88  
 Brønsted-Lowry acids and bases, 400–403  
 Buckminsterfullerene, 340, 340, 341  
 Bucky balls, 340, 340  
 Buffers, 423–426  
   blood as, 425  
   composition of, 424  
   Henderson-Hasselbach equation, 495  
   pH of, 495–496  
 Buffer capacity, 426  
 Buoyancy, 84  
 Burning, *see* Combustion  
 Butane ( $\text{C}_4\text{H}_{10}$ ), W9*t*  
*n*-Butane, W6, W7, W9  
*n*-Butyl group, W9*t*  
*Sec*-Butyl group, W9*t*  
*Tert*-Butyl group, W9*t*
- C**
- Cade, John, 124  
 Cadmium (Cd), 460  
 Cadmium bars, 530  
 Calcium (Ca), 71, 186, 235, 243, 254*t*, 257  
 Calcium bromide ( $\text{CaBr}_2$ ), 257  
 Calcium carbide ( $\text{CaC}_2$ ), W16  
 Calcium carbonate ( $\text{CaCO}_3$ ), 69, 69, 71, 124, 145, 153, 186, 365, 398–400, W4  
 Calcium chloride ( $\text{CaCl}_2$ ), 68, 388  
 Calcium citrate ( $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ ), 71, 186  
 Calcium gluconate ( $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ ), 186  
 Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), W16  
 Calcium ion ( $\text{Ca}^{2+}$ ), 158, 498, 501  
 Calcium oxalate ( $\text{CaC}_2\text{O}_4$ ), 497, 498, 501  
 Calcium oxide (CaO), 118, 158, W16  
 Calcium perchlorate ( $\text{Ca}(\text{ClO}_4)_2$ ), 148  
 Calcium phosphate ( $\text{Ca}(\text{PO}_4)_2$ ), 71  
 Calcium sulfate ( $\text{CaSO}_4$ ), 122  
 Calculators, 19, A31–A35  
 Calorie (Cal, nutritional unit), 98–99, 212  
 Calorie (cal, energy unit), 96, 98  
 Canada, 428  
 Cancer, 372, 519, 527, 528  
 Carbohydrates, 146, W49–W52  
 Carbon (C):  
   allotropes of, 340, 340  
   atomic radius, 243  
   atomic structure, 59  
   bonding of, W4–W5  
   in combustion reactions, 143  
   double bonding of, 263, 264  
   electron affinity, 244*t*  
   electron configuration, 240  
   ionization energy, 243*t*  
   Lewis Dot symbols, 254*t*  
   mass of, 170, 171, 171*t*  
 Carbon-14 (isotope), 516*t*, 527  
 Carbonated beverages, 427  
 Carbonate ion ( $\text{CO}_3^{2-}$ ), 122*t*, 128*t*, 153*t*, 269, 400, 402, 450  
 Carbon dating, 527  
 Carbon dioxide ( $\text{CO}_2$ ), 318*t*, 483, W13  
   and carbon dating, 527  
   and climate change, 137  
   in combustion, 197  
   in combustion reactions, 143  
   composition of, 182  
   in decomposition reactions, 145  
   in dipole-dipole attractions, 335, 336  
   in Earth's atmosphere, 293  
   in fuel cells, 462  
   heat of reaction, 474–475  
   liberation of, by acids, 398  
   linear geometry of, 279, 279  
   solubility of, 369, 370  
   and VSEPR theory, 275  
 Carbonic acid ( $\text{H}_2\text{CO}_3$ ), 128*t*, 145, 398, 402, 425, 427  
 Carbon monoxide (CO), 144, 478  
 Carbon monoxide poisoning, 369  
 Carbon tetrachloride, 84*t*, 350*t*, 351*t*  
 Carbonyl sulfoxide (OCS), 335  
 Carboxyl group, W26  
 Carboxylic acids, W25–W28, W44, W53  
 Carvone, W24  
*Cassini* orbiter, 79, 348  
 Catalysts, 139*t*, 281, 477–478, 478  
   enzymes as, W58–W59  
   equilibrium and addition of, 482  
 Catalytic converters, 429, 478  
 Cathode, 458, 459  
 Cations:  
   defined, 67  
   from metals, 117  
 Cation hydrolysis, 421  
 Caustic solutions, *see* Bases  
 Celluloid™, W16  
 Cellulose, W52, W52  
 Cell walls, W45  
 Celsius scale, 38, 303  
 Centi- (prefix), 29  
 Cerebroside, W45, W46  
 Cesium (Cs), 115  
 Chalcogens, 113, 237  
 Chalk, 153  
 Characteristic (logarithmic), A25  
 Charles, Jacques, 302  
 Charles's law, 302–304, 319  
 Chemical bond, 8–9  
 Chemical changes, 82, 83, 83  
 Chemical compounds, 56  
 Chemical energy, 94  
 Chemical equations, 138–142  
   balanced, *see* Balanced equations  
   defined, 138  
   molecular, 150  
   net ionic, 150–151  
   nuclear, 512  
   symbols in, 139*t*  
   thermochemical, 211–213  
   total ionic, 150  
 Chemical nomenclature, 65, 109, 117–123, 125–128, 130  
   acids, 127–128  
   alcohols, W20–W21  
   aldehydes and ketones, W23  
   alkenes, W14  
   alkynes, W16  
   amides, W27  
   amines, W24  
   carboxylic acids, W26  
   classical method, 119  
   esters, W26  
   ethers, W22  
   metal-nonmetal binary compounds, 117–124, 126  
   nonmetal-nonmetal binary compounds, 125–126  
   organic compounds, W8–W11  
   with polyatomic ions, 121–123  
   polymers, W14  
   Stock Method, 119  
 Chemical properties, 82, 83, 83  
 Chemical reactions, 56, 138–162  
   acid-base reactions, 400–410  
   chemosynthesis, 146  
   combination reactions, 145  
   combustion, 143–144  
   conditions required for, 472–475  
   and conservation of mass, 83  
   decomposition, 145  
   double-replacement, 154–161  
   equations for, 138–142  
   heat energy in, 211–213  
   irreversible reactions, 481  
   limiting reactants in, 203–207  
   neutralization, 160–161  
   neutralization reactions, 408–410  
   oxidation-reduction reactions, *see* Oxidation-reduction reactions  
   percent yield, 208–210  
   precipitation, 154–158  
   rates of, 475–478  
   reversible reactions, 208, 479–480  
   single-replacement reactions, 150–152  
   stoichiometry of, 198–202  
   thermite reaction, 151  
 Chemiluminescence, 443  
 Chemistry:  
   defined, 51  
   origins of modern, 10  
 Chemosynthesis, 146  
 Chernobyl nuclear disaster, 530–532  
 China, 411  
 Chloramines, 496  
 Chlorate ion ( $\text{ClO}_3^-$ ), 122, 122*t*  
 Chloride ion ( $\text{Cl}^-$ ), 122, 153*t*, 256, 422, 447–450, 454, 497, 498  
 Chlorine (Cl), 114, 180–181, 234, 243, 243*t*, 245, 254*t*, 256, 438, 439, 447–448, 454, 454*t*, 463, 478

- Chlorine (Cl<sub>2</sub>), 273, 273  
 Chlorite ion (ClO<sub>2</sub><sup>-</sup>), 122, 122*t*, 128*t*  
 Chlorobenzene, W18  
 Chlorofluorocarbons, 478  
 Chloroform (CHCl<sub>3</sub>), 280  
 Chloromethane (CH<sub>3</sub>Cl), W20  
 Chlorophyll, 475  
 Chlorous acid (HClO<sub>2</sub>), 128*t*  
 Cholesterol, W47, W48  
 Choline, W45, W46, W47  
 Chromate ion (CrO<sub>4</sub><sup>2-</sup>), 122*t*, 450  
 Chromic chloride (CrCl<sub>3</sub>), 71  
 Chromic ion (Cr<sup>3+</sup>), 120*t*  
 Chromium (Cr), 71, 151*t*, 235, 447–448, 454*t*, 463  
 Chromium metal, 361  
 Chromosomes, W62  
 Chromous ion (Cr<sup>2+</sup>), 120*t*  
*cis* isomers, W45  
 Citral, W24  
 Classical method, 119  
 Classical physics, 225  
 Clement, N., 114  
 Climate, 62  
 Clinical trials, 13  
 Clones, W67  
 Coal, 427, W18  
 Cobalt (Co), 513  
 Cobalt-60 (isotope), 527, 528  
 Cobaltic ion (Co<sup>3+</sup>), 120*t*  
 Cobaltous ion (Co<sup>2+</sup>), 120*t*  
 Codeine, W25  
 Codons, W63  
 Coefficients:  
   chemical, 139, 140  
   in scientific notation, 23  
 Cofman, Donald, W16  
 Coinder, Jean Francois, 114  
 Cold fusion, 538  
 Collagen, W56  
 Colligative properties (of aqueous solutions), 384–389  
 Collision theory, 472–473  
 Colloidion™, W16  
 Color, perception of, 223  
 Combination reactions, 145, 145  
 Combined gas law, 305–307  
 Combustion, 94–95, 137, 212  
 Combustion reactions, 143–144, 145  
 Common logarithms, A23–A25  
 Complementary base pairs, W62  
 Compound(s), 65  
   binary ionic, 256–258  
   branched, W9  
   chemical, 56  
   defined, 52  
   formulas for, *see* Formulas  
   ionic, 67–71  
   metal-nonmetal binary, 117  
   molar mass, 179–181  
   mole composition, 182–184  
   molecular, 64–66  
   naming, *see* Chemical nomenclature  
   new discoveries of, 190  
   organic vs. inorganic, 117  
   percent composition, 184–186  
   unbranched, W9  
 Compressibility:  
   of gases, 294  
   of solids and liquids, 332  
 Concentration, 367–368  
   enzyme, W59  
   equilibrium and changes in, 481  
   and molality, 385–386  
   and molarity, 373–377  
   percent by mass, 370–373  
   percent by volume, 372  
   percent mass per unit volume, 372  
   and rate of reaction, 477  
 Condensation, 346  
   defined, 82  
   energy for, 350–352  
 Condensation polymers, W27  
 Condensed formulas, W7, W7*t*  
 Condensed states, *see* Liquid state; Solid state  
 Conductors, 382, 383  
 Conjugate acid-base pairs, 401–403  
 Conjugate acids, 401–403, 421  
 Conjugate bases, 401–403  
   buffering by, 423  
   of weak acids, 420–421  
 Containment buildings, 532  
 Continuous spectrum, 222  
 Conversion factors, 31  
 Copernicus, Nicolaus, 11  
 Copper (Cu), 55*t*  
   activity of, 151*t*  
   in Daniell cell, 458  
   in early human history, 9  
   electron configuration, 235  
   emission spectrum of, 221  
   ionic compounds, 71  
   in periodic table, 111  
   in redox reactions, 453, 454*t*, 455  
   in single-replacement reaction, 150, 151  
 Copper (II) sulfate (CuSO<sub>4</sub>), 179, 383  
 Copper (II) sulfate pentahydrate (CuSO<sub>4</sub> · 5H<sub>2</sub>O), 179, 179  
 Core meltdown, 531  
 Corrosion, 111, 152, 388  
 Coulomb's law, 243  
 Courtois, Bernard, 114  
 Covalent bond(s), 8, 65, 261  
 Covalent bonding, 260–264  
 Cracking, W13  
 Crater Lake, Oregon, 483  
 Crick, Francis, W60  
 “Critical mass,” 530  
 Cronin, Joe, 22  
 Crude oil, W12–W14, W18  
 Crust, Earth's, 53, 54  
 Crystals, growing, 497, 498  
 Crystal lattice, 338  
 Crystalline solids, 338–339, 341, 342  
 Cupric gluconate (Cu(C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>)<sub>2</sub>), 71  
 Cupric ion (Cu<sup>3+</sup>), 120*t*  
 Cupric sulfate (CuSO<sub>4</sub>), 71, 498, 498  
 Cuprous ion (Cu<sup>+</sup>), 120*t*  
 Curie (unit), 522  
 Curie, Irène, 524  
 Curie, Marie, 512  
 Curie, Pierre, 512  
 Cyalume™, 443  
 Cyanide ion (CN<sup>-</sup>), 122, 122*t*  
 Cyanide poisoning, 369  
 Cyanoacrylate ester, 411  
 Cyanogen (CN)<sub>2</sub>, 283  
 Cyclo- (prefix), W10  
 Cyclopropane, W10  
 Cyclopropene, W7*t*  
 Cyclosporine, 12  
 Cysteine, W54  
 Cytosine, W60, W60, W62
- D**  
 Dacron™, W27, W27–W28  
 Dalton, John, 10, 56, 57, 60, 138  
 Dalton's law of partial pressures, 313–316  
 Daniell cells, 458–459  
 Dark energy, 100  
 Dark matter, 100  
 Data, 11  
 Dating, with radioactive decay series, 517  
 Datriil™, W27  
 Davy, Sir Humphry, 114  
 Dead Sea, 362, 384  
 Deca- (prefix), 29, 125*t*  
 Decane (C<sub>10</sub>H<sub>22</sub>), W9*t*  
 Decay:  
   biological, 471  
   radioactive, 514  
 Decay series, radioactive, 516–517  
 Deci- (prefix), 29  
 Decimals:  
   conversion to/from fractions, A5  
   and percent, A7–A9  
 Decomposition reactions, 145, 145  
 Decongestants, 124  
 Democritus, 56, 57  
 Denaturation, W59  
 Dendrimers, W16  
 Density, 84–88  
   as conversion factor, 86–87  
   defined, 84  
   electron, 228  
   of gases, 294, 318, 318*t*, 319  
   as physical property, 84–86, 88  
   of solids and liquids, 294, 332  
   of solutions, 90–91  
 Deoxyribonucleic acid (DNA), 337, 337, W50, W60, W62  
 Deoxyribose, W61  
 Derivatives, W18  
 Derived units, 28  
 Desalination (of water), 388  
 Desormes, C., 114  
 Detergents, 158, W48  
 Deuterium (heavy hydrogen), 5, 6, 7  
 Dextro (D-) isomers, W50  
 Di- (prefix), 125*t*, W9  
 Diabetes, 369, 425, W50  
 Diamond(s), 50, 340, 340, 341  
 Diapers, 389  
 Diatomic molecules, 66, 115  
   in chemical reactions, 138  
   covalent bonding in, 260–261  
   moles of, 180–181  
 Dichromate ion (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), 122*t*, 447–448  
 Diethyl ether, 347, 347  
 Diffusion, 295–296  
 Digestion, 186



- Digoxin, 12  
 Dihydrogen phosphate ion ( $\text{H}_2\text{PO}_4^-$ ), 122*t*, 425  
 Dilution, of concentrated solutions, 375  
 Dimensional analysis, 31  
 Dimethylamine ( $(\text{CH}_3)_2\text{NH}$ ), 493*t*, W24  
 Dimethyl ether, 66, W7*t*, W22  
 Dimethylpropane, W9  
 Dinitrogen monoxide ( $\text{N}_2\text{O}$ ), 125*t*  
 Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), 125*t*, 427  
 Dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ), 125*t*  
 Dinitrogen trioxide ( $\text{N}_2\text{O}_3$ ), 125*t*  
 Dinosaurs, extinction of, 55  
 Dioxin, 195, 372  
 Dipeptides, W53  
 Diphenylhydramine, W25  
 Dipoles, 272–273  
   molecular, 279  
   permanent, 335  
 Dipole-dipole attractions, 335–336  
 Diprotic acids, 409  
 Direct linear relationships, graphing, A27–A29  
 Direct proportionality, A16–A18  
 Direct relationships, 305  
 Disaccharides, W51, W51, W52  
 Discrete spectra, 224  
 Disproportionated (term), 442  
 Distillation, 90, 90, W12  
 Disulfide bonds, W56–W57  
 Division:  
   rules for, 20–21, 24–25, A5–A6  
   in scientific notation, A21–22  
 DNA, *see* Deoxyribonucleic acid  
 Dolomite, 339  
*d* orbitals, 229, 229–230  
 Double bonds, 263, 264  
 Double-replacement reactions, 154–161  
 Downs cell, 463  
 Drunk driving, 207  
 Dry cell batteries, 459–460, 460  
 Dry ice, 346  
 Ductility, 110, 341  
 Dynamic equilibrium, 480
- E**  
 $E_a$ , *see* Activation energy  
 E.A. (electron affinity), 244
- Edison, Thomas, 437  
 Efficiency, 208  
 Effusion, 295–296  
 Egyptians, ancient, 10, 12  
 Electrical energy, 94  
 Electric automobiles, 461  
 Electricity, 110, 382, 437  
 Electrodes, 458–459  
 Electrolysis, 213, 463–464  
 Electrolytes, 382–383, 388–389  
 Electrolytic cells, 462–464, 463  
 Electromagnetic radiation, 222, 223  
 Electrons, 4–5, 58, 60*t*. *See also* Orbitals; Oxidation-reduction reactions  
   as beta particles, 513  
   imbalance of, 67  
   paired, 240  
   sharing of, 260–264  
   valence, 254–255  
 Electron affinity (E.A.), 244  
 Electron capture radiation, 513, 514  
 Electron clouds, 334–335. *See also* Orbitals  
 Electron configurations, 233–239  
   defined, 233  
   noble gas shorthand for, 234  
   normal order of filling, 233–235  
   using periodic table to determine, 235–239  
 Electron density, 228  
 Electronegativity, 272, 272, 336–337, 439–440  
 Electronic geometry, 275–276  
 Electroplating, 463, 463  
 Electrostatic forces, 58, 58, 67, 68, 225, 243, 258, W56  
 Elements, 5, 52–57, 53. *See also specific elements*  
   artificially produced, 513  
   composition of, 56–57  
   distribution of, 53–54  
   formulas for, 66  
   free, 52, 53  
   main group, 113  
   molar mass, 174  
   relative mass of, 170–172  
   representative, 113  
   symbols for, 6, 54, 54*t*, 55*t*  
   synthetic, 525  
   trace, 71  
 $E = mc^2$ , 7, 529  
 Emission spectra, 221–227  
 Emission spectrograph, 227  
 Emitted light, 223
- Empirical formulas, 187–189  
 Endothermic (term), 94, 95, 95, 197, 211  
 Endothermic processes, 349, 350, 474, 474  
 Endothermic reactions, 482  
 End point (of titrations), 379–380  
 Energy, 4, 79, 94, 94–100  
   activation, 473–474  
   for boiling and condensation, 350–352  
   bond, 475  
   chemical, 94  
   in chemical reactions, 472–474, 474  
   conservation of, 94  
   dark, 100  
   and dark matter, 100  
   defined, 94  
   electrical, 94  
   forms and types, 94–95  
   heat, 94–100, 211–213  
   ionization, 243–244, 243*t*  
   kinetic, 95, 95  
   light, 94  
   mechanical, 94  
   for melting and freezing, 349–350  
   nuclear, 94, 530–533  
   of orbitals, 230, 230  
   potential, 95, 95  
   radiant, 94  
 Energy levels, 225, 228  
 English system of measurements, 26–27, 27*t*, 29, 30  
 Enthalpy, 211, 474, 475  
 Enzymes, 275, 281, W58–W59. *See also* Proteins  
 Enzyme activity, W59, W59  
 Equations, chemical, *see* Chemical equations  
 Equilibrium, 346, 471, 479–501, 480  
   and changes in condition, 480–483  
   in chemical reactions, 405  
   dynamic, 480  
   equilibrium constant, 485–488  
   Le Châtelier's principle, 480–483  
   osmotic, 388  
   solubility equilibria, 497–501  
   of weak acids and bases, 489–496  
 Equilibrium constant ( $K_{eq}$ ), 485–488, 486*t*
- Equilibrium constant expression, 485  
 Equilibrium vapor pressure, 346  
 Essential amino acids, W53  
 Esters, W25–W28  
 Estrogen, W47, W48  
 Eth- (prefix), W9  
 Ethanal, W23  
 Ethanamide, W27  
 Ethane ( $\text{C}_2\text{H}_6$ ), W8, W9*t*  
 Ethanoic acid, W26  
 Ethanol, *see* Ethyl alcohol  
 Ethene ( $\text{C}_2\text{H}_4$ ), W13  
 Ether(s), W22, W51  
   diethyl, 347, 347, W22  
   dimethyl, 66, W7*t*, W22  
   ethyl, 350*t*, 351*t*  
   ethylmethyl, W22  
   ethyl propyl, W22  
 Ethyl alcohol (ethanol,  $\text{C}_2\text{H}_5\text{OH}$ ), 66, 84*t*, 207, 347, 347, 350*t*, 351*t*, W7*t*, W21, W52  
 Ethylbenzene, W18  
 Ethyl butanoate, W26  
 Ethyl chloride, 359  
 Ethylene ( $\text{C}_2\text{H}_4$ ), W15*t*, W16  
 Ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), 394, W21, W28  
 Ethyl ethanoate, W26  
 Ethyl ether, 350*t*, 351*t*  
 Ethyl formate, W26  
 Ethyl group, W9*t*  
 3-Ethylheptane, W9  
 Ethyl methanoate, W26  
 Ethylmethyl ether, W22  
 Ethylmethylpropylamine, W24  
 Ethyl propyl ether, W22  
 Ethyne, W16  
 Evaporation, 345  
 Excited states, 226, 229  
 Exothermic (term), 94–95, 197, 211  
 Exothermic processes, 349–351, 474–475  
 Exothermic reactions, 482  
 Explosives, 481  
 Exponents, 23  
 Extensive properties, 82  
 Extrapolation, 302
- F**  
 Factor-label method, 30–37  
   in multistep conversions, 35–37  
   in one-step conversions, 32–35

- Fahrenheit scale, 38  
 Families, of elements, 111  
 Fats, W45, W47  
 Fatty acids, W44–W45  
 FDA, *see* Food and Drug Administration  
 Federal Trade Commission (FTC), 99  
 Fermi, Enrico, 529  
 Fermi National Accelerator, 525  
 Ferric ion ( $\text{Fe}^{3+}$ ), 120*t*, 158  
 Ferrous fumarate ( $\text{FeC}_4\text{H}_2\text{O}_4$ ), 71  
 Ferrous gluconate ( $\text{Fe}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ ), 71  
 Ferrous ion ( $\text{Fe}^{2+}$ ), 120*t*  
 Ferrous sulfate ( $\text{FeSO}_4$ ), 71  
 Fertilizers, 169, 263  
 Fiber, W52  
 Fibrous proteins, W56, W56  
 Filtration, 89, 89  
 Fingerprinting, 411  
 Fire, 9–10. *See also* Combustion  
 Fireflies, 443  
 Fireworks, 221, 223  
 Fission, 529–532  
 Flocculants, 501  
 Fluorescence, 521  
 Fluorine (F), 217, 240, 243, 243*t*, 244*t*, 254*t*, 260–262, 440, 454, 454*t*  
 Fluorite, 339  
 Food, irradiation of, 527, 527  
 Food and Drug Administration (FDA), 11, 124  
 Fool's gold, *see* Pyrite  
*f* orbitals, 230, 230  
 Forensics, 227, 411, 527  
 Formal charge, 280–283  
 Formaldehyde ( $\text{H}_2\text{CO}$ ), 9, W23, W64  
 Formic acid ( $\text{HCHO}_2$ ), 492*t*, W26  
 Formulas, 65, 117–125, 127–129  
   acids, 127–129  
   for binary molecular compounds, 125  
   empirical, 187–189  
   metal-nonmetal binary ionic compounds, 117–124  
   molecular, 189–190  
   with polyatomic ions, 122–123  
   structural, 66  
 Formula units, 68  
 Formula weight, 178–181  
 Fossett, Steve, 319  
 Fossil fuels, 213, 530  
 Foxglove, 12  
 Fractions:  
   conversion of, to/from decimals, A5  
   multiplication and division of, A6–A7  
 France, 530  
 Free elements, 52, 53  
 Free radicals, 268, 519  
 Freeze drying, 345  
 Freezing, energy for, 349–350  
 Freezing point:  
   of aqueous solutions, 386–387  
   defined, 81  
 Freezing-point lowering (term), 386–387  
 Frisch, Otto, 529  
 Fructose, W49, W50  
 D-Fructose, W50, W59  
 FTC (Federal Trade Commission), 99  
 Fuels, combustion of, 144  
 Fuel cells, 213, 320, 461, 461–462  
 Fuel rods, 532  
 Fuller, Buckminster, 340  
 Functional groups, W20  
 Fundamental units, 28  
 Fusion, 532–534  
   cold, 538  
   heat of, 350, 350*t*  
   nuclear, 7–8  
   by sun, 534
- G**  
 D-Galactose, W50  
 Galactosemia, W52  
 Galaxies, 4, 100  
 Galileo Galilei, 11  
 Gallium (Ga), 111, 115, 235, 236, 243, 254*t*, 257*n*  
 Galvanic cells, *see* Voltaic cells  
 $\gamma$  radiation, 513, 514  
 $\gamma$  rays, 513  
 Gas(es), 293–323  
   in aqueous solutions, 369–370  
   and Avogadro's law, 307–308  
   Boyle's law and pressure of, 297–301  
   calculating equilibrium constant for, 485–488  
   Charles's law and volume of, 302–304  
   combined gas law, 305–307  
   and Dalton's law of partial pressures, 313–316  
   defined, 80, 81  
   equilibrium and pressure changes in, 482  
   Gay-Lussac's law and temperature of, 304–305  
   Graham's law and velocity of, 295–296  
   ideal, 311  
   ideal gas law, 310–312  
   kinetic molecular theory, 295  
   molar volume and density, 316–319  
   noble, 113, 117  
   stoichiometry of, 319–321  
 Gas constant, 310  
 Gas oil, W12  
 Gasoline, 84*t*, 144, 208, W12  
 Gay-Lussac, Joseph Louis, 114, 304  
 Gay-Lussac's law, 304–305  
 Geiger counter, 521, 522  
 Genes, W62  
 General Motors, 461  
 Genesis (term), W64  
 Genetics, W60–W64  
 Geometry:  
   bent, 276  
   electronic, 275–276  
   linear, 275, 276*t*, 277*t*, 279  
   molecular, 276–278  
   tetrahedral, 275, 276*t*, 277*t*, 279  
   trigonal planar, 275, 276*t*, 277*t*, 279  
   trigonal pyramidal, 276, 277*t*  
   V-shaped, 276, 277*t*  
 Germanium (Ge), 111, 243, 254*t*  
 Giant Hydron Collider, 525, 525  
 Giga- (prefix), 29  
 Glass, identifying origins of, 88, 227  
 Global warming, 137  
 Globular proteins, W56, W56  
 Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), 143, 281, 383, 474–475, 528, W49–W50, W51, W52, W52  
 D-Glucose, W50, W59  
 Glutamic acid, W54  
 Glutamine, W54  
 Glyceraldehyde, W49–W50  
 Glycerin, W48  
 Glycerol, W21–W22, W45, W47  
 Glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ), 263, W35, W53, W54, W55, W55  
 Glycine-valine, W55  
 Glycogen, W52  
 Glycolipids, W45, W46  
 Glycoside bond, W51  
 Goiter, 114  
 Gold (Au), 10, 55*t*, 84*t*, 91, 111, 151*t*, 243  
*The Graduate* (film), W16  
 Graham, Thomas, 295  
 Graham's law, 295–296  
 Grain alcohol, *see* Ethyl alcohol  
 Grain storage, 477  
 Gram (unit), 27, 29  
 Graphing, A27–A30  
 Graphite, 340, 340, 341, 460  
 Gravitation, Newton's law of universal, 11  
 Gravity, 6, 100  
 Great Lakes, 349  
 Great Salt Lake, 384  
 Greeks, ancient, 10  
 Greek prefixes, 125, 125*t*  
 Greenhouse effect, 530  
 Greenland, 62  
 Ground state, 226, 228  
 Groups (periodic table), 113, 255  
 Guanine, W60, W60, W62, W62
- H**  
 $\Delta H$ , 211, 474–475  
 Haber, Fritz, 481, 482  
 Haber process, 481  
 Hahn, Otto, 529  
 Half-lives ( $t_{1/2}$ ), 516  
 Half-reaction method (of balancing):  
   in acidic solutions, 447–449  
   in basic solution, 449–451  
 Half-reactions (redox reactions), 438–439  
 Halogens, 113, 117, 237  
   ion formation by, 256, 257  
   oxidation state, 440  
 Halon™, W15*t*  
 Hard water, 158, W48  
 Heart attacks, W28  
 Heartburn, 124  
 Heart disease, 12, W45  
 Heat, 6, 482  
   and enzymes, W59



- in neutralization reactions, 161  
 from radiation, 518–519  
 Heat energy, 94–95, 211–213  
 Heat exchange, 98, 99  
 Heat index, 346  
 Heating curves, 352–355  
 Heat of fusion, 350, 350*t*  
 Heat of the reaction (term), 474  
 Heat of vaporization, 351, 351*t*  
 Heavy hydrogen, *see* Deuterium  
 Hecto- (prefix), 29  
 Helium (He), 534  
 atomic radius, 243  
 atomic structure, 5, 6  
 density of, 318, 318*t*  
 electron configuration, 234, 236, 237, 240  
 formation of, 7  
 and Graham's law, 296  
 in hot air balloons, 319  
 Lewis Dot symbols, 254*t*  
 mass of, 171, 171*t*  
 valence electrons, 254  
 Helium nucleus, 512, 512  
 Hemochromatosis, 71  
 Hemoglobin, 369  
 Henderson-Hasselbach equation, 495  
 Henry's law, 369, 370  
 Hepta- (prefix), 125*t*  
 Heptane (C<sub>7</sub>H<sub>16</sub>), W9*t*  
 Hercules™, W15*t*  
 Hetero atoms, W7  
 Heterogeneous catalysts, 478  
 Heterogeneous mixtures, 89, 89  
 Hexa- (prefix), 125*t*  
 Hexane (C<sub>6</sub>H<sub>14</sub>), W9*t*  
 1,6-Hexanediamine, W27  
 2-Hexene, W14  
 Hexose, W49  
 Hg, *see* Mercury  
 High blood pressure, W28  
 High-throughput-screening (HTS), 12  
 Hill, Julian, W16  
 Hindenburg (airship), 319  
 H<sup>+</sup> ions, 399, 408, 409, 447–450, 454*t*, 459, 519  
 Hippocrates, W28  
 Hiroshima, Japan, 530  
 Histidine, W54  
 Hoffman, Felix, W28  
 Homogeneous catalysts, 478  
 Homogeneous mixtures, 89, 89–92  
 Homologous series, W8  
 Hot-air balloons, 302, 302, 319, 328  
 HTS (high-throughput-screening), 12  
 Human body, 53, 54, 522–523  
 Human Genome Project, W60  
 Hund's rule, 240  
 Hyatt, John Wesley, W16  
 Hydrates, 179  
 Hydrated (term), 365  
 Hydrazine (N<sub>2</sub>H<sub>4</sub>), 493*t*  
 Hydrobromic acid (HBr), 404  
 Hydrocarbons, 279, W3, W8  
 Hydrochloric acid (HCl), 398–401, 404, 408, 409, 422, 496  
 in aqueous solution, 148, 365–366, 366  
 as binary acid, 127*t*  
 in binary ionic compounds, 262  
 boiling point, 347*t*  
 in dipole-dipole attractions, 335  
 as electrolytes, 382  
 formation of, 127  
 pH of, 416*t*  
 polarity of, 273, 273  
 solubility of, 367*t*  
 Hydrocyanic acid (HCN), 127, 492*t*  
 Hydrofluoric acid (HF), 127*t*, 405, 480, 492*t*  
 Hydrogen (H), 534, W16  
 in acids, 129  
 activity of, 151*t*  
 atomic radius, 243  
 atomic structure, 5  
 Bohr model of, 225  
 bonding of, with nonmetals, 261–262, 262  
 density of, 318*t*  
 electron configuration, 233, 236, 240  
 emission spectrum of, 221, 224, 225, 225  
 in equilibrium, 480–482  
 as fuel, 213  
 in fuel cells, 461–463  
 in hot air balloons, 319  
 Lewis Dot symbols, 254*t*  
 liberation of, by acids, 398  
 in nonmetal-nonmetal binary compounds, 125  
 orbitals of, 228–229  
 oxidation state, 440  
 in redox reactions, 454*t*  
 Hydrogenation, W45  
 Hydrogen atom, 5, 5  
 Hydrogen bomb, 532  
 Hydrogen bonding, 336–337  
 and boiling point, 347  
 in DNA, W60, W62  
 and heat of fusion, 350  
 in proteins, W56  
 Hydrogen carbonate ion (HCO<sub>3</sub><sup>-</sup>), 122*t*  
 Hydrogen chloride (HCl), 127, 127*t*  
 Hydrogen cyanide (HCN), 9, 275, 280  
 Hydrogen fluoride (HF), 127*t*, 261–262, 337, 347, 347*t*, 383, 383  
 Hydrogen iodide (HI), 127*t*  
 Hydrogen oxide, *see* Water  
 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 65, 66, 139  
 Hydrogen phosphate ion (HPO<sub>4</sub><sup>2-</sup>), 425  
 Hydrogen sulfate ion (HSO<sub>4</sub><sup>-</sup>), 122*t*, 420  
 Hydrogen sulfide (H<sub>2</sub>S), 127, 127*t*, 146, 205–206, 262, 347, 347*t*, 444  
 Hydrogen sulfite ion (HSO<sub>3</sub><sup>-</sup>), 122*t*  
 Hydroiodic acid (HI), 127*t*, 404  
 Hydrolysis, 420–422, 460  
 anion, 420–421  
 cation, 421  
 Hydronium ions (H<sub>3</sub>O<sup>+</sup>), 399, 400–402, 404–406, 413–417, 420, 421, 424, 425, 480, 490, 495  
 Hydrophilic (term), W48  
 Hydrophobic (term), W48  
 Hydrophobic interaction, W56  
 Hydrosulfuric acid (H<sub>2</sub>S), 127*t*  
 Hydroxide ion (OH<sup>-</sup>), 122, 122*t*, 153*t*, 159–160  
 Hydroxybenzene, W18  
 Hydroxyl group, W20  
 Hyperbaric chambers, 369  
 Hyperventilation, 425  
 Hypo- (prefix), 122  
 Hypobromous acid (HBrO), 492*t*  
 Hypochlorite ion (ClO<sup>-</sup>), 122, 122*t*, 262–263, 420, 424, 449–450, 490, 495, 496  
 Hypochlorous acid (HClO), 490, 492*t*, 495, 496  
 Hypothesis(-es), 11, 55  
 I  
 Ibuprofen, W27, W28  
 -ic (suffix), 119, 120*t*  
 Ice, 84*t*, 388  
 "Ice-Man," 527  
 -ide (suffix), 127, 128  
 Ideal gas law, 310–312  
 Identical twins, W64  
 I.E., *see* Ionization energy  
 Immiscible (term), 364  
 Improper fractions, A5  
 Indicators, chemical, 161, 379, W14  
 Indigestion, 124  
 Indium (In), 236  
 Industrial Revolution, 137  
 Inert electrodes, 460  
 Inflammation, W28  
 Infrared light, 223  
 Initiators, W14  
 Inner transition metals, 114, 237  
 Inorganic compounds, 117  
 defined, W4  
 naming, 117–123, 125–128  
 Insoluble (term), 148, 368  
 Inspection, balancing equations by, 140–142  
 Instantaneous dipole-induced dipole forces, 334–335  
 Instantaneous dipoles, 335  
 Insulators, 382  
 Insulin, W50  
 Intensive properties, 82  
 Intermolecular forces, 334–337, 346  
 International Thermonuclear Experimental Reactor (ITER), 533  
 Intravenous solutions, 388–389  
 Inverse proportionality, A17  
 Inverse relationships, 305  
 Iodide ion (I<sup>-</sup>), 153*t*  
 Iodine (I), 71, 112, 114, 513, 513  
 Iodine-131 (isotope), 516, 516*t*, 528  
 Ions. *See also* Anions; Cations  
 defined, 67  
 and hydrolysis, 422  
 Lewis structures of, 266  
 naming, 117  
 polyatomic, 69–70  
 from radiation, 519  
 spectator, 150–151  
 and strong acids, 148  
 Ion-dipole forces, 365

- Ion-electron method (of balancing), 447–451  
 in acidic solutions, 447–449  
 in basic solutions, 449–451
- Ionic bonds, 9, 68, 258
- Ionic bonding, 255–259
- Ionic compounds, 67–71  
 in aqueous solutions, 364–365  
 empirical formulas, 187  
 formulas for, 67–69  
 formula weights, 178–179  
 Lewis structures for, 266–267  
 physical state, 258  
 of polyatomic ions, 69–70
- Ionic radii, 244–245
- Ionic solids, 339, 339
- Ionization, 365–366, 404–405, 407  
 acid and base ionization constants, 490–496  
 autoionization, 413  
 buffering vs., 424–425  
 and radiation, 519
- Ionization energy (I.E.), 243–244, 243*t*
- Ionizing radiation, 519
- Ion product ( $K_w$ ), 413–414
- Ireland, 207
- Iridium, 55
- Iron (Fe), 8, 55*t*, 71, 454*t*, 455  
 activity of, 151*t*  
 in human body, 71  
 melting point, 341
- Iron-59 (isotope), 528
- Irreversible reactions, 481
- Isobutane, W6, W7, W9
- Isobutyl group, W9*t*
- Isoleucine, W54
- Isomers, W6, W7, W7*t*  
 cis, W45  
 dextro, W50  
 levo, W50  
 optical, W50  
 trans, W45
- Isopentane, W7*t*
- Isopropyl alcohol (propanol, C<sub>3</sub>H<sub>8</sub>O), 144, 360, W7*t*, W21
- Isopropyl group, W9*t*
- Isotonic (term), 388
- Isotopes, 5, 61–62, 511  
 radioactive, 512  
 stability of, 514
- Isotopic mass, 62
- Isotopic notation, 6, 61
- ite (suffix), 122, 128
- ITER (International Thermonuclear Experimental Reactor), 533
- IUPAC (International Union of Pure and Applied Chemistry), W8–W9
- J**
- Japan, 207
- Joint Institute for Nuclear Research, 525
- Joliot, Frédéric, 524
- Joule (unit), 28*t*, 96
- Jupiter, 311
- K**
- $K_a$ , *see* Acid ionization constant
- Kahlbaum, G. W. A., W16
- $K_b$ , *see* Base ionization constant
- K.E., *see* Kinetic energy
- Kelvin (unit), 28*t*
- Kelvin scale, 40, 302, 303
- $K_{eq}$ , *see* Equilibrium constant
- Kerosene, 84*t*, W12
- Ketones, W22–W24
- Ketose, W49
- Kidney disease, 425
- Kidney stones, 497, 501
- Kilo- (prefix), 29
- Kilocalorie (unit), 98
- Kilogram (unit), 28*t*, 29
- Kilopascal (unit), 298
- Kinetic energy (K.E.), 95, 476, 476–477  
 in chemical reactions, 473–474  
 of gases, 295  
 and vaporization, 345, 345
- Kinetic molecular theory (kinetic theory), 295, 300–301, 301  
 and Charles law/Gay-Lussac law, 305  
 and density, 318  
 for solids and liquids, 332–334
- Krishe, W., W16
- Krypton (Kr), 235, 254*t*
- Krypton-94 (isotope), 529
- L**
- Lactase, 281
- Lactose, 281, W51, W51, W52
- Lactose intolerance, 281
- Lakes, volcanic crater, 483
- Lake Monoun, Cameroon, 483
- Lake Nyos, Cameroon, 483
- $\lambda$  (wavelength), 222
- Lanthanide contraction, 250
- Lanthanides, 114, 237
- Lanthanum (La), 237
- Lasers, 411
- Latent prints, 411
- Lattice, 258
- Lavoisier, Antoine, 293
- Laws, 11
- Law of conservation of energy, 94
- Law of conservation of mass, 83, 138, 293
- Laxatives, W52
- LD<sub>50</sub> dose, 523
- Lead (Pb), 55*t*, 84*t*, 151*t*, 454*t*, 459  
 Lead-206 (isotope), 517  
 Lead-207 (isotope), 517  
 Lead-208 (isotope), 517  
 Lead-210 (isotope), 517  
 Lead-214 (isotope), 517  
 Lead-acid batteries, 459, 463  
 Lead (II) chloride, 498
- Le Châtelier's principle, 480–483
- Leclanché, S. A., 459
- Lemon grass, oil of, W24
- Leucine, W54
- Leukemia, 12, 519
- Levo (L) isomers, W50
- Lewis, G. N., 254*n*
- Lewis dot symbols, 254–257, 255*t*
- Lewis structures:  
 of benzene, W18  
 of covalent bonds, 260–264  
 and formal charge, 282–283  
 of organic molecules, W5–W6  
 rules for writing, 264–270
- Life, origin of, W64
- Ligaments, W56
- Light:  
 emitted, 223  
 gamma ray emission, 513  
 infrared, 223  
 reflected, 223  
 ultraviolet, 223
- Light energy, 94, 222, 222–223, 223, 226
- Lightning, 263, 437
- Lightning bugs, 443
- Light waves, 222
- Limestone, 153, 156, 428
- Limiting reactants, 203–207
- Linear geometry, 275, 276*t*, 277*t*, 279
- Linear relationships, 302
- Line spectra, 224, 226
- Lipids, W44–W49  
 complex, W45–W47  
 fatty acids in, W44–W45  
 nonsaponifiable, W44  
 saponifiable, W44  
 steroids, W47–W49
- Liquid (term), 80
- Liquid sodium, 361
- Liquid state, 332–337, 343–355  
 boiling point, 347–348  
 dipole-dipole attractions, 335–336  
 and energy for boiling and condensation, 350–352  
 and energy for melting and freezing, 349–350  
 and heating curves, 352–355  
 hydrogen bonding, 336–337  
 intermolecular forces, 334–337, 346  
 and kinetic theory, 332–334  
 London forces, 334–335  
 surface tension, 343–344  
 vapor pressure, 345–346  
 and viscosity, 344
- Liter (unit), 27, 28*t*
- Lithium (Li), 5–6, 6, 84*t*, 111, 234, 240, 243*t*, 244*t*, 254*t*, 257
- Lithium batteries, 460–461
- Lithium carbonate (LiCO<sub>3</sub>), 124
- Lithium citrate (LiC<sub>6</sub>H<sub>5</sub>O<sub>7</sub>), 124
- Lithium ion (Li<sup>+</sup>), 124
- Lithium oxide (Li<sub>2</sub>O), 257
- Litmus paper, 398
- Lobes (orbital), 229
- Lock-and-key model (enzyme activity), W59, W59
- Logarithms, A23–A26, A35
- Logarithmic scales, 419
- London forces, 334–335  
 of alkanes, W12  
 between amino acids, W56  
 in lipids, W45
- Los Alamos National Laboratory, 411
- Luciferase, 443
- Luciferin, 443
- Lucite™, W15*t*
- Lye, 160, 404, W48. *See also* Sodium hydroxide
- Lysine, W54

- M**
- M, *see* Molarity
- m*, *see* Molality
- Magnesium (Mg), 71, 84*t*, 151*t*, 234, 243, 243*t*, 244, 244*t*, 245, 254*t*, 256, 454, 454*t*
- Magnesium chloride (MgCl<sub>2</sub>), 118
- Magnesium hydroxide (Mg(OH)<sub>2</sub>), 124, 367–368, 367*t*, 407
- Magnesium ion (Mg<sup>2+</sup>)
- Magnesium oxide (MgO), 71, 145
- Magnetite, 188, 188–189
- Main group (of elements), 113
- Malachite, 9, 9
- Malleability, 110, 341
- Maltose, W51, W51
- Manganese (Mn), 240
- Manganic ion (Mn<sup>3+</sup>), 120*t*
- Manganous ion (Mn<sup>2+</sup>), 120*t*
- Manhattan Project, 530
- Manic-depressive disorder, 124
- Mantissa (logarithmic), A25
- Marble, 153, 365
- Mark Nutritionals Inc., 99
- Marlex™, W15*t*
- Mars, 51, 146, 348, 359
- Mass:
  - conservation of, 83, 138, 293
  - conversion of, to volume, 87
  - converting to/from moles, 174–177
  - defined, 27
  - determining, in reactions, 200–202
  - molar, 174, 179–181
  - relative, 170–172
  - weight vs., 29
- Mass number, 6, 61
- Mass ratio, 171
- Mass-to-mass calculations, 202
- Mathematical operations, 19–21, A2–A9
- Matter, 56, 79
  - antimatter, 513
  - chemical properties of, 82, 83
  - classification of, 90, 91
  - dark, 100
  - defined, 51
  - density of, 84–88
  - origin of, 4–9
  - physical states of, 80–82, 81
- Measurement(s):
  - defined, 16
  - English system of, 26–27, 27*t*, 29, 30
  - metric system of, 27–29, 30
  - numerical value of, 16
- Mechanical energy, 94
- Medicine:
  - amines used in, W25
  - and radiation, 528
- Mega- (prefix), 29
- Meitner, Lise, 529
- Melmac™, W23
- Melting, energy for, 349–350
- Melting point(s), 81, 82, 338–342, 350*t*
- Mendeleev, Dmitri, 111, 112, 117
- Mercury (Hg), 55*t*, 84*t*, 115, 341, 460
- Mercury batteries, 460, 460
- Mercury (II) oxide (HgO), 145, 460
- Messenger RNA (mRNA), W62–W63, W63
- Metabolism, 143, 281
- Metals, 110, 110, 111, 113, 243
  - active, 111, 455
  - alkali, 113, 117, 154, 236, 440
  - alkaline earth, 113, 117, 236, 440
  - and cations, 117
  - as crystalline solids, 341, 342
  - inner transition, 114, 237
  - ion formation by, 257, 258
  - ions with multiple charges from, 119–121, 120*t*
  - ions with single charge from, 117–119
  - noble, 111
  - and octet rule, 255
  - rare earths, 114
  - strength of, as reducing agents, 453–454
  - transition, 114, 119, 237
- Metallic solids, 341, 342
- Metalloids, 111, 113
- Metallurgy, 9
- Metal-nonmetal binary compounds, 117–124, 126
- Metastable isotopes, 513
- Meter (unit), 27, 28*t*
- Meth- (prefix), W9
- Methanal, W23
- Methanamide, W27
- Methane (CH<sub>4</sub>), 65, 117, 262, 339, 348, W8, W9*t*, W13, W16, W20
- Methanoic acid, W26
- Methanol, *see* Methyl alcohol
- Methionine, W54
- Methyl alcohol (methanol, CH<sub>3</sub>OH), 204–205, 218, 366, 366, 394, W21, W23
- Methylamine, W24
- Methylbenzene, W18
- Methyl benzoate, W26
- Methyl group, W9*t*
- Methyl methacrylate, W15*t*
- Methylpropane, W9
- Methyl salicylate, W26
- Metric system, 27, 27–29, 29*t*, 30
- Meyer, Lothar, 111
- Micelles, W46, W47, W47, W48
- Micro- (prefix), 29
- Micro X-rays, 411
- Middle Ages, 10
- Milk of magnesia, 407
- Milky Way, 100
- Miller, Stanley, W64
- Milli- (prefix), 29
- Millirem (unit), 522
- Mining, 152
- Miscible (term), 364
- Mixtures:
  - heterogeneous, 89
  - homogeneous, 89–92
- mm of Hg (unit), 297, 298
- Model(s):
  - ball-and-stick, W6
  - defined, 225
- Modern atomic theory, 56–57, 138, 221–246
  - electron configurations, 233–239
  - emission spectra and Bohr model, 222–227
  - orbitals, 228–231, 240–242
  - and periodic trends, 242–245
- Molality (*m*), 385–386
- Molarity (M), 373–377
  - determining, for an unknown, 379–380
  - molality vs., 386
- Molar mass, 174
  - and London forces, 335
  - and velocity of gases, 295–296
- Molar volume, 316, 316–318
- Mold, 471
- Mole (unit), 28*t*, 173–190
  - constants for, 316
  - converting to/from mass, 174–177
  - defined, 173–174
  - determining, in reactions, 199–202
  - empirical formulas from, 187–189
  - formula weight from, 178–181
  - mole composition of compounds, 182–184
  - and molecular formula, 189–190
  - and percent composition, 184–186
- Mole composition, 182–184
- Molecular compounds, 64–66
  - in aqueous solutions, 365–366
  - empirical formulas, 187
  - formula weight of, 178
  - Lewis structures for, 265–266
- Molecular dipoles, 279
- Molecular equations, 150
- Molecular formulas, 189–190
- Molecular geometry, 276–278
- Molecular solids, 339, 339
- Molecule(s), 9, 65
  - diatomic, *see* Diatomic molecules
  - movement of, in gases, 295
  - nonpolar, 279
  - polar, 278–280
- Mole ratio(s), 183, 199
- Mono- (prefix), 125*t*, 126
- Monohydrogen phosphate ion (HPO<sub>4</sub><sup>2-</sup>), 122*t*
- Monoprotic acids, 409
- Monosaccharides, W49–W50
- Montgolfier, Jacques-Étienne, 319
- Montgolfier, Joseph-Michel, 319
- mRNA, *see* Messenger RNA
- Multiple sclerosis, W45
- Multiplication:
  - rules for, 20–21, 24–25, A3–A4
  - in scientific notation, A21–22
- Multistep conversions, 35–37
- Multivitamins, 71
- Myelin sheath, W45
- Myristic acid, W44
- N**
- Nagasaki, Japan, 530
- Nano- (prefix), 29
- Nanometer, 242
- Nanotubes, W16
- Naproxen, W28

- Naphthalene, 346
- National Aeronautics and Space Administration (NASA), 462
- Natta, Giulio, W16
- Natural gas (CH<sub>4</sub>), 335, W12
- Neon (Ne), 234, 240, 244, 244*t*, 254*t*
- Neopentane, W7*t*, W9
- Nerve cells, W45
- Net ionic equations, 150–151
- Network solids, 340, 340
- Neutralization reactions, 160–161, 408–410
- Neutrons, 4, 6, 59, 60*t*
- Neutron activation analysis, 527
- Newton, Sir Isaac, 11
- Newtonian physics, 225
- Newton's law of universal gravitation, 11
- Nickel (Ni), 151*t*, 453, 454*t*, 455, 460
- Nickel-cadmium batteries, 460
- Nicotine, 195
- Nitrate ion (NO<sub>3</sub><sup>-</sup>), 69, 122*t*, 128*t*, 153*t*
- Nitric acid (HNO<sub>3</sub>), 128*t*, 148, 399, 404, 408, 409, 427, 444
- Nitric oxide (NO), 125*t*, 268, 444, 474, 474, 478
- Nitride ion (N<sup>3-</sup>), 257
- Nitrite ion (NO<sub>2</sub><sup>-</sup>), 69, 69, 122*t*
- Nitrogen (N), 117, 125*t*, 240, 243, 243*t*, 244, 244*t*, 254*t*, 257, 262–264, 268, 293, 313, 474, 474, 480–482, 513
- Nitrogen (N<sub>2</sub>), 318*t*, 339, 369
- Nitrogen-14 (isotope), 524
- Nitrogenase, 263
- Nitrogen dioxide (NO<sub>2</sub>), 69, 69, 125*t*, 268, 296
- Nitrogen fixation, 263, 481
- Nitrogen monoxide (NO), 125*t*, 283
- Nitroglycerin, 194, W22
- Nitrosyl chloride (NOCl), 282–283
- Nitrous acid (HNO<sub>2</sub>), 492*t*
- Nitrous oxide (N<sub>2</sub>O), 125*t*
- Nobel Prize, 524
- Noble gases, 113, 117, 237, 254
- Noble metals, 111
- Nomenclature, chemical, *see* Chemical nomenclature
- Nona- (prefix), 125*t*
- Nonane (C<sub>9</sub>H<sub>20</sub>), W9*t*
- Nonconductors, 382
- Nonelectrolytes, 382, 383
- Nonlinear relationships, graphing, A29–A30
- Nonmetals, 110, 111, 111, 113 and anions, 117 covalent bonding by, 260–264 ion formation by, 257 and octet rule, 255
- Nonpolar bonds, 273
- Nonpolar molecules, 279, 279, 366
- Nonsaponifiable lipids, W44
- Nonvolatile solutes, 384*n*
- Normal boiling point, 347
- NSAIDs (nonsteroid inflammatory drugs), W28
- Nuclear chain reaction, 529–530, 530
- Nuclear chemistry, 511–535 applications of radioactivity, 526–528 effects of radiation, 518–520 fission, 529–532 fusion, 532–534 measuring radiation, 521–523 nuclear reactions, 524–526 radioactivity, 512–515 rates of decay, 516–517
- Nuclear energy, 94, 530–533
- Nuclear equations, 512
- Nuclear fusion, 7–8, 532–534
- Nuclear medicine, 528
- Nuclear reactions, 524–526, 529–532 fission, 529–532 fusion, 532–534 for transmutation, 524–526
- Nuclear reactors, 327, 520, 530, 531
- Nuclear testing, 519
- Nuclear weapons, 529–530, 532
- Nucleic acids, W60–W61
- Nucleons, 59, 524
- Nucleotides, W60, W61
- Nucleus, 5, 59
- Nuprin™, W27
- Nylon™, W16, W27, W27
- O**
- Observations, 11
- Oceans, 363, 428
- Ocean vents, 146
- Octa- (prefix), 125*t*
- Octane (C<sub>8</sub>H<sub>18</sub>), 335, W9*t*, W13
- Octet rule, 254, 268, 280–282
- 3-Octyne, W16
- OH<sup>-</sup> ions, 399, 401, 407, 408, 413–416, 420, 421, 425, 450, 454, 454*t*, 460, 461, 490, 519, W24
- Oil, W45
- OIL RIG mnemonic, 439
- One-step conversions, 32–35
- Open-chain alkanes, W8
- Opportunity rover, 51
- Optical isomers, W50
- Optimal pH, W58
- Orbitals, 228–242 in covalent bonds, 261 *d*, 229, 229–230 defined, 228 diagrams of, 240–242 electron configurations in, 233–239 *f*, 230, 230 *p*, 229, 229 *s*, 228, 228
- Organic chemistry, W3–W30 alcohols, W20–W22 aldehydes and ketones, W22–W24 alkanes, W8–W13 alkenes, W13–W16 alkynes, W16–W17 amines, W24–W25 aromatic compounds, W17–W18 bonding, W4–W7 carboxylic acids, esters, and amides, W25–W28 ethers, W22
- Organic compounds, 117 defined, W4 naming, 125*n*
- Orlon™, W15*t*
- Osmosis, 387–388
- Osmotic pressure, 387–388, 388
- Osteoporosis, 71, 186, 501
- ous (suffix), 119, 120*t*
- Ovarian cancer, 12
- Oxalate ion (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), 122*t*, 498, 501
- Oxalic acid, W26
- Oxidation, W50*n*
- Oxidation number, 440
- Oxidation-reduction reactions (redox reactions), 438–465 about, 438–439 defined, 439 in electrolytic cells, 462–464 half-reactions, 438–439 ion-electron method of balancing, 447–451 oxidation state method of balancing, 444–446 oxidation states in, 439–442 spontaneous, 453–458, 454, 457 in voltaic cells, 457–462
- Oxidation state method (of balancing), 444–446
- Oxidation states, 439–442
- Oxides, acids as, 426–428
- Oxide ion (O<sup>2-</sup>), 256, 257
- Oxidized (term), 438
- Oxidizing agent(s), 439, 453–454
- Oxyacids, 128–129, 267
- Oxyanions, 122
- Oxygen (O), W13 activation energy, 474, 478 atomic radius, 243 density of, 318*t* in Earth's atmosphere, 293, 313 electron affinity, 244*t* electron configuration, 240 in fuel cells, 461, 463 ionization energy, 243*t* isotopes of, 62 Lewis Dot symbols, 254*t* and octet rule, 268 oxidation state, 440 in ozone, 296 as polyatomic ion, 262–264 reactions involving, 143–146 in redox reactions, 439, 454*t* solubility of, 369
- Oxygen-17 (isotope), 524
- Ozone (O<sub>3</sub>), 269, 269–270, 293, 296, 478
- P**
- Pacific yew, 12, 12
- Paired electrons, 240
- Palladium, 462, 478
- Palmitic acid, W44
- Paraffin (C<sub>24</sub>H<sub>50</sub>), 335
- Partial pressures, 313–315, 315
- Particle accelerators, 524–525
- Parts per billion (ppb), 372
- Parts per million (ppm), 186, 372
- Pascal (unit), 28*t*
- Passive electrodes, 460



- Path of reaction, 474
- Pauli exclusion principle, 240
- Pb, *see* Lead
- Penta-, 125*t*
- Pentane (C<sub>5</sub>H<sub>12</sub>), W9*t*
- N*-Pentane, W7*t*
- 2-Pentanone, W23
- Pentose, W49
- Pentyl acetate, W26
- Peptide bonding, W53, W55–W56, W63
- Per- (prefix), 122
- Percent, and decimals, A7–A9
- Percent by mass (concentration), 370–373
- Percent by volume, 372
- Percent composition, 184–186
- Percent mass per unit volume, 372
- Percent yield, 208–210
- Perchlorate ion (ClO<sub>4</sub><sup>−</sup>), 69, 122, 122*t*, 128*t*, 153*t*
- Perchloric acid (HClO<sub>4</sub>), 128*t*, 399, 404
- Periods (periodic table), 113
- Periodic law, 112
- Periodic table, 109, 110–115, 112, 236
- and electron configurations, 233–235
- and modern atomic theory, 242–245
- origin of, 111–112
- predicting charge from, 117–118, 118
- theoretical basis of, *see* Modern atomic theory
- using, 112–115
- Permanent dipoles, 335
- Permanganate ion (MnO<sub>4</sub><sup>−</sup>), 122*t*, 450
- Persians, ancient, 9
- Perspiration, 345, 411
- PET (positron emission tomography), 528, 528
- Petrochemicals, W13
- Petroleum, W12, W12
- pH, 415–427
- and acid/base ionization constants, 491–494
- and acidity, 416–419
- of blood, 425
- buffers, 423–426
- definition, 415–416
- effect of salts on, 420–422
- and enzymes, W58
- optimal, W58
- of soil, 422
- Phase, of matter, 89
- Phenol, W18
- Phenolphthalein, 410
- Phenylalanine, W54
- Phoenix* polar lander, 348
- Phosphates, W60
- Phosphate ion (PO<sub>4</sub><sup>3−</sup>), 122*t*, 128*t*, 153*t*, 282
- Phosphatidylcholine, W45, W47
- Phosphine (PH<sub>3</sub>), 215
- Phospholipids, W45, W47
- Phosphors, 521
- Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), 128*t*
- Phosphorus (P), 71, 117, 234, 243, 243*t*, 254*t*, 257, 262, 475–476, W64
- Phosphorus-30 (isotope), 524
- Photochemical smog, 296
- Photographic film, 521
- Photography, 156
- Photons, 222
- Photosynthesis, 137, 146, 443, 475
- Physics, 225
- Physical change, 82
- Physical properties, 80
- Physical states of matter, 80–82, 81. *See also* Liquid state; Solid state
- and chemical equations, 139
- of ionic compounds, 258
- and periodic table, 114, 115
- Pico- (prefix), 29
- Picometer, 242–243
- Pitchblende, 511
- p*K*<sub>a</sub>, 492, 492*t*
- p*K*<sub>b</sub>, 492, 493*t*
- Planck's constant, 223
- Plants, drugs from, 12
- Plastics, W16
- Plastic prints, 411
- Platelets, W28
- Platinum (Pt), 461, 462, 478
- Plexiglas™, W15*t*
- Plumbic ion (Pb<sup>4+</sup>), 120*t*
- Plumbous ion (Pb<sup>2+</sup>), 120*t*, 498
- Plum pudding model (of atom), 58, 58
- Plutonium (Pu), 525
- Plutonium-239 (isotope), 530
- Plutonium-242 (isotope), 516*t*
- POH, 415–417
- Point of equilibrium, 479
- Poisoning, 369, 527
- Polar bonds (polar covalent bonds), 272–274
- Polarity:
- induced, 335
- of organic molecules, W5
- and physical state, 335–336
- of soaps, W48
- and solubility, 366
- Polar molecules, 278–280, 365–366
- Pollution, 296
- Polonium (Po), 237, 512, 521
- Polonium-210 (isotope), 517
- Polonium-214 (isotope), 517
- Polonium-218 (isotope), 517, 521
- Poly- (prefix), W14
- Polyatomic ions, 69–70, 122*t*
- balancing equations with, 140
- covalent bonding in, 262–263
- naming compounds with, 121–124
- oxidation state, 440
- Polyethylene, W14, W16
- Polyfilm™, W15*t*
- Polymers, 389, W14, W15, W15*t*
- addition, W27
- condensation, W27
- Polyprotic acids, 409–410
- Polysaccharides, W52
- p orbitals, 229, 229
- Positron particle, 513
- Positron radiation, 513, 514
- Postulating (term), 225
- Potassium (K), 55*t*, 111, 151*t*, 234–235, 243, 254*t*
- Potassium chlorate (KClO<sub>3</sub>), 145
- Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), 207
- Potassium hydroxide (KOH), 399, 460
- Potassium nitrate (KNO<sub>3</sub>), 114, 122, 367*t*, 368
- Potassium sulfate (K<sub>2</sub>SO<sub>4</sub>), 365
- Potential energy, 95
- in chemical reactions, 473–474, 474
- and spontaneous chemical reactions, 457–458
- Powers (mathematical):
- and calculators, A34
- in scientific notation, A22–A23
- Precipitates, 154, 501
- Precipitation reactions, 154–158
- Precision, 16, 17
- Pressure:
- and boiling point, 82, 347
- changes in, and equilibrium, 482
- of gases, 294–295, 297–301
- and number of moles of gases, 307–308
- osmotic, 387–388, 388
- partial, 313–315, 315
- and solubility, 369–370
- and temperature of gases, 304–305
- units of, 298–299
- vapor, 345–346, 346
- and volume of gases, 299–301
- Pressure cookers, 347
- Priestly, Joseph, 293
- Primary structure (protein), W55, W56
- “Primordial soup,” W64
- Principal quantum number, 225
- Procter and Gamble, W48
- Products (chemical reaction), 138
- gases as, 319–321
- heat as, 211
- predicting from equilibrium constant, 485–486
- quantitative conversion to/from reactants, *see* Stoichiometry
- Progesterone, W47, W48
- Proline, W54
- Proof, W21
- Propane (C<sub>3</sub>H<sub>8</sub>), 359, W8, W9*t*
- Propanol, *see* Isopropyl alcohol
- 2-Propanol, W23
- Propanone, W7*t*, W23
- Propene, W7*t*
- Proper fractions, A5
- Properties, 65
- Proportionalities, A16–A18
- Propylene (C<sub>3</sub>H<sub>6</sub>), W15*t*
- N*-Propyl group, W9*t*
- Prostaglandins, W28
- Prostate cancer, 528
- Protactinium-234 (isotope), 517
- Proteins, 281, W53, W55–W57. *See also* Amino acids; Enzymes
- fibrous, W56, W56
- globular, W56, W56
- hydrogen bonding in, 337
- synthesis of, *see* Replication (of DNA)
- Protons, 4–5, 59, 60*t*
- fusion of, 7
- and isotopic notation, 6
- Proton acceptors, 400

- Proton donors, 400
- Pseudoephedrine hydrochloride ( $C_{10}H_{14}NOH_2 + Cl^-$ ), 124
- Pseudohalogens, 283
- Pseudo-noble gas configuration, 257*n*
- Psi (pounds per square inch), 298
- Ptolemy, Claudius, 11
- Pure substances, 65, 90, 384
- Purification, by recrystallization, 368
- Pyrite ( $FeS_2$ ), 201–202, 216
- Q**
- Q*, *see* Reaction quotient
- Quantized (term), 225
- Quantum mechanics, 5
- Quantum number, principal, 225
- Quarks, 59
- Quartz ( $SiO_2$ ), 338, 341
- Quinine, 194
- R**
- R* (gas constant), 310
- Radiant energy, 94
- Radiation, 512–528
- alpha, 512–514
  - applications of, 526–528
  - background, 522
  - beta, 513, 514
  - detectors, 521
  - effects of, 518–520
  - electromagnetic, 222
  - electron capture, 513, 514
  - gamma, 513, 514
  - half-lives, 516, 516*t*
  - ionizing, 519
  - measuring, 521–523
  - positron, 513, 514
  - radioactive decay series, 516–517
  - rates of decay, 516–517
- Radiation sickness, 523
- Radii:
- atomic, 242–243, 243
  - ionic, 244–245
- Radioactive decay, 514
- Radioactive decay series, 516–517
- Radioactive isotopes, 512
- decay of, 514
  - uses of, 527–528
- Radioactivity, artificially induced, 524
- Radium, 512
- Radium-226 (isotope), 516*t*, 517
- Radius (term), 242
- Radon (Rn), 521
- Radon-222 (isotope), 517, 521
- Radon detectors, 521, 521
- Rare earths, 114
- Rate of reaction, 475–478
- and activation energy, 475–476
  - and catalysts, 477–478
  - and concentration, 477
  - of enzymes, W59
  - and particle size, 477
  - and temperature, 476–477
- Rational drug design, 13
- Reactants, 138
- calculating excess, 205–206
  - gases as, 319–321
  - heat as, 211
  - limiting, 203–207
  - predicting from equilibrium constant, 485–486
  - quantitative conversion to/from products, *see* Stoichiometry
- Reactions:
- chemical, *see* Chemical reactions
  - nuclear chain, 529–530, 530
- Reaction coordinate, 474
- Reaction quotient (*Q*), 486–487
- Reactivity, 151, 152
- Rechargeable batteries, 460–461
- Recrystallization, 368, 368
- Red blood cells, 528
- Red giants, 7
- Redox reactions, *see* Oxidation-reduction reactions
- Reduced (term), 439
- Reducing agents, 439, 453–454
- Reduction potentials, 454
- Reflected light, 223
- Re-forming (crude-oil), W13
- Refractive index, 227
- Refractory ceramic tiles, 341
- Relative humidity, 346
- Rem (unit), 522
- Replication (of DNA), W62, W62–W63, W63
- Representative elements, 113
- electron configurations of, 236–237
  - monatomic ions of, 118
- Reproducibility, 11
- Resonance hybrids, 269
- Resonance structures, 269–270
- Reverse Polish Notation (RPN), A31
- Reversible reactions, 208, 479–480, 480
- Ribonucleic acid (RNA), W50, W60, W62
- Ribose, W49, W50, W61
- D-Ribose, W50
- Ribosomal RNA (rRNA), W63, W63
- Ribosomes, W63
- Richter scale, 416
- RNA (ribonucleic acid), W50, W60, W62
- Roentgen, Wilhelm, 511
- Room temperature, 114, 115
- Roots (mathematical), A4
- and calculators, A34
  - in scientific notation, A22–A23
- Rosy periwinkle, 12
- Rounding off, 19–22
- RPN (Reverse Polish Notation), A31
- rRNA, *see* Ribosomal RNA
- Rubbing alcohol, *see* Isopropyl alcohol
- Rubies, 258
- Ruminants, W52
- Rust, 82
- Rutherford, Ernest, 58, 59, 224, 511, 512, 524
- S**
- Salicylic acid, W27, W28
- Salts, 122–124
- acid, 409
  - from anhydrides, 427
  - formation of, 160, 408–411
  - and pH, 420–422
- Salt bridge, 458
- Saltpeeter, 114. *See also* Potassium nitrate
- Saponifiable lipids, W44
- Saponification, W46, W47
- Sapphires, 258
- Saturated (term), 367, W8
- Saturated fatty acids, W44–W45
- Saturation point, W59
- Saturn, 31
- Scale (hard water), 158
- Scandinavia, 428
- Scandium (Sc), 235, 237, 243
- Scanning tunneling microscope (STM), 57, 57
- Schoenbein, Christian Friedrich, W16
- Scientific method, 10–13
- Scientific notation, 22–25, A19–A26, A33–A34
- Scintillation counter, 521
- Scuba divers, 369
- Second (unit), 28*t*
- Secondary structure (protein), W55–W56, W56
- Seed crystals, 367
- Segré, Emilio, 529
- Selenium (Se), 243, 254*t*
- “Self-painting,” 456
- Semiconductors, 113
- Semipermeable membranes, 387, 388
- September 11, 2001, 341
- Serine, W54
- Shells, 228–231, 230, 231, 233–235
- Shroud of Turin, 527
- Siberia, 349
- Side-chains (amino acids), W53, W56
- Sievert (unit), 522
- Significant figure(s):
- defined, 16
  - and mathematical operations, 19–21
  - zero as, 17–18
- Silicon (Si), 234, 243, 243*t*, 254*t*, W5
- Silicon-30 (isotope), 524
- Silver (Ag), 55*t*, 111, 237, 454*t*, 455, 460, 463
- activity of, 151*t*
  - recovery of, 156
  - tarnishing of, 205–206
- Silver batteries, 460
- Silver chloride ( $AgCl$ ), 154, 155, 156, 367–368, 367*t*
- “Silver coating,” 456
- Silver nitrate ( $AgNO_3$ ), 207
- Single-replacement reactions, 150–152
- Singularity, 4
- SI system, 27, 28, 28*t*, 522
- Skin, human, 388, W56
- Smoke detectors, 520
- Soaps, 47, 344, W46, W48
- Sodium (Na), 55*t*
- activity of, 151*t*
  - atomic radius, 243, 243
  - in binary ionic compounds, 256
  - electron affinity, 244*t*
  - electron configuration, 234
  - emission spectrum of, 221, 224
  - in fuel cells, 463
  - ionic radius, 245



- ionization energy, 243*t*, 244  
Lewis Dot symbols, 254*t*  
liquid sodium, 361  
in periodic table, 111  
in redox reactions, 454, 454*t*, 455
- Sodium acrylate, 389  
Sodium bicarbonate, 421  
Sodium bisulfate (NaHSO<sub>4</sub>), 496  
Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), 158, 496  
Sodium chloride (NaCl), 118, 179, 256  
in aqueous solution, 148, 364–365, 365  
in binary ionic compounds, 256  
in combination reactions, 145  
crystal structure of, 67, 67, 68  
as electrolyte, 382, 388, 388  
in equilibrium, 497, 498  
formation of, 438, 438, 439  
in fuel cells, 463, 464  
heat of fusion and melting point, 350, 350*t*  
heat of vaporization and boiling point, 351*t*  
ionic bonding in, 273, 273–274  
in neutralization reactions, 160  
solubility of, 367*t*, 368  
in solution, 90
- Sodium chromate (Na<sub>2</sub>CrO<sub>4</sub>), 179  
Sodium hydroxide (NaOH), 394, 399–400, 408, 409, 416*t*, 427, 460  
Sodium iodide (NaI), 71  
Sodium ion (Na<sup>+</sup>), 158, 497  
Sodium polyacrylate, 389  
Sodium stearate, W48
- Soil:  
drugs from, 12  
fertility of, 428  
pH of, 422
- Solar energy, 461, 463  
Solar System, 11
- Solid(s):  
amorphous, 338  
crystalline, 338–339, 341, 342  
defined, 80  
ionic, 339, 339  
metallic, 341, 342  
molecular, 339, 339  
network, 340, 340
- Solid state, 332–342, 349–350, 352–355  
dipole-dipole attractions, 335–336  
energy for melting and freezing, 349–350  
and heating curves, 352–355  
hydrogen bonding, 336–337  
intermolecular forces, 334–337  
and kinetic theory, 332–334  
London forces, 334–335  
melting point, 338–342  
sublimation, 346
- Solubility, 154, 367*t*  
defined, 367  
determining, from solubility product constant, 500  
and equilibrium, 497–501  
of ionic compounds, 153–154, 153*t*  
and polarity, 366  
and temperature/pressure, 367–370, 368
- Solubility product constant ( $K_{sp}$ ), 498–501
- Soluble (term), 148, 368
- Solutes, 148, 384*n*
- Solutions, 90, 148–149  
alkaline, *see* Bases  
aqueous, *see* Aqueous solutions  
brine, 388  
buffer, 495–496  
concentrated, 375  
density of, 90–91  
intravenous, 388–389  
making, in laboratories, 375  
solid, 91  
strongly acidic, 416  
strongly basic, 416  
weakly acidic, 416  
weakly basic, 416
- Solvent, 148  
*s* orbitals, 228, 228
- Space program, 213, 461, 476
- Space shuttle, 341
- Spearmint, oil of, W24
- Specific gravity, 87
- Specific heat, 96–98, 96*t*, 351, 353, 354
- Spectator ions, 150–151
- Spectrum(—a):  
continuous, 222  
discrete, 224  
emission, 221–227  
line, 224
- Speed, 28
- Sphingolipids, W45, W46
- Sphingomyelin, W45, W46
- Sphingosine, W45, W46
- Spirit* rover, 51
- Spitteler, A., W16
- Spontaneous redox reactions, 453–458, 454, 457
- Stainless steel, 91
- Standard temperature and pressure (STP), 306
- Stannic ion (Sn<sup>4+</sup>), 120*t*  
Stannous ion (Sn<sup>2+</sup>), 120*t*
- Stars, 7–8
- Starch, W52, W52
- Steric acid, W44
- Steroids, W47, W48
- STM, *see* Scanning tunneling microscope
- Stock Method, 119, 126
- Stoichiometry, 198–202, 319  
of aqueous solutions, 377–380  
of gases, 319–321  
and mole ratio, 199  
procedure for problems, 201
- Stone Age, 9
- STP (standard temperature and pressure), 306
- Strassman, Fritz, 529
- Stratosphere, 296, 478
- Strong acids, 148–149, 159–161  
neutralization of, 408  
in water, 399
- Strong bases, 159–161  
in neutralization reactions, 408–410  
in water, 399–400
- Strong electrolytes, 382, 383
- Strongly acidic solutions, 416
- Strongly basic solutions, 416
- Strontium, 221
- Strontium-90 (isotope), 519
- Structural formulas, 66
- Styran™, W15*t*  
Styrene, W15*t*  
Styrofoam™, W15*t*
- Sublimation, 346, 346
- Subshells, 229–231, 230, 231, 233–235
- Substances, pure, 65, 90, 384
- Substituents, W9
- Substrate (enzymatic), W59
- Subtraction:  
rules for, 19–20, A2–A3  
in scientific notation, A20–A21
- Sucrase, 281, W59
- Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), 65, 281, 367, 367*t*, W51, W51, W59
- Sudafed, 124, 124
- Sugars, in DNA, W60
- Sulfate ion (SO<sub>4</sub><sup>2-</sup>), 122, 122*t*, 128*t*, 153*t*
- Sulfide ion (S<sup>2-</sup>), 153*t*
- Sulfite ion (SO<sub>3</sub><sup>2-</sup>), 122, 122*t*, 128*t*, 265
- Sulfur (S), 234, 243, 243*t*, 245, 254*t*
- Sulfur dioxide (SO<sub>2</sub>), 201–202, 276, 282, 335, 335, 426–427
- Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 128*t*, 182, 183*t*, 207, 280–282, 398, 404, 408, 409, 409, 427, 459
- Sulfurous acid (H<sub>2</sub>SO<sub>3</sub>), 128*t*, 427
- Sulfur trioxide (SO<sub>3</sub>), 426–427
- Sumerians, ancient, 12
- Sun, 7, 11, 94
- Superconducting Super Collider, 525
- Superglue, 411
- Supernova, 8, 8, 534
- Supersaturated (term), 367
- Surface tension, 343–344, 344
- Sweden, 207
- Swimming pools, 496
- Symbols (for elements), 6, 54, 54*t*, 55*t*
- Syrup, 344, 344
- T**
- Table salt, 84*t*, 114, 122, 148, 258, 338, 385. *See also* Sodium chloride (NaCl)
- Tamoxifen, 10–11
- Taxol, 12
- Teflon™, W15*t*
- Television, 223
- Tellurium (Te), 111, 112
- Temperature:  
changes in, and equilibrium, 482  
defined, 38  
and kinetic energy, 345  
measurement of, 38–40  
during phase changes, 353, 353  
and physical state, 81–82  
and pressure of gas, 304–305  
and rate of reaction, 476, 476–477  
room, 114, 115  
and solubility, 368, 368–369  
and volume of gases, 302–304

- Tera- (prefix), 29  
 Terephthalic acid, W28  
 Tertiary structure (protein), W55, W56  
 Testosterone, W47, W48  
 Tetra- (prefix), 125*t*  
 Tetrafluoroethylene (C<sub>2</sub>F<sub>4</sub>), W15*t*  
 Tetrahedral geometry, 275, 276*t*, 277*t*, 279  
 Thallium (Tl), 236, 257*n*  
 Theoretical maximum, 210  
 Theoretical yield, 208–211  
 Theory(-ies), 11, 55  
 Thermal expansion, 332  
 Thermite reaction, 151, 216  
 Thermochemical equations, 211–213  
 Thermometer, 38  
 Thomson, J. J., 58  
 Thorium (Th), 237, 512, 512–513  
 Thorium-230 (isotope), 517  
 Thorium-232 (isotope), 517  
 Thorium-234 (isotope), 516*t*, 517  
 Three Mile Island accident, 531  
 Threonine, W54  
 Thymine, W60, W60, W62  
 Thyroid, 528  
 Tide™, W48  
 Tin (Sn), 55*t*, 151*t*, 454*t*  
 Tire gauges, 298  
 Titan, 79, 348  
 Titration, 410  
 Titrations, 379–380  
 Torr (unit), 298  
 Torricelli, Evangelista, 297–298  
 Total ionic equations, 150  
 Toluene, W18  
 Trace elements, 71  
 Transcription, W62, W63  
 Trans fatty acids, W45  
 Transfer RNA (tRNA), W63, W63  
*trans* isomers, W45  
 Transition metals, 114  
   electron configurations of, 237  
   ions from, 119  
 Translation, W63, W63  
 Transmutation, 524  
 Tri- (prefix), 125*t*, W9  
 Triglycerides, W44  
 Trigonal planar geometry, 275, 276*t*, 277*t*, 279  
 Trigonal pyramidal geometry, 276, 277*t*  
 Triple bonds, 263, 264  
 Triple-helix structure (proteins), W56, W56  
 Triprotic acids, 409  
 Tritium, 532  
 Triton, 114  
 tRNA, *see* Transfer RNA  
 Tryptophan, W54  
 Tungsten (W), 55*t*, 341, 342  
 Tygon™, W15*t*  
 Tylenol™, W27  
 Tyrosine, W54
- U**  
 Ulcers, W28  
 Ultraviolet light, 223, 411  
 Unbranched compounds, W9  
 Uncertainty, 19  
 Unit(s):  
   conversion of, by factor-label method, 30–37  
   defined, 16  
   fundamental vs. derived, 28  
   selecting, for concentration, 373  
 United States, 124, 207, 521, 530  
 U.S. Atomic Energy Commission, 520  
 Unit factors, 32  
 Unit maps, 32  
 Unsaturated (term), 367, W13  
 Unsaturated fatty acids, W45, W47  
 Uracil, W61, W62  
 Uranium (U), 511–512, 512, 521  
 Uranium-234 (isotope), 517  
 Uranium-235 (isotope), 517, 530  
 Uranium-238 (isotope), 516–517, 516*t*, 517, 520, 525, 529  
 Uranium enrichment, 296  
 Urea (H<sub>2</sub>NCONH<sub>2</sub>), W4
- V**  
 Valence electrons, 254–255  
 Valence shell electron-pair repulsion (VSEPR) theory, 275  
 Valine, W53, W54, W55, W55  
 Valine-glycine, W55  
 Vaporization, 345, 351, 351*t*  
 Vapor pressure, 345–346, 346, 384, 384  
 Vapor pressure lowering (term), 384–385  
 Velocity (of gases), 295–296  
 Vincristine, 12  
 Vinyl chloride (C<sub>2</sub>H<sub>3</sub>Cl), W15*t*, W17  
 Viscosity, 344  
 Visible prints, 411  
 Volatile (term), 346  
 Volatility, W12  
 Volcanic crater lakes, 483  
 Voltaic cells, 457–462  
   batteries, 459–461  
   Daniell cells, 458–459  
   fuel cells, 461–462  
 Volume:  
   conversion of, to mass, 86–87  
   defined, 27  
   and physical state, 80, 81  
   and pressure of gases, 299–301  
   of solids and liquids, 332  
   and temperature of gases, 302–304  
 VSEPR theory, 275  
 V-shaped geometry, 276, 277*t*
- W**  
 Water (H<sub>2</sub>O), 454*t*  
 Water (H<sub>2</sub>O), 9, 66, 84*t*, 90, 117, 138, 139, 262, 280, 474–475, 480  
   acids in, 399  
   amphiprotic nature of, 401–402  
   autoionization of, 413  
   bases in, 399–400  
   boiling point, 347, 347*t*  
   as combustion product, 143  
   as driver of neutralization, 408–410  
   electrolysis of, 463  
   formula for, 65  
   hard, 158, 501, W48  
   heat energy and phase of, 349, 349  
   heat energy from creation of, 211  
   heating curve of, 352–355  
   heat of fusion, 350, 350*t*  
   heat of vaporization, 351, 351*t*  
   hydrogen bonding, 336, 336–337  
   ion product of, 413–414  
   on Mars, 348  
   molecular geometry of, 276  
   molecular structure, 65, 65  
   physical states of, 331, 333, 333–334  
   production of, 476  
   properties of, 82  
   as solvent, *see* Aqueous solutions  
   stoichiometry of production, 203, 204  
   surface tension, 343, 344  
   vapor pressure and temperature, 347, 347  
   viscosity, 344  
 Water-softening, 158  
 Water treatment, 501  
 Watson, James, W60  
 Watt, James, 437  
 Wavelength (λ), 222  
 Wave mechanical model (of hydrogen atom), 228  
 Weak acids, 416, 489–496  
 Weak bases, 416, 489–496  
 Weak electrolytes, 382–383, 383  
 Weak molecular acids, 404–406  
 Weak molecular bases, 407  
 Weather, 62  
 Weight:  
   counting by, 170–171  
   defined, 29  
   formula, 178–181  
 Weight loss, 99  
 White phosphorus, 475–476, 476  
 Williams, Ted, 22  
 Willow trees, W28  
 Wintergreen, oil of, W26  
 Wöhler, Friedrich, W4  
 Work, 94  
 World Trade Center, 341  
 World War I, 481
- X**  
 Xenon (Xe), 513, 513  
 X-rays, 511, 513
- Y**  
 -yne (suffix), W16  
 Yucatan Peninsula, 55
- Z**  
 Zero, as significant figure, 17–18  
 Ziegler, Karl, W16  
 Zinc (Zn), 235, 243, 399, 453, 454*t*, 458, 460  
   activity of, 151*t*  
   in single-replacement reaction, 150, 151  
 Zinc sulfide, 521  
 Zwicky, Fred, 100

## Atomic Masses of the Elements

| Name          | Symbol    | Atomic Number | Atomic Mass | Name           | Symbol    | Atomic Number | Atomic Mass |
|---------------|-----------|---------------|-------------|----------------|-----------|---------------|-------------|
| Actinium*     | <b>Ac</b> | 89            | 227         | Meitnerium*    | <b>Mt</b> | 109           | 268         |
| Aluminum      | <b>Al</b> | 13            | 26.981538   | Mendelevium*   | <b>Md</b> | 101           | 258         |
| Americium*    | <b>Am</b> | 95            | 243         | Mercury        | <b>Hg</b> | 80            | 200.59      |
| Antimony      | <b>Sb</b> | 51            | 121.760     | Molybdenum     | <b>Mo</b> | 42            | 95.94       |
| Argon         | <b>Ar</b> | 18            | 39.948      | Neodymium      | <b>Nd</b> | 60            | 144.24      |
| Arsenic       | <b>As</b> | 33            | 74.92160    | Neon           | <b>Ne</b> | 10            | 20.1797     |
| Astatine*     | <b>At</b> | 85            | 210         | Neptunium*     | <b>Np</b> | 93            | 237         |
| Barium        | <b>Ba</b> | 56            | 137.327     | Nickel         | <b>Ni</b> | 28            | 58.6934     |
| Berkelium*    | <b>Bk</b> | 97            | 247         | Niobium        | <b>Nb</b> | 41            | 92.90638    |
| Beryllium     | <b>Be</b> | 4             | 9.012182    | Nitrogen       | <b>N</b>  | 7             | 14.00674    |
| Bismuth       | <b>Bi</b> | 83            | 208.98038   | Nobelium*      | <b>No</b> | 102           | 259         |
| Bohrium*      | <b>Bh</b> | 107           | 264         | Osmium         | <b>Os</b> | 76            | 190.23      |
| Boron         | <b>B</b>  | 5             | 10.811      | Oxygen         | <b>O</b>  | 8             | 15.9994     |
| Bromine       | <b>Br</b> | 35            | 79.904      | Palladium      | <b>Pd</b> | 46            | 106.42      |
| Cadmium       | <b>Cd</b> | 48            | 112.411     | Phosphorus     | <b>P</b>  | 15            | 30.973762   |
| Calcium       | <b>Ca</b> | 20            | 40.078      | Platinum       | <b>Pt</b> | 78            | 195.078     |
| Californium*  | <b>Cf</b> | 98            | 251         | Plutonium*     | <b>Pu</b> | 94            | 244         |
| Carbon        | <b>C</b>  | 6             | 12.0107     | Polonium*      | <b>Po</b> | 84            | 209         |
| Cerium        | <b>Ce</b> | 58            | 140.116     | Potassium      | <b>K</b>  | 19            | 39.0983     |
| Cesium        | <b>Cs</b> | 55            | 132.90545   | Praseodymium   | <b>Pr</b> | 59            | 140.90765   |
| Chlorine      | <b>Cl</b> | 17            | 35.4527     | Promethium*    | <b>Pm</b> | 61            | 145         |
| Chromium      | <b>Cr</b> | 24            | 51.9961     | Protactinium   | <b>Pa</b> | 91            | 231.03588   |
| Cobalt        | <b>Co</b> | 27            | 58.933200   | Radium*        | <b>Ra</b> | 88            | 226         |
| Copper        | <b>Cu</b> | 29            | 63.546      | Radon*         | <b>Rn</b> | 86            | 222         |
| Curium*       | <b>Cm</b> | 96            | 247         | Rhenium        | <b>Re</b> | 75            | 186.207     |
| Darmstadtium* | <b>Ds</b> | 110           | 271         | Rhodium        | <b>Rh</b> | 45            | 102.90550   |
| Dubnium*      | <b>Db</b> | 105           | 262         | Roentgenium*   | <b>Rg</b> | 111           | 272         |
| Dysprosium    | <b>Dy</b> | 66            | 162.500     | Rubidium       | <b>Rb</b> | 37            | 85.4678     |
| Einsteinium*  | <b>Es</b> | 99            | 252         | Ruthenium      | <b>Ru</b> | 44            | 101.07      |
| Erbium        | <b>Er</b> | 68            | 167.26      | Rutherfordium* | <b>Rf</b> | 104           | 261         |
| Europium      | <b>Eu</b> | 63            | 151.964     | Samarium       | <b>Sm</b> | 62            | 150.36      |
| Fermium*      | <b>Fm</b> | 100           | 257         | Scandium       | <b>Sc</b> | 21            | 44.955910   |
| Fluorine      | <b>F</b>  | 9             | 18.9984032  | Seaborgium*    | <b>Sg</b> | 106           | 266         |
| Francium*     | <b>Fr</b> | 87            | 233         | Selenium       | <b>Se</b> | 34            | 78.96       |
| Gadolinium    | <b>Gd</b> | 64            | 157.25      | Silicon        | <b>Si</b> | 14            | 28.0855     |
| Gallium       | <b>Ga</b> | 31            | 69.723      | Silver         | <b>Ag</b> | 47            | 107.8682    |
| Germanium     | <b>Ge</b> | 32            | 72.61       | Sodium         | <b>Na</b> | 11            | 22.989770   |
| Gold          | <b>Au</b> | 79            | 196.96655   | Strontium      | <b>Sr</b> | 38            | 87.62       |
| Hafnium       | <b>Hf</b> | 72            | 178.49      | Sulfur         | <b>S</b>  | 16            | 32.066      |
| Hassium*      | <b>Hs</b> | 108           | 277         | Tantalum       | <b>Ta</b> | 73            | 180.9479    |
| Helium        | <b>He</b> | 2             | 4.002602    | Technetium*    | <b>Tc</b> | 43            | 98          |
| Holmium       | <b>Ho</b> | 67            | 164.93032   | Tellurium      | <b>Te</b> | 52            | 127.60      |
| Hydrogen      | <b>H</b>  | 1             | 1.00794     | Terbium        | <b>Tb</b> | 65            | 158.92534   |
| Indium        | <b>In</b> | 49            | 114.818     | Thallium       | <b>Tl</b> | 81            | 204.3833    |
| Iodine        | <b>I</b>  | 53            | 126.90447   | Thorium        | <b>Th</b> | 90            | 232.0381    |
| Iridium       | <b>Ir</b> | 77            | 192.217     | Thulium        | <b>Tm</b> | 69            | 168.93421   |
| Iron          | <b>Fe</b> | 26            | 55.845      | Tin            | <b>Sn</b> | 50            | 118.710     |
| Krypton       | <b>Kr</b> | 36            | 83.80       | Titanium       | <b>Ti</b> | 22            | 47.867      |
| Lanthanum     | <b>La</b> | 57            | 138.9055    | Tungsten       | <b>W</b>  | 74            | 183.94      |
| Lawrencium*   | <b>Lr</b> | 103           | 262         | Uranium        | <b>U</b>  | 92            | 238.0289    |
| Lead          | <b>Pb</b> | 82            | 207.2       | Vanadium       | <b>V</b>  | 23            | 50.9415     |
| Lithium       | <b>Li</b> | 3             | 6.941       | Xenon          | <b>Xe</b> | 54            | 131.29      |
| Lutetium      | <b>Lu</b> | 71            | 174.967     | Ytterbium      | <b>Yb</b> | 70            | 173.04      |
| Magnesium     | <b>Mg</b> | 12            | 24.3050     | Yttrium        | <b>Y</b>  | 39            | 88.90585    |
| Manganese     | <b>Mn</b> | 25            | 54.938049   | Zinc           | <b>Zn</b> | 30            | 65.39       |
|               |           |               |             | Zirconium      | <b>Zr</b> | 40            | 91.224      |

\* This element has no stable isotopes. The atomic mass given is that of the isotope with the longest known half-life.

## Names, Formulas, and Charges of Common Ions

| Positive Ions (Cations) |                             |                  | Negative Ions (Anions) |                                     |                                    |
|-------------------------|-----------------------------|------------------|------------------------|-------------------------------------|------------------------------------|
| 1+                      | Ammonium                    | $\text{NH}_4^+$  | 1-                     | Acetate                             | $\text{C}_2\text{H}_3\text{O}_2^-$ |
|                         | Copper(I)<br>(Cuprous)      | $\text{Cu}^+$    |                        | Bromate                             | $\text{BrO}_3^-$                   |
|                         | Hydrogen                    | $\text{H}^+$     |                        | Bromide                             | $\text{Br}^-$                      |
|                         | Potassium                   | $\text{K}^+$     |                        | Chlorate                            | $\text{ClO}_3^-$                   |
|                         | Silver                      | $\text{Ag}^+$    |                        | Chloride                            | $\text{Cl}^-$                      |
|                         | Sodium                      | $\text{Na}^+$    |                        | Chlorite                            | $\text{ClO}_2^-$                   |
| 2+                      | Barium                      | $\text{Ba}^{2+}$ |                        | Cyanide                             | $\text{CN}^-$                      |
|                         | Cadmium                     | $\text{Cd}^{2+}$ |                        | Fluoride                            | $\text{F}^-$                       |
|                         | Calcium                     | $\text{Ca}^{2+}$ |                        | Hydride                             | $\text{H}^-$                       |
|                         | Cobalt(II)                  | $\text{Co}^{2+}$ |                        | Hydrogen carbonate<br>(Bicarbonate) | $\text{HCO}_3^-$                   |
|                         | Copper(II)<br>(Cupric)      | $\text{Cu}^{2+}$ |                        | Hydrogen sulfate<br>(Bisulfate)     | $\text{HSO}_4^-$                   |
|                         | Iron(II)<br>(Ferrous)       | $\text{Fe}^{2+}$ |                        | Hydrogen sulfite<br>(Bisulfite)     | $\text{HSO}_3^-$                   |
|                         | Lead(II)                    | $\text{Pb}^{2+}$ |                        | Hydroxide                           | $\text{OH}^-$                      |
|                         | Magnesium                   | $\text{Mg}^{2+}$ |                        | Hypochlorite                        | $\text{ClO}^-$                     |
|                         | Manganese(II)               | $\text{Mn}^{2+}$ |                        | Iodate                              | $\text{IO}_3^-$                    |
|                         | Mercury(II)<br>(Mercuric)   | $\text{Hg}^{2+}$ |                        | Iodide                              | $\text{I}^-$                       |
| 3+                      | Nickel(II)                  | $\text{Ni}^{2+}$ | Nitrate                | $\text{NO}_3^-$                     |                                    |
|                         | Tin(II)<br>(Stannous)       | $\text{Sn}^{2+}$ | Nitrite                | $\text{NO}_2^-$                     |                                    |
|                         | Zinc                        | $\text{Zn}^{2+}$ | Perchlorate            | $\text{ClO}_4^-$                    |                                    |
|                         | Aluminum                    | $\text{Al}^{3+}$ | Permanganate           | $\text{MnO}_4^-$                    |                                    |
|                         | Antimony(III)               | $\text{Sb}^{3+}$ | Thiocyanate            | $\text{SCN}^-$                      |                                    |
|                         | Arsenic(III)                | $\text{As}^{3+}$ | 2-                     | Carbonate                           | $\text{CO}_3^{2-}$                 |
|                         | Bismuth(III)                | $\text{Bi}^{3+}$ |                        | Chromate                            | $\text{CrO}_4^{2-}$                |
|                         | Chromium(III)               | $\text{Cr}^{3+}$ |                        | Dichromate                          | $\text{Cr}_2\text{O}_7^{2-}$       |
|                         | Iron(III)<br>(Ferric)       | $\text{Fe}^{3+}$ |                        | Oxalate                             | $\text{C}_2\text{O}_4^{2-}$        |
|                         | Titanium(III)<br>(Titanous) | $\text{Ti}^{3+}$ |                        | Oxide                               | $\text{O}^{2-}$                    |
| 4+                      | Manganese(IV)               | $\text{Mn}^{4+}$ |                        | Peroxide                            | $\text{O}_2^{2-}$                  |
|                         | Tin(IV)<br>(Stannic)        | $\text{Sn}^{4+}$ |                        | Silicate                            | $\text{SiO}_3^{2-}$                |
|                         | Titanium(IV)<br>(Titanic)   | $\text{Ti}^{4+}$ |                        | Sulfate                             | $\text{SO}_4^{2-}$                 |
| 5+                      | Antimony(V)                 | $\text{Sb}^{5+}$ |                        | Sulfide                             | $\text{S}^{2-}$                    |
|                         | Arsenic(V)                  | $\text{As}^{5+}$ |                        | Sulfite                             | $\text{SO}_3^{2-}$                 |
|                         |                             |                  | 3-                     | Arsenate                            | $\text{AsO}_4^{3-}$                |
|                         |                             |                  |                        | Borate                              | $\text{BO}_3^{3-}$                 |
|                         |                             |                  |                        | Phosphate                           | $\text{PO}_4^{3-}$                 |
|                         |                             |                  |                        | Phosphide                           | $\text{P}^{3-}$                    |
|                         |                             |                  |                        | Phosphite                           | $\text{PO}_3^{3-}$                 |

## Prefixes and Numerical Values for SI Units

| Prefix | Symbol | Numerical value           | Power of 10 equivalent |
|--------|--------|---------------------------|------------------------|
| exa    | E      | 1,000,000,000,000,000,000 | $10^{18}$              |
| peta   | P      | 1,000,000,000,000,000     | $10^{15}$              |
| tera   | T      | 1,000,000,000,000         | $10^{12}$              |
| giga   | G      | 1,000,000,000             | $10^9$                 |
| mega   | M      | 1,000,000                 | $10^6$                 |
| kilo   | k      | 1,000                     | $10^3$                 |
| hecto  | h      | 100                       | $10^2$                 |
| deka   | da     | 10                        | $10^1$                 |
| —      | —      | 1                         | $10^0$                 |
| deci   | d      | 0.1                       | $10^{-1}$              |
| centi  | c      | 0.01                      | $10^{-2}$              |
| milli  | m      | 0.001                     | $10^{-3}$              |
| micro  | $\mu$  | 0.000001                  | $10^{-6}$              |
| nano   | n      | 0.000000001               | $10^{-9}$              |
| pico   | p      | 0.000000000001            | $10^{-12}$             |
| femto  | f      | 0.0000000000000001        | $10^{-15}$             |
| atto   | a      | 0.0000000000000000001     | $10^{-18}$             |

## SI Units and Conversion Factors

| Length                     |  | Mass                          |  | Volume                                      |  |
|----------------------------|--|-------------------------------|--|---|--|
| <b>SI unit: meter (m)</b>  |  | <b>SI unit: kilogram (kg)</b> |  | <b>SI unit: cubic meter (m<sup>3</sup>)</b> |  |
| 1 meter                    | = 1000 millimeters<br>= 1.0936 yards                   | 1 kilogram                    | = 1000 grams<br>= 2.20 pounds                        | 1 liter                                     | = 1000 milliliters<br>= $10^{-3}$ m <sup>3</sup> |
| 1 centimeter               | = 0.3937 inch  | 1 gram                        | = 1000 milligrams                                    |   | = 1 dm <sup>3</sup>                              |
| 1 inch                     | = 2.54 centimeters<br>(exactly)                        | 1 pound                       | = 453.59 grams<br>= 0.45359 kilogram                 | 1 gallon                                    | = 1.0567 quarts                                  |
| 1 kilometer                | = 0.62137 mile   |                               | = 16 ounces  |   | = 8 pints  |
| 1 mile                     | = 5280 feet  | 1 ton                         | = 2000 pounds  |   | = 3.785 liters                                   |
|                            | = 1.609 kilometers                                     |                               | = 907.185 kilograms                                  | 1 quart                                     | = 32 fluid ounces                                |
| 1 angstrom                 | = $10^{-10}$ meter                                     | 1 ounce                       | = 28.3 grams   |   | = 0.946 liter                                    |
|                            |  | 1 atomic<br>mass unit         | = $1.6606 \times 10^{-27}$ kilograms                 | 1 fluid<br>ounce                            | = 4 cups<br>= 29.6 mL                            |
| <b>Temperature</b>         |  | <b>Energy</b>                 |  | <b>Pressure</b>                             |  |
| <b>SI unit: kelvin (K)</b> |  | <b>SI unit: joule (J)</b>     |  | <b>SI unit: pascal (Pa)</b>                 |  |
| 0 K                        | = $-273.15^\circ\text{C}$<br>= $-459.67^\circ\text{F}$ | 1 joule                       | = $1 \text{ kg m}^2/\text{s}^2$<br>= 0.23901 calorie | 1 pascal                                    | = $1 \text{ kg}/(\text{m s}^2)$                  |
| K                          | = $^\circ\text{C} + 273.15$                            | 1 calorie                     | = 4.184 joules                                       | 1 atmosphere                                | = 101.325 kilopascals                            |
| $^\circ\text{C}$           | = $\frac{(\text{F} - 32)}{1.8}$                        |                               |  |   | = 760 torr                                       |
| $^\circ\text{C}$           | = $\frac{5}{9}(\text{F} - 32)$                         |                               |  |   | = 760 mm Hg                                      |
| $^\circ\text{F}$           | = $1.8(^\circ\text{C}) + 32$                           |                               |  |   | = 14.70 pounds<br>per square inch (psi)          |

# The Modern Periodic Table of the Elements

| Periods | IA<br>(1)             | IIA<br>(2)           | IIIB<br>(3)           | IVB<br>(4)          | VB<br>(5)            | VIB<br>(6)           | VII B<br>(7)        | VIII B<br>(8) (9) (10) | IB<br>(11)            | IIB<br>(12)        | IIIA<br>(13)          | IVA<br>(14)         | VA<br>(15)           | VIA<br>(16)          | VIIA<br>(17)          | Noble gases<br>VIIIA<br>(18) |                      |                      |
|---------|-----------------------|----------------------|-----------------------|---------------------|----------------------|----------------------|---------------------|------------------------|-----------------------|--------------------|-----------------------|---------------------|----------------------|----------------------|-----------------------|------------------------------|----------------------|----------------------|
| 1       | 1<br>H<br>1.00794     |                      |                       |                     |                      |                      |                     |                        |                       |                    | 5<br>B<br>10.811      | 6<br>C<br>12.011    | 7<br>N<br>14.00674   | 8<br>O<br>15.9994    | 9<br>F<br>18.99840    | 2<br>He<br>4.00260           |                      |                      |
| 2       | 3<br>Li<br>6.941      | 4<br>Be<br>9.01218   |                       |                     |                      |                      |                     |                        |                       |                    | 13<br>Al<br>26.98154  | 14<br>Si<br>28.0855 | 15<br>P<br>30.97376  | 16<br>S<br>32.066    | 17<br>Cl<br>35.4527   | 10<br>Ne<br>20.1797          |                      |                      |
| 3       | 11<br>Na<br>22.98977  | 12<br>Mg<br>24.3050  |                       |                     |                      |                      |                     |                        |                       |                    | 31<br>Ga<br>69.723    | 32<br>Ge<br>72.61   | 33<br>As<br>74.92159 | 34<br>Se<br>78.96    | 35<br>Br<br>79.904    | 18<br>Ar<br>39.948           |                      |                      |
| 4       | 19<br>K<br>39.0983    | 20<br>Ca<br>40.078   | 21<br>Sc<br>44.95591  | 22<br>Ti<br>47.88   | 23<br>V<br>50.9415   | 24<br>Cr<br>51.9961  | 25<br>Mn<br>54.9380 | 26<br>Fe<br>55.847     | 27<br>Co<br>58.93320  | 28<br>Ni<br>58.69  | 29<br>Cu<br>63.546    | 30<br>Zn<br>65.39   | 49<br>In<br>114.82   | 50<br>Sn<br>118.710  | 51<br>Sb<br>121.75    | 36<br>Kr<br>83.80            |                      |                      |
| 5       | 37<br>Rb<br>85.4678   | 38<br>Sr<br>87.62    | 39<br>Y<br>88.90585   | 40<br>Zr<br>91.224  | 41<br>Nb<br>92.90638 | 42<br>Mo<br>95.94    | 43<br>Tc<br>98.9072 | 44<br>Ru<br>101.07     | 45<br>Rh<br>102.90550 | 46<br>Pd<br>106.42 | 47<br>Ag<br>107.8682  | 48<br>Cd<br>112.411 | 52<br>Te<br>127.60   | 53<br>I<br>126.90447 | 54<br>Xe<br>131.29    |                              |                      |                      |
| 6       | 55<br>Cs<br>132.90543 | 56<br>Ba<br>137.327  | 57<br>*La<br>138.9055 | 72<br>Hf<br>178.49  | 73<br>Ta<br>180.9479 | 74<br>W<br>183.85    | 75<br>Re<br>186.207 | 76<br>Os<br>190.2      | 77<br>Ir<br>192.22    | 78<br>Pt<br>195.08 | 79<br>Au<br>196.96654 | 80<br>Hg<br>200.59  | 81<br>Tl<br>204.3833 | 82<br>Pb<br>207.2    | 83<br>Bi<br>208.98037 | 84<br>Po<br>208.9824         | 85<br>At<br>209.9871 | 86<br>Rn<br>222.0176 |
| 7       | 87<br>Fr<br>223.0197  | 88<br>Ra<br>226.0254 | 89<br>†Ac<br>227.0278 | 104<br>Rf<br>261.11 | 105<br>Db<br>262.114 | 106<br>Sg<br>263.118 | 107<br>Bh<br>262.12 | 108<br>Hs<br>(265)     | 109<br>Mt<br>(266)    | 110<br>Ds<br>(269) | 111<br>Rg<br>(272)    | 112<br>Uub<br>(277) | 114<br>Uuq<br>(285)  | 116<br>Uuh<br>(289)  |                       |                              |                      |                      |

|                      |                       |                     |                      |                      |                      |                      |                       |                      |                       |                       |                       |                       |                      |
|----------------------|-----------------------|---------------------|----------------------|----------------------|----------------------|----------------------|-----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|
| 58<br>Ce<br>140.115  | 59<br>Pr<br>140.90765 | 60<br>Nd<br>144.24  | 61<br>Pm<br>144.9127 | 62<br>Sm<br>150.36   | 63<br>Eu<br>151.965  | 64<br>Gd<br>157.25   | 65<br>Tb<br>158.92534 | 66<br>Dy<br>162.50   | 67<br>Ho<br>164.93032 | 68<br>Er<br>167.26    | 69<br>Tm<br>168.93421 | 70<br>Yb<br>173.04    | 71<br>Lu<br>174.967  |
| 90<br>Th<br>232.0381 | 91<br>Pa<br>231.0359  | 92<br>U<br>238.0289 | 93<br>Np<br>237.0482 | 94<br>Pu<br>244.0642 | 95<br>Am<br>243.0614 | 96<br>Cm<br>247.0703 | 97<br>Bk<br>247.0703  | 98<br>Cf<br>242.0587 | 99<br>Es<br>252.083   | 100<br>Fm<br>257.0951 | 101<br>Md<br>258.10   | 102<br>No<br>259.1009 | 103<br>Lr<br>260.105 |

\*

†