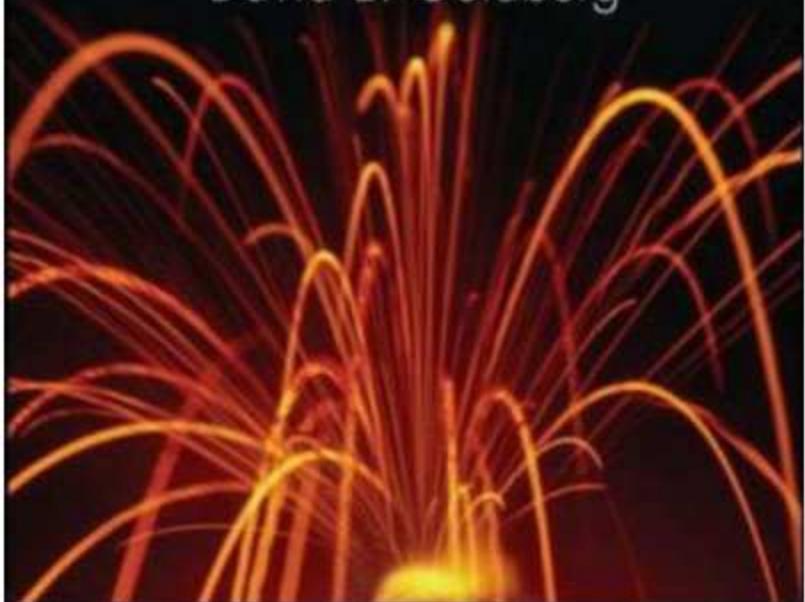


Fundamentals of
Chemistry

Fifth Edition

David E. Goldberg



Chemistry

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Goldberg • *Fundamentals of Chemistry, Fifth Edition*

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Preface

Chernistry is a dynamic and rapidly changing field. It is an extraordinarily interesting subject to study and an intriguing one to teach. The diversity of knowledge of the beginning student presents a unique challenge to the student and to the teacher. This text is written primarily for use in courses designed to prepare students who wish to pursue a science major requiring a comprehensive course in general chemistry. These students, in most cases, have never taken a course in chemistry or have had limited instruction in the basic math necessary to solve chemistry problems, so a chemistry course can be very threatening to them.

To address this issue, this text has four major goals:

1. To provide a clear, consistent methodology that a student can follow to develop conceptual and quantitative problem-solving skills.
2. To engage the student by relying heavily on analogies that relate chemistry to daily life.
3. To anticipate the points where students are apt to have difficulty and to smooth the path to understanding by explaining in detail what the pitfalls are and how to avoid them.
4. To present, at one time, points that may be easily confused with one another so that students can avoid making the errors. For example, if a radioactive decay problem asks for the number of atoms that have *disintegrated* instead of the number *remaining* after a certain time, a student might easily make a mistake. If in one problem both the number disintegrated and the number remaining are required, the student can hardly make that same mistake. In a given chapter some early problems ask related questions together and later ones ask them separately to ensure that the differences are not forgotten.

Developing Problem-Solving Skills

ORGANIZING THEIR THOUGHTS

Students have numerous demands on their time, so helping them organize their thoughts and identifying the key concepts is important. This book has several ways to accomplish this task.

8

Chemical Reactions

■ 8.1 The Chemical Equation
■ 8.2 Balancing Equations
■ 8.3 Predicting the Products of Chemical Reactions
■ 8.4 Acids and Bases



A reaction liberating energy

Review Clues

Section 8.1	Section 7.4
Section 8.2	Section 5.1
Section 8.3	Section 5.4
Section 8.4	Section 6.3

Objectives

8.1	To interpret a balanced chemical equation in terms of mole ratios of reactants and products
8.2	To balance chemical equations—that is, to get the same number of atoms of each element on each side
8.3	To predict the products of thousands of chemical reactions by categorizing reactions
8.4	To predict the products of the reactions of acids with bases and metals, and to use a specialized nomenclature for acid-base reactions

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CHAPTER 5 ■ Chemical Bonding

Summary

Chemical formulas identify the numbers, types, and molecules. The formula unit implies that the atoms are held together by some kind(s) of chemical bonds. When they are not combined with other elements, hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, and iodine exist as diatomic molecules (Figure 5.2).

In formulas for binary compounds, the more electropositive element is written first. A formula unit represents the collection of atoms in the formula. Subscripts in a formula indicate the numbers of atoms of the elements in each formula unit. For example, the formula unit H_2O has two hydrogen atoms and one oxygen atom. Formula units of uncombined elements, such as Ne , are atoms. Formula units of covalently bonded atoms are called molecules. Formula units of ionic compounds do not have any special name. In formulas, atoms bonded in special groups may be enclosed in parentheses. A subscript following the closing parenthesis multiplies everything within the parentheses. For example, a formula unit of $\text{Ba}(\text{ClO}_4)_2$ contains one barium atom, two chlorine atoms, and eight oxygen atoms. Formulas for hydrates have a centered dot preceding a number and the formula for water, such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, placed between the element symbol and the closing parenthesis (Section 5.1).

Atoms of main group elements tend to accept, donate, or share electrons to achieve the electronic structure of the nearest noble gas. Metal atoms tend to donate electrons and thereby become positive ions. When combining with metals, nonmetal atoms tend to accept electrons and become negative ions. The number of electrons donated or accepted by each atom depends to a great extent on the periodic group number; each atom tends to attain a noble gas configuration. The attraction of oppositely charged ions is called an ionic bond. Transition and inner transition metal atoms donate their valence electrons first, but ordinarily do not achieve noble gas configurations. Most of them can also lose electrons from an inner shell and thus can form cations with different charges (Section 5.2).

Electron dot diagrams can be drawn for atoms, ions, and molecules, using a dot to represent each valence electron. These diagrams are most useful for main group elements. The diagrams help in visualizing simple reactions and structures of polyatomic ions and molecules (Section 5.3).

Formulas for ionic compounds may be deduced from the charges on the ions, since all compounds have zero net charge. Given the constituent elements, we can predict the formula for binary compounds of most main group metals. We cannot do so for most transition metals because they have many oxidation states and valence electrons. (Given the specific ions, we can write a formula for any ionic compound.) Conversely, given a formula for an ionic compound, we can deduce the charges on its ions. Writing correct formulas for compounds and identifying the ions in compounds from their formulas are two absolutely essential skills (Section 5.4).

Nominal atoms can share electrons with other nonmetal atoms, forming covalent bonds. In electron dot diagrams, the shared electrons are counted as being in the outermost shell of *each* of the bonded atoms. A single bond consists of one shared electron pair; a double bond consists of two shared electron pairs; a triple bond consists of three shared electron pairs. Macromolecules result from covalent bonding of millions of atoms or more into giant molecules.

Drawing electron dot diagrams for structures containing only atoms that obey the octet rule can be based by subtracting the number of valence electrons available from the number required to get an octet (or duet) around each nonmetal atom. The difference is the number of electrons to be shared in the covalent bonds. For an ion, we must subtract 1 available electron for each positive charge on the ion and add 1 available electron for each negative charge. Main group elements require 8 electrons in their outermost electrons; but each hydrogen atom requires 2; and each other nonmetal atom requires 8. Atoms in some compounds do not follow the octet rule (Section 5.5).

Items for Special Attention

- Because formulas are used to represent unbonded atoms, covalently bonded molecules (Section 5.5), and ionically bonded compounds (Section 5.2), a formula unit can represent an atom, a molecule, or the simplest unit of an ionic compound (Figure 5.8). For example, He represents an uncombined atom; P_2 represents a molecule of an element; CO_2 represents a molecule of a compound;
- NaCl represents one pair of ions in an ionic compound.
- The seven elements that occur in the form of diatomic molecules (Figure 5.2) form such molecules *only when these elements are uncombined with other elements*. When combined in compounds, they may have one, two, three,

Chapter Outline At the beginning of each chapter, the outline of the entire chapter is listed to introduce students to the topics presented in the chapter. This outline also provides the instructor with a quick topic summary for organizing lecture material.

Chapter Objectives At the beginning of each chapter, the learning objectives are presented to alert the student to the key concepts covered in the chapter. These enable students to preview the material and become aware of the topics they are expected to master. These are also a valuable study tool for students when they are reviewing.

Review Clues At the beginning of each chapter except the first, there is a list of Review Clues. These clues provide students the opportunity to go back to previous sections in the book or to Appendix 1 and review or relearn material pertinent to the present chapter.

Chapter Summary At the end of each chapter is a summary designed to help the student identify important concepts and help them review for quizzes and tests.

Items for Special Attention At the end of every chapter, this unique section highlights and emphasizes key concepts that often confuse students. This section anticipates students' questions and problem areas and helps them avoid many pitfalls.

Various Problem-Solving Methods

Many problems are worded to show students that very different questions may sound similar and that the same question may be presented in very different words. This will encourage students to try to understand concepts rather than to memorize solutions.

All Examples have the solutions following the stated problem. The solutions range from a simple statement (Example 1.4 on pages 6–7) to a short explanation (Example 3.1 on page 78) to a step-by-step solution (Example 7.13 on pages 194–195). Side-by-side examples are also presented with the general method for the technique presented on the left and a specific example of the method on the right (pages 193–194).

After most numbered examples, a practice problem is presented for the students to practice the problem-solving method. The complete answers are presented in Appendix 4. The students will then use these methods to solve the end-of-chapter problems.

The end-of-chapter problems have new variables while maintaining the same skill pattern. The end-of-chapter problems provide practice for the student using the skills presented in the chapter. Solutions to the problems numbered in red are provided in Appendix 5.

SELF-TESTING AND REVIEWING



Snapshot Review

ChemSkill Builder 3.6

- We classify matter so that we can learn the general properties of each type to enable us to answer specific questions about individual samples.
- All substances have definite compositions.

A. Does the compound baking soda have a definite composition?



Self-Tutorial Problems

8.1 Assign each of the following types to one of the five classes of reactions presented in Section 8.3:

Reactants	Products
(a) 2 elements	1 compound
(b) 1 compound	2 elements
(c) 2 compounds	2 different compounds
(d) 1 element + 1 compound	1 element + 1 compound
(e) 1 compound	1 element + 1 compound
(f) 1 compound + O ₂	2 or more compounds
(g) 1 element + 1 compound	1 compound

8.2 Explain how to recognize that O₂ and MgO will not react with each other in a single substitution reaction.

8.3 Rewrite the following equations with integral coefficients:

- CdF₂(s) + $\frac{1}{2}$ F₂(g) → CdF₃(s)
- CoCl₃(s) + $\frac{1}{2}$ Co(s) → $\frac{3}{2}$ CoCl₂(s)
- CuCl₃(s) + $\frac{1}{2}$ Cl₂(g) → CuCl₂(s)
- $\frac{2}{3}$ H₃PO₄(aq) + CaCO₃(s) → $\frac{1}{3}$ Ca₃(PO₄)₂(s) + H₂O(l) + CO₂(g)
- NH₃(g) + $\frac{5}{4}$ O₂(g) → NO(g) + $\frac{3}{2}$ H₂O(g)

8.4 Write a balanced chemical equation for each of the following reactions:

- SO₂(g) + PCl₃(s) → SOCl₂(l) + POCl₃(l)
- SO₂(g) + Cl₂(g) → SO₂Cl₂(l)

8.5 What is the difference, if any, among (a) the reaction of sodium with chlorine, (b) the combination of sodium and chlorine, and (c) the formation of sodium chloride from its elements?

8.6 Consider the reaction of aqueous chlorine with aqueous zinc iodide.

- Identify the reaction type.
- Write correct formulas for all reactants and products.
- Write a balanced equation.

8.7 Explain how a catalyst resembles a marriage broker.

8.8 A certain double substitution reaction produced silver chloride and potassium acetate. What were the reactants?

8.9 Can a single substitution reaction occur between an element and a compound of that same element?

8.10 Can a double substitution reaction occur between two compounds containing one ion in common?

8.11 Are oxides of reactive metals or oxides of unreactive metals more likely to decompose into their two elements when heated?

8.12 What type of reaction is the following? What are the products?

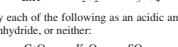


8.13 In a certain double substitution reaction, CrCl₃ is a reactant. Is Cr(NO₃)₃ or Cr(NO₃)₂ more likely to be a product?

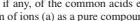
8.14 Do the classes of reactions described in Section 8.3 include all possible types of chemical reactions?

8.15 Which table in this chapter should be used when working with single substitution reaction, and which ones with double substitution reactions?

8.16 Which of the following compounds are acids?



8.17 Classify each of the following as an acidic anhydride, a basic anhydride, or neither:



8.18 Which, if any, of the common acids exist completely in the form of ions (a) as a pure compound and (b) in aqueous solution?

8.19 What products are expected in each of the following cases?

(a) KClO₃ is heated in the presence of MnO₂ as a catalyst.

(b) KClO₃ is heated in the presence of MnO₂.

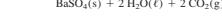
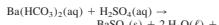
(c) KClO₃ and MnO₂ are heated together.

(d) KClO₃ is heated.

8.20 What type of substance can act as an acid but does not have hydrogen written first in its formula?

8.21 What is the difference between “acidic” and “acetic”?

8.22 Give two reasons why the following reaction produces products:



Snapshot Review At the end of each chapter section, a *Snapshot Review* appears. Students are provided a short synopsis of the section and then asked a question or two to test their comprehension of the concept(s). Answers to the *Snapshot Review* questions are provided at the end of each chapter.

ChemSkill Builder At the end of chapter sections, where applicable, a ChemSkill Builder icon appears. ChemSkill Builder is an online electronic homework program that generates questions for students in a randomized fashion with a constant mix of variables. The icon lets the student know which sections of ChemSkill Builder to practice for the chemical skills relating to the specific content of the text. The correlation to ChemSkill Builder by James D. Spain and Harold J. Peters is enhanced by the increased number of topics covered there. Log on at www.mhhe.com/csb.

Self-Tutorial Problems This end-of-chapter section presents problems in simple form designed as teaching devices. Many are from everyday life, and they emphasize the importance of identifying the information needed to answer questions, thus advancing analytical skills. By considering different terms that look or sound alike in a single problem, the students can more easily distinguish and learn both. (see Problems 5.1, 5.5, and 5.6 on pages 153–154)

Engaging Student Interest

ANALOGIES

Frequent use of analogies to daily life helps students understand that chemistry problems are not significantly different from everyday problems. For example, calculations involving dozens of pairs of socks and moles of diatomic molecules can be carried out by the same methods (see Problems 7.4 and 7.5 on page 201). Oxidizing and reducing agents can be compared conceptually to hand towels and wet hands (Example 16.11 on page 441). Specific heat calculations are like those involving room rates at a resort (Example 14.5 on page 384).

REAL-WORLD PROBLEMS

Students are engaged in the study of a topic by use of a real-world problem. The students easily understand by frequently using analogies to apply the scientific concept to a normal daily event. In working with conceptual problems, the use of chemistry in the real world is brought alive to the student. (See Problem 7.130 on page 205)

ITEMS OF INTEREST

Periodically throughout the book the students will find *Items of Interest* within the textual material. These items demonstrate the use of chemistry in the present and future. An example is the industrial Solvay process in Chapter 8 on page 222.

ART PROGRAM

Today's students are much more visually oriented than any previous generation and many are principally visual learners. We have attempted to develop this style of learning through the expanded use of color and illustrations. Each chapter is amply illustrated with accurate, colorful diagrams that clarify difficult concepts and enhance learning.

Content Changes in the Fifth Edition

Changes in the fifth edition include:

- The addition of a *NEW Chapter 17* on Electrochemistry, with calculation of potentials and of stoichiometric quantities from electrical quantities and vice versa. Six new in-chapter examples and *forty* end-of-chapter problems were added, as well as two tables, Table 17.1 “Electrical Variables and Units” and Table 17.2 “Standard Reduction Potentials.”
- The addition of a *NEW Section 19.5* on Polyprotic Acids, with Table 19.4 on “Selected Dissociation Constants of Polyprotic Acids”.
- Changes in positions of several sections for better flow of ideas:
 - Chapter 2: Presentation of Exponential Numbers before The Metric System
 - Chapter 12: Presentation of Dalton’s Law immediately after Ideal Gas Law

- Five new Item of Interest additions:
 - Chapter 10: Ion mass in food chemistry
 - Chapter 14: High heat capacity and heat of vaporization of water
 - Chapter 17: Purification process for copper
 - Galvanic cell reactions
 - Chapter 19: H₂S, a dangerous but useful gas
- New Enrichment Box on Controlled Experiments in Chapter 13
- The elimination of Section 16.6 on Equivalents and Normality from Chapter 16. These concepts are available online for instructors who want them; contact your McGraw-Hill Sales Representative.

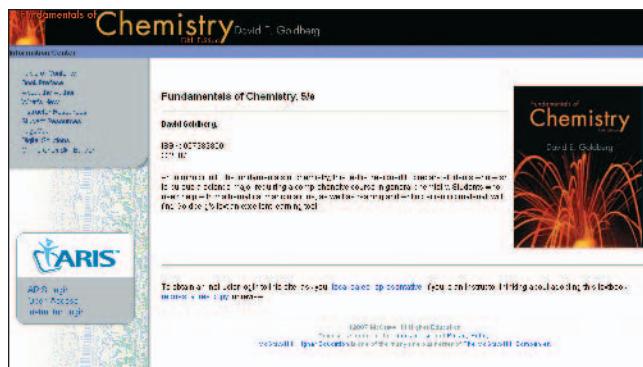
In addition, the entire book has been examined for accuracy, and the problems and examples have been amended. More in-chapter examples and end-of-chapter problems have been added as well. The artwork has been upgraded to further student interest and understanding.

Major pedagogy retained by the author includes:

- Asking questions in a way so students can understand concepts rather than memorize has been retained and hopefully improved.
- Multiple-part questions that ask the same question in several different ways, or that ask quite different questions in similar-sounding ways, have been retained. (For example, see Problem 18.6 where equilibria involving solid and gaseous iodine are both presented in a single problem.)
- Increase in the number of problems and examples; full solutions are given, either in the appendices or the instructor's manual.

Supplemental Materials

INSTRUCTOR RESOURCES



ARIS—Assessment, Review, and Instruction System.

ARIS is a complete, online tutorial, electronic homework, and course management system, designed for greater ease of use than any other system available. Instructors can create and share course materials and assignments with colleagues with a few clicks of the mouse. All assignments, quizzes, and question tutorials are directly tied to text-specific materials, but instructors can also edit questions, import their own content, and create announcements and due dates for assignments.

ARIS has automatic grading and reporting of

homework, quizzing, and testing. All student activity within McGraw-Hill's ARIS is automatically recorded and available through a fully integrated gradebook that can be downloaded to Excel. Log on at www.mhhe.com/goldberg.

Instructor's Manual and Solution Manual is found in the *Fundamentals of Chemistry*, Fifth Edition ARIS website under the Instructor Center.

The Instructor's Manual contains the test bank questions, suggestions on how to organize the course and answers to the end-of-chapter problems.

Instructor's Testing and Resource CD-ROM contains the electronic format for the test bank questions allowing the instructors to edit or create their own test templates. The Test Bank is formatted for easy integration into any course management system.

Digital Content Manager CD-ROM is a multimedia collection of visual resources allowing instructors to utilize artwork from the text in multiple formats to create customized classroom presentation, visually based tests and quizzes, dynamic course content, or attractive support materials. The Digital Content Manager is a cross-platform CD containing an image library, a photo library, and a table library.



ChemSkill Builder is an online tool containing more than 1500 algorithmically generated questions, each with tutorial feedback. There is a direct correlation between student time investment in this program and increased problem-solving ability. A record of student work is maintained in an online gradebook so that homework can be done at home, in a dorm room, or in a university lab. Log on at www.mhhe.com/csb

STUDENT RESOURCES

ARIS—Assessment, Review, and Instruction System. ARIS is a complete, online tutorial, and electronic homework system, designed for greater ease of use than any other system available. All assignments, quizzes, and question tutorials are directly tied to text-specific materials.

ARIS has automatic grading and reporting of homework, quizzing, and testing. All student activity within ARIS is automatically recorded and available to the instructor. Log on at www.mhhe.com/goldberg.



ChemSkill Builder challenges the students' knowledge of introductory chemistry with an array of individualized problems. The ChemSkill

Builder icon in the text lets the student know which section of ChemSkill Builder to practice for the chemical skills relating to the specific content of the text. Log on at www.mhhe.com/csb

How to Study Science is written by Fred Drewes of Suffolk County Community College. This excellent workbook offers students helpful suggestions for meeting the considerable challenge of a science course. It offers tips on how to take notes and how to get the most out of laboratories, as well as how to overcome science anxiety. The book's unique design helps to rouse critical thinking skills, while facilitating careful note taking on the part of the student.

ChemSkill Builder

Welcome to ChemSkill Builder!

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Assignable
Algorithmic

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Technical Support

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For technical support go to www.mhhe.com/support

3000 Solved Problems in Chemistry is written by David E. Goldberg. This Schaum's solved problem manual provides 3000 solved problems. It provides problem-solving strategies and helpful hints in studying.

Acknowledgments

The preparation of a textbook is a family effort, and the quality of the final product is a reflection of the dedication of all the family members. First, I would like to thank my wife, without whose patience and support this project would not have been possible. Second, I would like to thank the scores of my fellow chemists and my students who have taught me much in the past and continue to do so. Learning is a never-ending process, and I continue to learn from my colleagues and students. Please let me know about any errors that I have not eliminated from this edition. I would also like to thank the members of my extended family at McGraw-Hill, without whom there would not have been a text: my developmental editor, Lorraine Buczek, my managing developmental editor, Shirley Oberbroeckling, my project manager, Jayne Klein, and my publisher, Thomas Timp. I gratefully acknowledge the invaluable help of the following dedicated reviewers, who provided expert suggestions and the needed encouragement to improve the text:

John R. Allen <i>Southeastern Louisiana University</i>	Kirsten L Murphy <i>University of Wisconsin–Milwaukee</i>
Bob Blake <i>Texas Tech University</i>	D.K. Philbin <i>Allan Hancock College</i>
David A. Boyajian <i>Palomar College</i>	Elsa C. Santos <i>Colorado State University</i>
Steve Gentemann <i>Southwestern Illinois College</i>	Mark W. Schraf <i>West Virginia University</i>
Claudia M.S. Hein <i>Diablo Valley College</i>	Mary C. Setzer <i>University of Alabama in Huntsville</i>
James R. Jeitler <i>North Idaho College</i>	Jeffrey S. Temple <i>Southeastern Louisiana University</i>
Marc Lord <i>Columbus State Community College</i>	Jacquelyn A. Thomas <i>Southwestern College</i>
Lydia J. Martinez Rivera <i>University of Texas at San Antonio</i>	

To the Student

This book is designed to help you learn the fundamentals of chemistry. To be successful, you must master the concepts of chemistry and acquire the mathematical skills necessary to solve problems in this quantitative science. If your algebra is rusty, you should polish it up. Appendix 1 reviews the algebra used in basic chemistry and also shows how to avoid mistakes while solving chemistry problems with your scientific calculator. The factor label method is introduced in Chapter 2 to show you how to use units to help with problem solutions. You can help yourself by using the standard symbols and abbreviations for various quantities (such as *m* for mass, *m* for meter, mol for moles, and M for molarity). Always use the proper units with your numerical answers; it makes a big difference whether your roommate's pet is 6 inches long or 6 feet long!

Many laws, generalizations, and rules are presented in the study of basic chemistry. Most students can master these. Successful students, however, not only know them but also know *when to use each one*. Word problems are the biggest hurdle for most students who do have difficulty with chemistry. The best way to learn to do word problems is to practice intensively. Review the Examples and do the Practice Problems until you feel confident that you understand the concepts and techniques involved. (Do not try to memorize solutions; there are too many different ways to ask the same questions, and many similar-sounding questions are actually quite different.) Do the Snapshot Review items at the end of each section. Do as many of the end-of-chapter problem as you possibly can to see whether you have mastered the material.

You should not try to speed-read chemistry. Mere reading of a section will not generally yield full comprehension of the material. You must be able to solve the problems to be sure that you have really mastered the concepts. Many of the problems sound alike but are very different (for example, Problems 5.10, 7.4, 7.5, and 11.9), and many others sound different but are essentially the same (for example, Problems 3.5, 5.16, 8.5, and 8.19). These will help you develop careful reading habits and prepare you for the questions asked on examinations.

Problems from everyday life that are analogous to scientific problems are included to help you understand certain points better (for example, Problems 7.4 and 7.5). Other problems are first presented in parts to help you work through the solution and later appear as a single question, as is more likely to occur on examinations. Some of the problems are very easy; these are generally intended to emphasize an important point. After solving one of these problems, ask yourself why such a question was asked. Make sure you understand the point.

Make sure you understand the scientific meaning of each new term introduced. For example, the word "significant" as used in Chapter 2 means something

To the Student

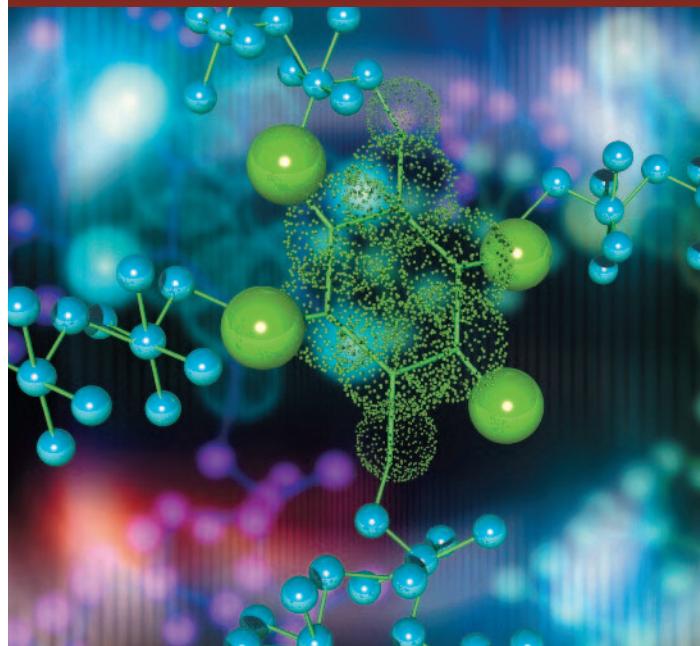
xix

entirely different from its meaning in everyday conversation; be sure you understand the difference. Key terms are **boldfaced** when they are first introduced in the text. A list of these terms is given at the end of each chapter. A complete glossary of all important terms is provided at the end of the book.

Other materials to aid your study include lists of standard symbols and abbreviations for variables, units, and subatomic particles, found in Appendix 2. A summary of the mathematical equations used in the book is presented in Appendix 3. The solutions to all Practice Problems and selected end-of-chapter problems are provided in Appendices 4 and 5, respectively. The selected end-of-chapter problem numbers are printed in red. A periodic table is printed inside the front cover of the book, and a table of the elements appears inside the back cover. Let these tools help you succeed!

1

Basic Concepts



A representation of atoms bonded together

- 1.1 Classification of Matter
- 1.2 Properties
- 1.3 Matter and Energy
- 1.4 Chemical Symbols
- 1.5 The Periodic Table
- 1.6 Laws, Hypotheses, and Theories

Objectives

- 1.1 To classify matter into types to make manageable the wealth of information about matter
- 1.2 To use properties to help identify substances
- 1.3 To distinguish among matter, mass, and weight, as well as between matter and energy
- 1.4 To write the symbols for the important elements and the names of these elements from the symbols
- 1.5 To begin to classify the elements in a systematic manner. To identify periods, groups, and sections of the periodic table by name and/or number
- 1.6 To distinguish among laws, hypotheses, and theories

Chemistry is the study of matter and energy. Matter includes all the material things in the universe. In Section 1.1, we will learn to classify matter into various types—elements, compounds, and mixtures—based on composition. Properties—the characteristics by which samples of matter may be identified—are discussed in Section 1.2.

Energy may be defined as the ability to do work. We often carry out chemical reactions for the sole purpose of changing energy from one form to another—for example, we pay large sums of money for fuels to burn in our homes or cars. The relationship between energy and matter, an important one for chemists, is explored in Section 1.3.

Symbols, introduced in Section 1.4, are used to represent the elements. The periodic table, introduced in Section 1.5, groups together elements with similar properties. Chemical symbols and the periodic table are both designed to decrease the effort required to learn a great deal of chemistry. Section 1.6 presents scientific laws, hypotheses, and theories that generalize and explain natural phenomena.

For convenience, chemistry is often divided into the following five subdisciplines: organic chemistry, inorganic chemistry, analytical chemistry, physical chemistry, and biochemistry. **Organic chemistry** deals with most compounds of carbon. These compounds are introduced systematically in Chapter 20. **Inorganic chemistry** deals with all the elements and with compounds that are not defined as organic. **Analytical chemistry** involves finding which elements or compounds are present in a sample or how much of each is present. **Physical chemistry** deals with the properties—especially quantitative (measurable) properties—of substances. **Biochemistry** deals with the chemistry of living things.

These subdivisions of chemistry are somewhat arbitrary. A chemist specializing in any one of the first four subdivisions uses all of them and often biochemistry as well. A biochemist uses all five specializations. For example, the modern organic chemist often uses inorganic compounds to convert starting materials to desired products and then analyzes the products and measures their properties. In addition, many organic chemists now are investigating compounds of biological interest.

The importance of science in general and of chemistry in particular in our everyday lives can hardly be overstated. For example, color television, computers, and modern copy machines all stem from chemical advances of the past few decades. (Color TV requires compounds that glow intensely in red, blue, or green when bombarded with electron beams. Computers work with “chips” made from specially treated metalloids. Copy machines require materials that “remember” how much light has fallen on them.) However, today’s and tomorrow’s chemists are still faced with monumental tasks—cleaning up the environment and providing sufficient food for an ever-growing world population to mention just two.

1.1 Classification of Matter

Matter is defined as anything that has mass and occupies space. All the materials in the world are composed of a few more than a hundred elements. **Elements** are the simplest form of matter and cannot be broken down chemically into simpler, stable substances. They can be thought of as building blocks for everything in the universe. The same elements that make up the Earth also

1.1 ■ Classification of Matter**3**

make up the Moon, as shown by actual analysis of rock samples from the Moon. Moreover, indirect evidence obtained from analysis of light from stars shows that the rest of the universe is composed of the same elements.

Clearly the number of different combinations of elements must be huge to get all the varieties of matter in the universe. But elements can combine in only two fundamentally different ways: by physical changes to form mixtures or by chemical changes to produce compounds. **Chemical changes**, also called **chemical reactions**, change the composition (or structure) of a substance. **Physical changes** do not alter the composition. The breaking of glass into small pieces is an example of a physical change. The glass still has the same composition and the same properties as before, but its external form is changed. The burning of charcoal (mostly carbon) in air (or in pure oxygen) to get carbon dioxide, a colorless gas, is an example of a chemical reaction. Not only the form of the material but also its composition has changed. The gas has both carbon and oxygen in it, but the charcoal had no oxygen and the oxygen had no carbon.

If a sample of matter cannot be broken down into simpler substances by ordinary chemical means, the sample is an element. [Ordinary chemical means includes any methods except nuclear reactions (Chapter 21).] An element has a definite set of properties. A **compound** is a chemical combination of elements that has its own set of properties and a **definite composition**. For example, pure water obtained from any natural source contains 88.8% oxygen and 11.2% hydrogen by mass. Compounds can be separated into their constituent elements only by chemical reaction. Elements and compounds are the two types of **substances**, often referred to as pure substances.

EXAMPLE 1.1

The percentage of carbon in a small box of the pure substance sucrose (table sugar) is 42.1%. (a) Is sucrose an element or a compound? (b) What is the percentage of carbon in a large box of the same substance?

Solution

- Sucrose is a compound; it contains more than one element.
- The larger sample is also 42.1% carbon because a given compound always contains the same percentage of each of its elements, no matter what the size of the sample.

Two or more substances—elements, compounds, or both—can combine physically to produce a mixture. A mixture can be separated into its components by physical means. **Mixtures** are physical combinations of substances that have properties related to those of their components but that do not have definite compositions. They can be either **heterogeneous** or **homogeneous mixtures**. In heterogeneous mixtures, two or more different types of matter can be seen to be present with the naked eye or a good optical microscope. Homogeneous mixtures, also called **solutions**, look alike throughout, even under a microscope.

Both types of pure substances are usually homogeneous (but can be heterogeneous, as in ice water).

ITEM OF INTEREST

The difference between elements and compounds is illustrated in human nutrition:

A. *Vitamins* are complex compounds of carbon, hydrogen, and several other elements. A vitamin owes its activity to the nature of the compound as a whole, and any slight change in it can destroy its nutritional value.

B. About 20 elements are called *minerals*. They also play a role in human nutrition. The minerals known to be essential for good health are calcium, phosphorus, potassium, sulfur, sodium, chlorine, magnesium, iron, manganese, copper, iodine, cobalt, fluorine, and zinc. Traces of silicon, boron, arsenic, strontium, aluminum, bromine, molybdenum, selenium, and nickel may also be required. These elements are eaten in the form of their compounds, but it does not matter much which compounds.

Heating a vitamin will destroy its potency by breaking the compound into other compounds. In contrast, heating a compound that contains one of the essential minerals might destroy the compound, but it will not change the mineral into another element. For example, calcium citrate can be changed into another calcium-containing compound, but the calcium is still present.

ITEM OF INTEREST

The word *homogenize* is related to the term *homogeneous*, but as used in everyday conversation, it does not mean exactly the same thing. For example, homogenized milk is not really homogeneous; we can see individual particles of cream under a microscope. Truly homogeneous liquids are transparent (though not always colorless). If we cannot recognize objects viewed through a thin layer of liquid, the liquid is not homogeneous.

Table 1.1 Classification of Matter

Pure substances
Elements
Compounds
Mixtures
Heterogeneous mixtures
Homogeneous mixtures (solutions)

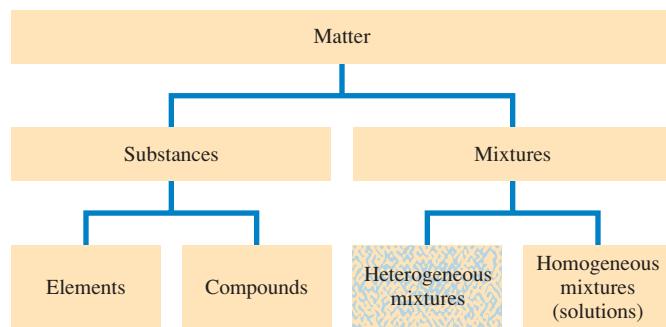
EXAMPLE 1.2

If we stir a teaspoon of sugar into a glass of water and a teaspoon of mud into another glass of water, the sugar will disappear into the water (dissolve), but the mud will not (Figure 1.2). Which mixture is a solution?

Solution

The sugar forms a solution—a homogeneous mixture—with the water. The mud and water form a heterogeneous mixture. Particles of mud are easy to see in the mud-water mixture, but seeing any sugar particles in the sugar-water solution is impossible, no matter how hard we look (even with a microscope).

Practice Problem 1.2 When solid iodine is added to ethyl alcohol, a colorless liquid, it forms a uniform, transparent liquid mixture with a deep color. Is the mixture homogeneous or heterogeneous?

1.1 ■ Classification of Matter**Figure 1.1** Classification of Matter**EXAMPLE 1.3**

Classify each of the following statements as true or false:

- Every mixture contains two or more free elements.
- Every compound is a substance.
- Every compound contains two or more elements.
- Every mixture contains two or more compounds.
- Every substance is a compound.
- All mixtures are homogeneous.
- Every mixture contains two or more substances.

Solution

- False (They may contain compounds and only one or no free elements.)
- True
- True
- False (They may contain free elements or compounds or both.)
- False (Some are free elements.)
- False (Some are heterogeneous.)
- True

Figure 1.2 Sugar Plus Water, and Mud Plus Water

- (a) Sugar dissolves in water and is not distinguishable from the water; a solution is formed. (b) Mud does not dissolve in water; a heterogeneous mixture is formed.



(a)



(b)

Practice Problem 1.3 Classify each of the following statements as true or false:

- (a) Every mixture contains two or more elements.
- (b) All mixtures are heterogeneous.
- (c) Every substance contains two or more elements.
- (d) All homogeneous samples are solutions.



Snapshot Review



ChemSkill Builder 3.6

- We classify matter so that we can learn the general properties of each type to enable us to answer specific questions about individual samples.
- All substances have definite compositions.

A. Does the compound baking soda have a definite composition?

1.2 Properties

Every substance has a definite set of properties. **Properties** are the characteristics by which we can identify something. For example, we know that pure water is a colorless, odorless, tasteless substance that is a liquid under the conditions usually found in an ordinary room. Water puts out fires, and it dissolves sugar and salt. Liquid water can be changed into a gas (called water vapor or steam) by heating it, or into a solid (ice) by cooling it. Salt has a different set of properties from water; sugar has yet another set.

Chemical properties are the characteristic ways a substance can react to produce other substances. **Physical properties** are the ways a substance can be identified without changing its characteristic composition. For example, water can react with very active metals to produce hydrogen and another compound. That reactivity is a chemical property of water. Water can also freeze to ice at 0°C (equal to 32°F) or it can evaporate to water vapor, neither of which changes it from H₂O. These are physical properties of water.

Some properties of a sample of a substance depend on the quantity of the sample. These properties are called **extensive properties**. For example, the weight of a solid sample depends on how much of the substance is present. Other properties, such as color and taste, do not depend on how much is present. These properties are known as **intensive properties**. Intensive properties are much more useful for identifying substances.

EXAMPLE 1.4

- (a) Sample A weighs twice as much as sample B. Is it possible to tell which sample is iron and which is powdered sugar?
- (b) Sample A is attracted by a magnet and sample B is a white powder. Is it possible to tell which sample is iron and which is powdered sugar?

1.2 ■ Properties**7****Solution**

- (a) The weight of a sample is an extensive property that does not tell anything about the material's identity.
- (b) The intensive properties described enable us to tell which of the two samples is iron (the magnetic one) and which is powdered sugar (the white one).

Practice Problem 1.4 Which is heavier, (a) bricks or straw? (b) one package of cheese or two of those packages of cheese? (c) Which of these uses of the word *heavier* describes an intensive property and which an extensive property?

Some of the most important intensive properties that chemists use to identify substances are ones that they measure; they are called **quantitative properties**. Two such properties are the freezing point and the normal boiling point of a substance, which are the temperatures at which a liquid freezes to form a solid and boils to form a gas under normal atmospheric conditions, respectively. We will discuss quantitative properties in more detail in Chapter 2.

We can distinguish compounds from mixtures because of the characteristic properties of compounds. Mixtures have properties like those of their constituents. The more of a given component present in a mixture, the more the properties of the mixture will resemble those of that component. For example, the more sugar we put into a glass of water, the sweeter is the solution that is produced.

An experiment will illustrate how properties are used to distinguish between a compound and a mixture. We place small samples of iron filings and powdered sulfur on separate watch glasses to investigate their properties (Figure 1.3a). We note that both are solids. We place the samples in separate test tubes and then hold a magnet beside the first tube (Figure 1.3b). We find that the iron is attracted to the magnet. When we hold the magnet next to the tube with the sulfur, nothing happens; the sulfur is not attracted by the magnet.

When we pour carbon disulfide, a colorless, flammable liquid, on the sulfur sample, the solid sulfur disappears, and the liquid turns yellow. The sulfur has **dissolved**, forming a solution with the carbon disulfide. When we pour carbon disulfide on the iron, nothing happens; the iron stays solid, and the liquid stays colorless. If we had large pieces of each element, we could pound them with a hammer and find that the sulfur is brittle and easily powdered but that the iron does not easily break into small pieces. Iron is **malleable**—that is, it can be pounded into various shapes. Table 1.2 lists the properties discussed so far of the two elements.

Next we pour some iron filings and some powdered sulfur into a large test tube and stir them together. The sample appears to be a dirty yellow, but if we look closely, we can see yellow specks and black specks. If we hold a magnet next to the test tube (Figure 1.3c), the black particles (with some yellow particles clinging to them) are attracted by the magnet. When we pour some carbon disulfide on the sample, the liquid turns yellow. We pour off that liquid and pour on more carbon disulfide until no yellow solid remains in the sample. When we evaporate the carbon disulfide in a fume hood, we get a

Caution: Carbon disulfide is both explosive in air and poisonous.

Figure 1.3 Iron, Sulfur, and a Mixture of the Two

- (a) Iron filings (black) and powdered sulfur (yellow).
- (b) The iron is attracted by the magnet, but the sulfur is not.
- (c) The iron filings in a mixture of iron and sulfur are still attracted by the magnet. (Some of the powdered sulfur sticks to the iron filings, but the sulfur is not attracted by the magnet.)



(a)



(b)



(c)

yellow solid again. If we place a magnet next to the black material left in the large test tube, we find that it is attracted to the magnet. It seems that mixing the two samples of elements has not changed their properties. The sulfur is still yellow and still soluble in carbon disulfide; the iron is still black and still attracted by a magnet. The two elements have retained their properties and their identities; they are still elements. This combination of the two is a mixture. A mixture does not have a definite composition, and it has properties related to the properties of its components.

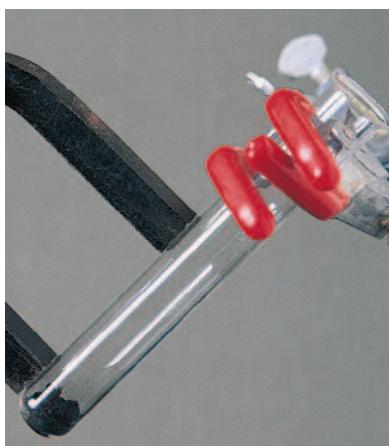
Now we place two new, carefully measured samples of iron filings and powdered sulfur in another large test tube and heat the mixture strongly with a Bunsen burner. After a time, a red glow appears in the bottom of the tube and gradually spreads throughout the sample. This is evidence of a

Table 1.2 Some Properties of Iron, Sulfur, and an Iron-Sulfur Compound

Iron	Sulfur	Iron-Sulfur Compound
Solid	Solid	Solid
Shiny	Dull	Dull
Magnetic	Not magnetic	Not magnetic
Black	Yellow	Black
Malleable	Brittle	Brittle
Insoluble in carbon disulfide	Soluble in carbon disulfide	Insoluble in carbon disulfide

1.2 ■ Properties**9**

(a)



(b)

Figure 1.4 Reaction of Iron and Sulfur

(a) When a mixture of iron and sulfur is heated, the two elements react. Some sulfur is vaporized and then deposits on the test tube wall.
 (b) The pulverized product of the reaction is not attracted by a magnet.

chemical reaction. Some sulfur escapes into the gas phase because of the heat and then deposits on the test tube wall (Figure 1.4a). A black solid results from the chemical reaction. When we remove the solid from the test tube (we may have to break the tube to get it out), we can pulverize the solid with a hammer—that is, it is brittle. If we try to dissolve the material in carbon disulfide, it does not dissolve. If we bring the magnet close to it, it is not attracted (Figure 1.4b). This material has its own set of properties: a dull black color, brittleness, insolubility in carbon disulfide, lack of attraction to a magnet (see Table 1.2). It is a compound—a chemical combination of iron and sulfur.

EXAMPLE 1.5

After a certain substance is heated in air until no further reaction takes place, a metal is left that has a mass 58.5% of that of the original substance. After another substance is heated in air, a white powder is left that has a mass of 138% of that of the original substance. Can you tell whether the reactants and the products are elements or compounds?

Solution

The first substance is a compound. When it is heated, it decomposes into a metallic material that is left behind and some gaseous product that escapes into the air. Because the metal has less mass than the original substance, it is simpler. The original substance is decomposable—it is not an element. The metal product might or might not be decomposable, so we cannot tell from the information given whether it is an element or a compound.

The second substance combined with something in the air; it gained mass. The powdery product is therefore a combination of substances and cannot be an element. We do not know if the original substance can be decomposed (it was not decomposed in this experiment), so we cannot tell if it is an element or a compound.

Practice Problem 1.5 A certain sample of a shiny substance is heated in air. Afterward, a white powder with twice the mass is present. Is the change a chemical reaction? Is the powder an element?

Snapshot Review

- Each substance has its own characteristic set of properties.
- Extensive properties depend on how much sample is present; intensive properties do not.
- Intensive properties are useful for identifying substances.

- A. Consider the statement: “There is 1 liter (L) of colorless soda in the can.” Which of the two properties is intensive and which is extensive?
- B. A certain familiar substance freezes at 0°C. Does this property help identify the substance?



ChemSkill Builder 1.2

1.3 Matter and Energy

Matter is anything that has mass and occupies space. All the material things in the universe are composed of matter, including anything we can touch as well as the planets in the solar system and all the stars in the sky.

The **mass** of an object measures how much matter is in the object. Mass is directly proportional to weight at any given place in the universe. If we leave the surface of the Earth, our mass remains the same, but our weight changes. An astronaut positioned between two celestial bodies such that their gravitational attractions pull equally in opposite directions is weightless, but the astronaut's mass remains the same as it is on Earth. Because chemists ordinarily do their work on the Earth's surface and because mass and weight are directly proportional here, many chemists use the terms *mass* and *weight* interchangeably, but we must remember that they differ.

Energy is the capacity to do work. We cannot hold a sound or a beam of light in our hands; they are not forms of matter but forms of energy. Some of the many forms of energy are outlined in Table 1.3. Energy cannot be created or destroyed, but it can be converted from one form to another. This statement is known as the **law of conservation of energy**.

Table 1.3 Forms of Energy

Heat
Chemical
Nuclear
Mechanical
Kinetic (energy of motion)
Potential (energy of position)
Electrical
Sound
Electromagnetic (light)
Visible light
Ultraviolet
X-rays
Gamma rays
Infrared
Radio waves
Microwaves
Solar*

*Solar energy is a combination of several forms of light.

EXAMPLE 1.6

What desired energy conversion is exhibited by (a) use of a flashlight and (b) an automobile consuming gasoline?

Solution

- Chemical energy is converted to electrical energy, which is converted to light.
- Chemical energy is converted to kinetic energy.

Practice Problem 1.6 What desired energy conversion is exhibited by (a) an alternator in a car recharging the battery and (b) automobile brakes in use?



ENRICHMENT

In 1905, Albert Einstein (1879–1955) published his theory that the mass of a sample of matter is increased as the energy of the sample is increased. For example, a baseball in motion has a very slightly greater mass than the same baseball at rest. The difference in mass is given by the famous equation

$$E = mc^2$$

In this equation, E is the energy of the object, m is the *mass difference*, and c^2 is a very large constant—the square of the velocity of light:

$$\begin{aligned}c^2 &= (300,000 \text{ kilometers/second})^2 \\&= 90,000,000,000 \text{ kilometers}^2/\text{second}^2 \\&= (186,000 \text{ miles/second})^2 \\&= 34,600,000,000 \text{ miles}^2/\text{second}^2\end{aligned}$$

For macroscopic bodies such as a baseball, the increase in mass because of the added energy is so small that it is not measurable. It was not even discovered until the beginning of the twentieth century. At atomic and subatomic levels, however, the conversion of a small quantity of matter into energy is very important. It is the energy source of the Sun and the stars, the atomic bomb, the hydrogen bomb, and nuclear power plants.

Chemistry is the study of the interaction of matter and energy and the changes that matter undergoes. (In nuclear reactions, tiny quantities of matter are actually converted to relatively large quantities of energy. See Chapter 21.)



Snapshot Review

- Matter has mass and occupies space.
- Mass is a measure of the quantity of matter in a sample (but energy also has a mass equivalent).

A. Which has a greater mass—an automobile or a sewing thimble?

1.4 Chemical Symbols

Because the elements are the building blocks of all materials in the universe, we need an easy way to identify and refer to them. For this purpose, each chemical element is identified by an internationally used **symbol** consisting of one or two letters. The first letter of an element's symbol is always capitalized. If the symbol has a second letter, it is a lowercase (small) letter. The symbol is an abbreviation of the element's name, but some symbols represent names in languages other than English. The 10 elements whose symbols and names have different first letters are listed in Table 1.4. A list of the names and symbols of the first 109 elements, along with some other information, is presented in a table inside the back cover of this book. In that table, the elements are alphabetized according to their names, but duplicate entries appear under the initial letter of the symbols for the elements in Table 1.4.

The most important symbols for beginning students to learn are given in Figure 1.5. The names of these elements and their symbols must be memorized. The elements indicated by pink shading should be learned first. Don't bother to memorize the numbers shown in the boxes with the elements.

Chemists write symbols together in **formulas** to identify compounds. For example, the letters CO represent a compound of carbon and oxygen. Be careful to distinguish the formula CO from the symbol Co, which represents the element cobalt. The capitalization of letters is very important! Formulas are sometimes written with subscripts to tell the relative proportions of the elements present. For example, H_2O represents water, which has two atoms of hydrogen for every atom of oxygen present. More about formulas will be presented in Section 5.1.

Table 1.4 Elements Whose Names and Symbols Begin with Different Letters

Name	Symbol
Antimony	Sb
Gold	Au
Iron	Fe
Lead	Pb
Mercury	Hg
Potassium	K
Silver	Ag
Sodium	Na
Tin	Sn
Tungsten	W

EXAMPLE 1.7

Which of the elements of Table 1.4 are not among the most important elements to learn (see Figure 1.5)?

Solution

Antimony (Sb) and tungsten (W).

12

CHAPTER 1 ■ Basic Concepts

Figure 1.5 Elements Whose Names and Symbols Should Be Learned

The elements shown with a pink background are most important in this course. Those with a blue background are also important. It is not necessary to memorize the (atomic) numbers.



Snapshot Review



ChemSkill Builder
1.4. 3.1

- The first letter in a symbol for an element is always capitalized; the second letter, if any, is small (lowercase).
 - Memorize the names and symbols of the elements in Figure 1.5 by the end of the first few weeks of this course.

- A. How many different elements are represented in the formula CoCO_3 ?

1.5 The Periodic Table

In Section 1.2, we learned a few of the properties of sulfur and of iron. Do we have to learn the properties of all 100 or so elements individually, or are there some ways to ease that burden? For over 140 years, chemists have arranged the elements into groups with similar chemical characteristics, which makes it easier to learn their properties. This grouping of the elements has been refined to a high degree, and the modern **periodic table** is the result. A full periodic table is shown inside the front cover of this book. The elements numbered 104 and up in that table have only recently been produced and in such infinitely small quantities that their chemical properties are unmeasured. Therefore, we will almost totally ignore them in the remainder of this book.

1.5 ■ The Periodic Table**13**

We will explore several uses for the periodic table in this section, as well as a number of terms associated with it. This table will be used extensively throughout the rest of this course and in subsequent chemistry courses.

All the elements in any horizontal row of the periodic table are said to be in the same **period**. There are seven periods, the first consisting of just two elements. The second and third periods contain 8 elements each, and the next two contain 18 elements each. The sixth period has 32 elements (including 14 inner transition elements numbered 57 through 71, located at the bottom of the table), and the last period is not yet complete. The periods are conventionally numbered with the Arabic numerals 1 through 7 (Figure 1.6).

EXAMPLE 1.8

Which element begins the fourth period of the periodic table? Which element ends it? How many elements are in that period?

Solution

Potassium (K) begins the period, Krypton (Kr) ends it, and there are 18 elements in the period.

Practice Problem 1.8 Which element begins the second period of the periodic table? Which element ends it? How many elements are in that period?

The elements in any vertical column in the periodic table are in the same **group**, or **family**. They have similar chemical properties, which change gradually from each one to the one below it. In some groups, the elements are very

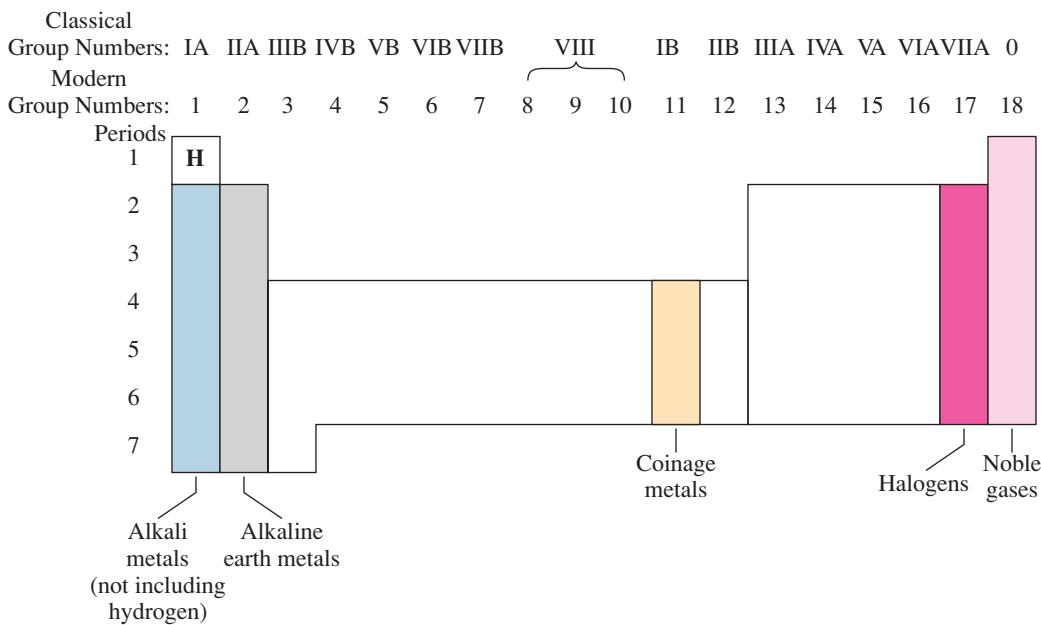


Figure 1.6 Groups and Periods

similar, in others, less so. The groups have been given two sets of group numbers (shown in Figure 1.6). The classical group numbers are Roman numerals followed by a letter A or B. These are more useful for beginning students in learning about atomic structure and bonding. The elements in two groups having the same number have some chemical similarities, especially in the formulas of some of their compounds. A chemical formula (Section 5.1) shows the ratio of atoms of each of its elements to every other element. For example, water, H_2O , has two hydrogen atoms for each of its oxygen atoms, and carbon dioxide, CO_2 , has one carbon atom for every two atoms of oxygen. Examples of the periodic similarities of compounds are BaO and CdO , with barium in group IIA and cadmium in group IIB, as well as KMnO_4 and KClO_4 , with manganese in group VIIB and chlorine in group VIIA. The modern group numbers are given as Arabic numerals. The classical group numbers will be used throughout this book, with the modern group numbers sometimes added in parentheses afterward.

Be careful. Some periodic tables have hydrogen located above fluorine as well as above lithium. Hydrogen is neither an alkali metal nor a halogen.

Five groups have family names (see Figure 1.6). The **alkali metals** include all the elements of group IA (1) except hydrogen. The **alkaline earth metals** are the elements of periodic group IIA (2), and the **coinage metals** are those of group IB (11). The **halogens** form group VIIA (17), and the **noble gases** constitute group 0 (18).

EXAMPLE 1.9

Is each of the following sets of elements in the same period or in the same group? Which set has the more similar chemical properties?

- (a) N, P, As (b) Li, C, F

Solution

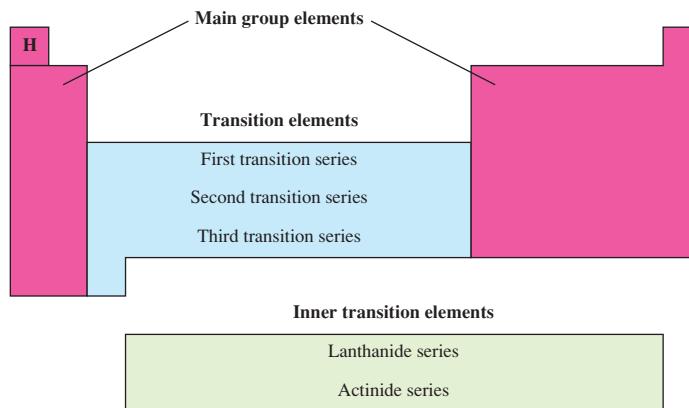
Set (b) is in the same period (2); set (a) is in the same group (VA). Set (a) has the more similar chemical properties.

Practice Problem 1.9 Is sulfur more likely to be similar to selenium (Se) or to chlorine in its chemical properties?

Another major classification of the elements in terms of the periodic table is shown in Figure 1.7. Three areas are defined and named the **main group elements**, the **transition elements**, and the **inner transition elements**. The main group elements are the simplest to learn about, and they will be studied first. The transition elements include some of the most important elements in our everyday lives, such as iron, nickel, chromium, zinc, and copper. The transition elements are often divided into four rows of elements, called the first, second, third, and fourth transition series. The elements of the fourth transition series except for actinium (Ac), and those of the main group elements above 112, are artificial; they are not found in nature. The two inner transition series fit into the periodic table in periods 6 and 7, right after lanthanum (La) and actinium (Ac), respectively. The inner transition elements include a few important elements, including uranium and plutonium. The first series of inner transition elements is called the lanthanide series, after lanthanum, the element that precedes

1.5 ■ The Periodic Table**15**

Figure 1.7 Main Group Elements, Transition Elements, and Inner Transition Elements



them; the second series is called the actinide series, after actinium, the element that precedes them. These elements are conventionally placed below the others so as not to make the periodic table too wide. None of the actinide elements to the right of uranium has been found in nature; they all are artificial. All of the elements in the actinide series are radioactive.

EXAMPLE 1.10

In what period are the actinide elements found?

Solution

The actinide elements, 90–103, follow element 89 and therefore are in period 7.

Practice Problem 1.10 In what period are the lanthanide elements found?

EXAMPLE 1.11

The symbols for how many transition elements are included in the periodic table inside the front cover of the text?

Solution

There are 37 (including the new artificial elements).

Practice Problem 1.11 How many inner transition elements are there?

We can also divide the elements into metals and nonmetals because each of these classes has some distinctive properties common to all their members. For example, metals generally have a metallic luster (a glossy or shiny appearance) and are generally malleable (can be pounded into thin sheets) and **ductile** (can be drawn into a wire); nonmetals are generally brittle. Metals conduct electricity; most nonmetals do not.

In the periodic table, the **metals** are to the left of a stepped line starting to the left of boron (B) and continuing downward and to the right, ending to the left of astatine (At) (Figure 1.8). Except for hydrogen, all the **nonmetals** are to the right of this line. As we can see, the metallic elements greatly outnumber the nonmetallic elements. The properties of the elements vary gradually across the periodic table. Several of the elements near the stepped line have some properties of metals and some properties of nonmetals; they are sometimes called **metalloids**.

EXAMPLE 1.12

Which of the following elements are metals, and which are nonmetals?

Solution

- (a) Calcium is a metal. (b) Phosphorus is a nonmetal.
(c) Nickel is a metal. (d) Carbon is a nonmetal.

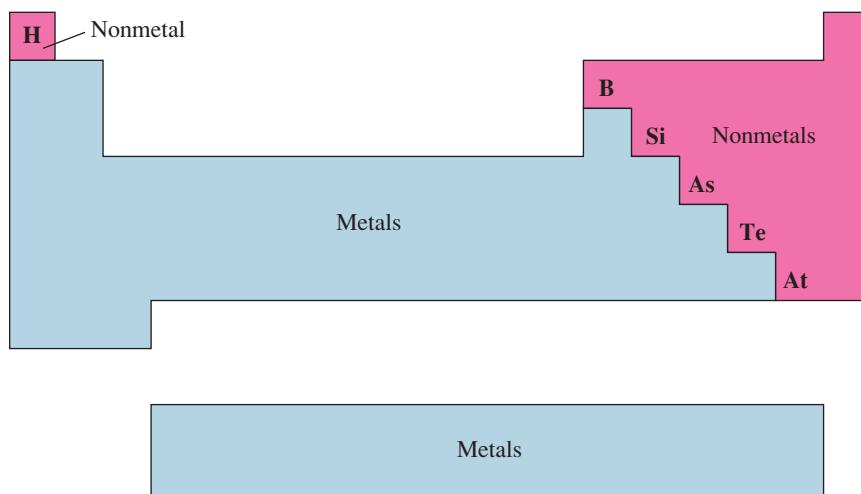
Practice Problem 1.12 Classify each of the following as metal or nonmetal:

- (a) The carbon in a “lead” pencil (b) Silver

Hydrogen is unique in its properties. It is placed on the side of the stepped line with the metals because it has many chemical properties similar to those of metals. In some periodic tables, it is also placed in another position, above the halogens, because of its nonmetallic chemical and physical properties. It actually does not fit comfortably in either position because it is neither an alkali metal nor a halogen, it is placed in the center on still other periodic tables to reflect its unique properties.

Figure 1.8 Metals and Nonmetals

The symbols adjacent to the stepped line are the metalloids.



1.6 ■ Laws, Hypotheses, and Theories**17****EXAMPLE 1.13**

Use the periodic table to identify each of the following:

- (a) The fifth element of the first transition series
- (b) The element of the fourth period that is also in group VB
- (c) The last lanthanide
- (d) The seventh transition element
- (e) The second actinide metal
- (f) The first element of group VIII
- (g) The third halogen
- (h) The first alkaline earth metal
- (i) The first coinage metal

Solution

- (a) Mn
- (b) V
- (c) Lu
- (d) Co
- (e) Pa
- (f) Fe
- (g) Br
- (h) Be
- (i) Cu

Practice Problem 1.13 Identify the second noble gas.

**Snapshot Review**

- The elements are classified in the periodic table for much the same reasons that matter is classified as described in Section 1.1.
 - Elements in the same periodic group have similar chemical properties.
 - Learn the nomenclature of the table. For example, when the instructor states that “main group elements are easiest to understand,” we must know which elements are in the main groups.
- A. What are the atomic numbers (the integers) of the third transition series of elements?
 - B. What element that is not naturally occurring has the smallest atomic number?

1.6 Laws, Hypotheses, and Theories

So many facts are available to scientists as they do experiments and observe natural phenomena that the data must be classified so that they can be learned and understood. When a large group of scientific observations is generalized into a single statement, that statement is called a **law**. For example, when a pen drops, it falls downward. When a ball drops, it falls downward. These and millions of other such observations are grouped together and generalized as the law of gravity. A law is a general statement about observable facts.

After organizing observed data into a law, scientists try to explain the law. A statement that attempts to explain why a law is true is called a **hypothesis**. If the hypothesis becomes generally accepted, it becomes a **theory**. Einstein explained the law of gravity with his theory of relativity. Laws and theories are

necessary because learning or remembering all the data that have been observed over the ages is impossible.

One of the most important laws in chemistry is the **law of conservation of mass**. This law states that, in any chemical reaction or physical change, the total mass present after the change is equal to the total mass present before the change. This law will be further explained in Section 3.1. Section 3.2 will present John Dalton's explanation of the law, in which he proposed that the particles that make up matter can rearrange themselves in various ways but cannot be created or destroyed. That explanation is a theory; it explains the law. If the particles that make up the materials before and after the change are the same, the total mass must also be the same.

The way new generalities are accepted by the scientific community as being true has been loosely codified into a system known as the **scientific method**. The steps of this method are

1. State the problem clearly.
2. Do further experiments. Many scientists test the generality with experiments, repeating each other's work and doing other experiments related to those.
3. Interpret the results. See if the generality explains all the results, new and old.
4. Accept the law. If all the data support the law, it is generally accepted by the scientific community as true. If later, further experiments are in conflict with the law, it is modified or abandoned altogether.

An example of how the scientific method works is the establishment of the law of constant composition of compounds, also called the law of definite proportions. The initial statement, based on the work of Antoine Lavoisier (1743–1794), was that every sample of a given compound is composed of the same percentage of each of its elements as any other sample of the same compound. That concept was subjected to many tests, in which other scientists measured and remeasured the compositions of many samples of a wide range of compounds. Claude-Louis Berthollet (1748–1822) showed that gaseous combinations of carbon and oxygen had compositions ranging from 27.29% carbon to 42.88% carbon; and thus the composition was not definite. He therefore stated that the proposed law was incorrect. However, Joseph Louis Proust (1754–1826) found that Berthollet's samples were *mixtures* of two compounds—carbon monoxide and carbon dioxide—and that when either compound was analyzed by itself, it always had the same composition. The law of definite proportions was firmly established by his work. An explanation of the law of definite proportions was proposed by John Dalton in 1803 (Section 3.2). His hypothesis generated a great deal of additional work, all of which supported his ideas, which made the hypothesis into a theory.

All samples of a given compound have the same percentage of each of its elements.



Snapshot Review

- Generalities about empirical observations are called *laws*; accepted explanations of these laws are called *theories*.

- A. Is the law of definite proportions (Chapter 3) an explanation or a collection of observations?

■ Summary**19**

Key Terms

Key terms are defined in the Glossary.

alkali metal (1.5)	group (1.5)	noble gas (1.5)
alkaline earth metal (1.5)	halogen (1.5)	nonmetal (1.5)
analytical chemistry (intro)	heterogeneous mixture (1.1)	organic chemistry (intro)
biochemistry (intro)	homogeneous mixture (1.1)	period (1.5)
chemical change (1.1)	hypothesis (1.6)	periodic table (1.5)
chemical property (1.2)	inner transition element (1.5)	physical change (1.1)
chemical reaction (1.1)	inorganic chemistry (intro)	physical chemistry (intro)
chemistry (1.3)	intensive property (1.2)	physical property (1.2)
coinage metal (1.5)	law (1.6)	property (1.2)
compound (1.1)	law of conservation of energy (1.3)	quantitative property (1.2)
definite composition (1.1)	law of conservation of mass (1.6)	scientific method (1.6)
dissolve (1.2)	main group element (1.5)	solution (1.1)
ductile (1.5)	malleable (1.2)	substance (1.1)
element (1.1)	mass (1.3)	symbol (1.4)
energy (1.3)	matter (1.3)	theory (1.6)
extensive property (1.2)	metal (1.5)	transition element (1.5)
family (1.5)	metalloid (1.5)	
formula (1.4)	mixture (1.1)	

Summary

Matter includes every material thing in the universe. To be able to understand such a wide variety of items, we must classify matter. Matter is divided into pure substances and mixtures. Pure substances may be elements or compounds. Mixtures may be either heterogeneous or homogeneous. Elements are the fundamental building blocks of matter and cannot be broken down to simpler substances by chemical or physical means. Compounds are chemical combinations of elements; they have their own sets of properties and have definite compositions. A physical combination of substances results in a mixture, whose components retain most of their properties. Mixtures do not have definite compositions. Homogeneous mixtures, called solutions, look alike throughout, but some parts of a heterogeneous mixture can be seen to be different from other parts. (Section 1.1)

Properties are the characteristics by which we can identify samples of matter. Intensive properties, such as color and brittleness, do not depend on the size of the sample, but extensive properties, such as volume, do. Intensive properties are more important in identifying substances. We can determine whether a combination of substances is a mixture or a compound by its properties. When we combine samples of matter, the result has more matter present than any of the original samples. When we break down a sample, each of the resulting products is composed of less matter than the starting sample. (Section 1.2)

Matter is anything that has mass and occupies space. Mass is a measure of the quantity of matter in a sample. The mass of an object does not change with its position in the universe. On the surface of the Earth, mass is directly proportional to weight, and we determine the mass of an object by “weighing” it. Energy is the ability to do work and comes in many forms (Table 1.3). Energy cannot be created or destroyed, but it can be converted from one form to another. Chemistry is the study of the interaction of matter and energy and the changes that matter undergoes. (Section 1.3)

Each element has a chemical symbol consisting of one or two letters. The first letter (or the only one) is always written as a capital letter; the second, if present, is always written as a lowercase (small) letter. Associating the names of the most important elements (shown in Figure 1.5) with their symbols, and their symbols with their names, is a necessary skill. (Section 1.4)

The periodic table is a classification scheme for elements that is tremendously useful in learning the properties of the elements. It consists of seven periods and 16 classical groups, or families (18 in a more modern but less useful version). Several of the groups have names, which beginning students need to learn. The elements are separated into metals and nonmetals on the periodic table. They are also subdivided into main group elements, transition elements, and inner transition elements. (Section 1.5)

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CHAPTER 1 ■ Basic Concepts

A statement that summarizes innumerable scientific facts and enables scientists to predict what will happen in a certain type of situation in the future is called a law. (For example, the law of gravity enables us to predict that if we drop something, it will fall downward. This law resulted from innumerable observations.) One of the most important

laws in chemistry is the law of conservation of mass, which states that mass cannot be created or destroyed in any chemical reaction or physical change. An explanation that is proposed to explain why a law works is called a hypothesis. If the explanation is accepted by the scientific community, it is known as a theory. (Section 1.6)

Items for Special Attention

- Be sure to use the correct capitalization and abbreviations throughout the study of chemistry. Small differences can completely change the meaning of a term. For example, Co and CO are different substances.
 - The word *homogeneous* does not necessarily refer to a homogeneous mixture. Most samples of pure substances are also homogeneous (but some, such as ice water, are heterogeneous).

- The elements in a given group of the periodic table have similar properties. This fact can help us learn a great deal of chemistry with less effort than would otherwise be required.
 - Like some groups of the periodic table, some portions of periods have special names. For example, the first transition series (elements 21–30) is part of the fourth period.

Answers to Snapshot Reviews

- 1.1 A. Because all compounds (a type of substance) have definite compositions and baking soda is a compound, it must have a definite composition.
 - 1.2 A. The lack of color is intensive; the volume, 1 liter (L), is extensive.
 - B. The property certainly helps identify the substance. Many people would guess that it is water without further data, but that is risky.

- 1.3 A. The automobile has the greater mass—there is more matter present.

1.4 A. Three (Co, C, and O).

1.5 A. 57 and 72–80
B. Po (84)

1.6 A. It is a collection of observations. That is why it is called a law.

Self-Tutorial Problems

- 1.1 A chemist in which branch of chemistry most often deals with the chemistry of compounds of carbon?
 - 1.2 Would it be considered unusual for an organic chemist to analyze a new compound, even though analysis is considered to be the function of an analytical chemist?
 - 1.3 Which of the following are samples of matter, and which are samples of energy?
 - (a) A tree
 - (b) A beam of light
 - (c) The exhaust gas from a car
 - (d) The output of an electric heater
 - 1.4 As seen in Figure 1.1, state which class of matter is *not* homogeneous.
 - 1.5 All brands of pure aspirin are the same compound. If you need aspirin, how should you choose a brand to buy?
 - 1.6 What property of water is most often desired to be affected by the presence in water solution of ethylene glycol, antifreeze?

- 1.7 Name as many properties of aluminum as you can think of. Indicate which ones are chemical properties.

1.8 Explain the difference between the results of hitting a piece of steel on a hard surface with a hammer and similarly hitting a pane of glass. Use the word *brittle* in your explanation.

1.9 How many elements are present in each of the following?

(a) HF and Hf (b) No and NO

(c) Si and SI₂ (d) PoCl₂ and POCl₃

(e) Ni(CO)₄ (f) NiCO₃

1.10 Cm is the chemical symbol for curium, named after the famous scientist Madam Curie. Why wasn't the symbol C, Cu, or Cr used instead?

1.11 Write the names from the symbols for the following:

(a) The first 18 elements in the periodic table

(b) The second 18 elements in the periodic table

(c) The rest of the elements shown in Figure 1.5

■ Problems**21**

1.12 Write the symbols from the names for the following:

- (a) The first 18 elements in the periodic table
- (b) The second 18 elements in the periodic table
- (c) The rest of the elements shown in Figure 1.5

1.13 Which classical periodic group number is used for each of the following families?

- | | |
|--------------------|---------------------------|
| (a) Alkali metals | (b) Alkaline earth metals |
| (c) Coinage metals | (d) Halogens |
| (e) Noble gases | |

1.14 Which classical transition group has the most elements?

1.15 Are the nonmetals main group elements, transition elements, or inner transition elements?

1.16 Do elements in the same period or elements in the same group have similar chemical properties?

1.17 Does each main group have more or fewer elements than a typical transition group?

1.18 (a) In which group of the periodic table is S?

- (b) In which period is S?

- (c) What type of element is S—a main group element, a transition element, or an inner transition element?

1.19 Why do scientists accept a new law?

- (a) Scientific societies accept it.
- (b) It explains most of the observations.
- (c) The government says to accept it.
- (d) Prominent scientists say to accept it.
- (e) Many scientists check the law and find it correct.

1.20 Calculate the percentage of main group elements in the periodic table.

Problems

1.1 Classification of Matter

1.21 (a) When pure water is cooled below 0°C (32°F), it freezes (solidifies). When the solid is warmed above that temperature, it melts again. Its composition does not change during the entire process. Are these chemical or physical changes?

(b) When gaseous ethylene is treated with a tiny quantity of a certain other substance, it solidifies. It is difficult to cause the solid to re-form a gas. Is the solidification a chemical or a physical change?

1.22 What kind of change—chemical or physical—is the dissolving of sugar in (a) hot tea? (b) iced tea?

1.23 What kind of change—chemical or physical—accompanies each of the following?

- (a) The conversion of two elements to a compound
- (b) The conversion of two compounds into a solution
- (c) The combination of an element and a compound into another compound
- (d) The conversion of a compound to an element and another compound
- (e) The separation of a mixture into its components

1.24 In a certain experiment, two separate samples of matter are mixed, and a great deal of heat is generated. Is this more likely to be a chemical or a physical change?

1.25 Classify each of the following as a compound or mixture. If it is impossible to tell, explain why.

- (a) A solid combination of iron and oxygen, no part of which is attracted by a magnet
- (b) A material containing 88.8% oxygen and 11.2% hydrogen

(c) A material that is explosive and that contains 88.8% oxygen and 11.2% hydrogen

(d) A material that consists of blue particles and red particles

(e) A material containing only hydrogen and oxygen that is a gas under ordinary room conditions

1.26 Classify each of the following as a compound or a mixture:

(a) Bubbling carbonated water

(b) Salt water

(c) Iced tea

(d) The liquid formed by a certain combination of oxygen and hydrogen gases

1.2 Properties

1.27 Bromine melts at -7.2°C ; sodium melts at 97.81°C . A certain combination of the two melts at 747°C . Is the combination a mixture or a compound?

1.28 Classify each of the following as an element, a compound, or a mixture:

(a) Solid iodine (a dark violet solid)

(b) A homogeneous combination of sodium and iodine that is a white solid

(c) A homogeneous combination of iodine and alcohol (tincture of iodine), which retains a dark color and the liquid state of the alcohol

1.29 If 3 dozen donuts costs \$10.50 and 10 dozen donuts costs \$35.00, is the price of donuts intensive or extensive?

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- 1.30 Classify the following materials as homogeneous or heterogeneous:
- White paint
 - Milk
 - Household ammonia (ammonia gas dissolved in water)
 - A glass of pure water containing an ice cube (also pure water)
 - A teaspoon of sugar in a glass of warm water after having been stirred thoroughly
 - A cola drink with no bubbles visible
 - A cola drink with bubbles
- 1.31 Electricity is passed through 14.40 grams (g) of a pure substance, and 5.66 grams of one material and 8.74 grams of another material are produced. Is the original substance an element or a compound?
- 1.32 Elemental nitrogen and hydrogen are both odorless.
- What is the odor of a mixture of the two gases?
 - Explain why ammonia, a compound of nitrogen and hydrogen only, smells so strongly.
- 1.33 Which of the following properties are extensive and which are intensive?
- | | |
|--------------------|----------------|
| (a) Length | (b) Color |
| (c) Price per unit | (d) Total cost |
| (e) Volume | (f) Mass |
| (g) Boiling point | (h) Speed |
- 1.34 Classify each of the following as a chemical change or a physical change:
- Melting ice by spreading salt on an icy sidewalk
 - Striking a match
 - Breaking a piece of metal by bending it back and forth
 - Baking a cake
 - Rubbing your hands together to get them warm
 - Using a tea bag
 - Cooking a hot dog
- 1.35 When some salt is added to water, a solution is formed. State several ways in which you can tell that the combination is a solution rather than a new compound.
- 1.36 List four or five properties you could use to distinguish between iron and aluminum. State which one(s) are chemical properties.
- 1.37 List four or five properties that enable us to distinguish between water and gasoline. State which one(s) are chemical properties.
- 1.38 A sample of a liquid is homogeneous. When it is cooled to 7°C, part of the liquid solidifies. The solid part is removed, and the liquid part is cooled further, but no other change takes place. Is the original liquid a compound or a solution?

CHAPTER 1 ■ Basic Concepts

- 1.39 A sample of a solid substance is heated under a stream of hydrogen gas, and a solid remains after the treatment that has a mass 63% of that of the original substance. Further treatment with hydrogen causes no further change. Is the original substance an element or a compound?
- 1.40 In the iron-sulfur experiment described in Section 1.2, heat was used to start a chemical reaction, which gave off more heat. Can you think of another example of a reaction that is started by heating and then gives off more heat?
- 1.41 When dinitrogen tetroxide, a colorless liquid, is warmed, a brown gas is formed. Is this change a chemical change or a physical change?
- ### 1.3 Matter and Energy
- 1.42 List as many kinds of energy as you can think of without consulting the text.
- 1.43 What is the mass of a 100-kilogram (kg) astronaut on the surface of the Moon, where gravity is 17% that on Earth?
- 1.44 For a given quantity of energy, the electricity produced by a battery is much more expensive than that provided by the electric company. Why do we still use batteries?
- 1.45 Explain the advantages and disadvantages of house current versus batteries for use in a home smoke detector.
- 1.46 How much energy is created when 1.00 kg of charcoal (mostly carbon) is burned in air?
- 1.47 What two changes in energy accompany the use of a flashlight?
- 1.48 Name a device commonly found on a car that changes:
- Chemical energy to electrical energy
 - Electrical energy to sound
 - Mechanical energy to heat
 - Electrical energy to chemical energy
 - Chemical energy to mechanical energy
 - Electrical energy to mechanical energy
 - Electrical energy to heat
- 1.49 Name one common device, not on a car, that performs each of the following conversions:
- Electrical energy to light
 - Electrical energy to sound
 - Chemical energy to heat
 - Chemical energy to mechanical energy
- ### 1.4 Chemical Symbols
- 1.50 Calculate the percentage of all elements in the Table of the Elements (inside back cover) whose names start with the letter P.

■ Problems

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- 1.51** How many elements are present in each of the following?
- OsSO_4
 - BN
 - NI_3
 - $\text{Sc}(\text{SCN})_3$
 - HF
 - Nb
 - CoCl_2
- 1.52** Beginning students often mix up the following elements. Give the name for each element.
- Mg and Mn
 - K and P
 - Na and S
 - Cu and Co
- 1.53** Write the symbol for each of the following elements:
- Mercury
 - Copper
 - Sodium
 - Antimony
 - Iron
 - Lead
 - Gold
 - Tungsten
 - Potassium
 - Silver
- 1.54** Without consulting any tables, write the names of the following elements:
- Fe and F
 - Ag and Au
 - Na and Ne
 - Sn and S
 - P and K
- 1.55** Name each of the following elements:
- Ag
 - Pb
 - K
 - W
 - Fe
 - Cu
 - Au
 - Na
 - Sb
 - Hg
- 1.56** Write the symbol for each of the following elements:
- Hydrogen
 - Helium
 - Lithium
 - Carbon
 - Nitrogen
 - Oxygen
 - Fluorine
 - Neon
 - Sodium
- 1.57** Without consulting any tables, write the symbols for the following elements:
- Potassium and phosphorus
 - Carbon, cadmium, and calcium
 - Boron, barium, and bismuth
 - Sodium and sulfur
 - Cobalt and copper
 - Magnesium and manganese
 - Iron and iodine
- ### 1.5 The Periodic Table
- 1.58** (a) What two elements are in group V of period 4?
 (b) What element(s) is (are) in group V of period 2?
- 1.59** Which element of periodic group IA is *not* an alkali metal?
- 1.60** Which of the following neighbors of nitrogen in the periodic table has chemical properties most like those of nitrogen—oxygen, carbon, or phosphorus?
- 1.61** Would you expect vanadium (V) or sulfur to act more like a typical metal?
- 1.62** Which two elements are most like potassium in chemical properties?
- 1.63** How many elements are in the first period of the periodic table? the second? the third? the fourth?
- 1.64** Which element is in group IV of the second transition series?
- 1.65** The formula of an oxide of phosphorus is P_2O_5 . Make an educated guess as to which one of the following formulas represents a real compound: S_2O_5 Ga_2O_5 As_2O_5
- 1.66** State the group number and period number of each of the following elements:
- Ca
 - Cd
 - Cl
- 1.67** Name the group and state the group number of each of the following elements:
- K
 - Ne
 - Be
 - Cl
 - Cu
- 1.68** Using the table inside the back cover of the text and the periodic table, determine:
- How many elements whose names start with the letter C are transition elements?
 - How many elements whose symbols start with the letter P are transition elements?
- 1.69** Using the table inside the back cover of the text and/or the periodic table, determine:
- How many elements whose names start with the letter S are main group elements?
 - How many elements whose symbols start with the letter P are inner transition elements?
- ### 1.6 Laws, Hypotheses, and Theories
- 1.70** Would an accepted generalization that explains why active metals react with acids be referred to as a law, hypothesis, or theory?
- 1.71** Suppose that you are a consultant to the National Science Foundation, an agency of the U.S. government. In a proposal for a \$1 million grant, a claim is made that a method will be developed to make 20 ounces (oz) of gold from 10 oz of gold and no other ingredients. Would you recommend that government money be spent on this proposed research? Explain your reasoning.
- 1.72** Suppose that you are a consultant to the National Science Foundation. In a proposal for a \$10 million grant, a claim is made that a method will be developed to make a machine that produces twice as much energy as it uses up, with no permanent changes in matter. Would you recommend that government money be spent on this proposed research? Explain your reasoning.

24**CHAPTER 1 ■ Basic Concepts****General Problems**

- 1.73 (a) A chemist in which branch of chemistry is most likely to determine the number of parts per million of an impurity in a city's drinking water?
- (b) A chemist in which branch of chemistry determines the electrical conductivity of a metal already prepared by another chemist?
- (c) A chemist develops a pharmaceutical to help patients with thyroid problems. In what branch of chemistry is this chemist working?
- 1.74 Na_2SO_4 is the formula for a certain sulfur compound. Which of the following formulas is most likely to be the formula for a chromium compound?
- (a) Na_3CrO_4 (b) Na_2CrO_4 (c) NaCrO_4
- 1.75 A chemist uses a compound of carbon, hydrogen, and oxygen to separate a metal from the rest of a sample to determine the metal's percentage in the sample. What branch of chemistry is the chemist practicing?
- 1.76 Ratios are generally intensive. Explain why.
- 1.77 (a) Predict the color of a solution of a blue substance dissolved in a yellow substance.
- (b) Can you predict the color of a compound of a blue substance and a yellow substance?
- (c) Explain your answers.

- 1.78 Explain the following statements sometimes made in everyday conversation:
- (a) "Oil and water do not mix."
- (b) "Gasoline and alcohol do not mix."
- 1.79 A nutritionist recommends more iron and less sodium in the diet of a patient with a blood problem. Does the nutritionist advocate eating iron metal, but not sodium metal? Explain.
- 1.80 What kind of electrical device has the advantage of portability like a dry cell but better economy?
- 1.81 (a) Count the number of each of the following types of elements in Figure 1.5: main group elements, transition elements, inner transition elements. Now calculate the percentage of each type important enough for you to learn of all the elements in that type. For example, what percentage of all the main group elements, is important for you to learn (from Figure 1.5)?
- (b) Which type of element do you think will be most important in this course? Which will be second most important?



Various types of laboratory glassware

2

Measurement

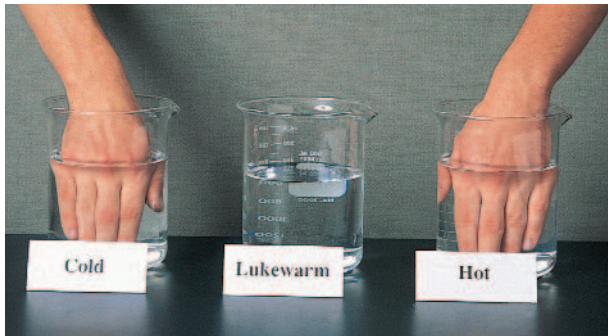
- 2.1 Factor Label Method
- 2.2 Exponential Numbers
- 2.3 The Metric System
- 2.4 Significant Digits
- 2.5 Density
- 2.6 Temperature Scales

Review Clues

- | | |
|-------------|--------------------|
| Section 2.1 | Appendix 1 |
| Section 2.2 | Appendix 1 |
| Section 2.3 | Appendix 1 |
| Section 2.4 | Elementary algebra |
| Section 2.5 | Elementary algebra |

Objectives

- | | |
|-----|--|
| 2.1 | To use the units of a measurement to help to do calculations involving that measurement |
| 2.2 | To use exponential notation to work with very large and very small numbers |
| 2.3 | To use the basic elements of the metric system—a system of units and prefixes designed to make scientific calculations as easy as possible |
| 2.4 | To use the correct number of digits to indicate the precision of a measurement or a calculated result |
| 2.5 | To calculate density, volume, or mass, given the other two, and to use density to identify substances |
| 2.6 | To distinguish among Fahrenheit, Celsius, and Kelvin temperature scales |



(a)



(b)

Figure 2.1 Hot and Cold Experiment

When the hands are moved from position (a) to position (b), the hand from the cold water feels hot and the hand from the hot water feels cold, even though they are both in water of the same lukewarm temperature. Try it.

Measurement is the heart of modern science, and even the social sciences are becoming more quantitative. Measurements make identifications of substances more precise and enable more scientific generalities to be made. For example, even ancient peoples knew that when objects were dropped, they fell downward. Measurements involving gravity enabled Sir Isaac Newton (1642–1727) to determine that the same laws of gravity that govern the fall of an object here on Earth also govern the motions of the Moon and the planets in the solar system.

A simple project will convince anyone that measuring things quantitatively tells more than qualitative estimates, especially those made using the human senses: Fill one beaker with cold water, a second beaker with hot water, and a third beaker with a mixture of equal amounts of hot and cold water. Place one hand in the cold water and the other hand in the hot water at the same time (Figure 2.1). Leave them there for 2 minutes (min). Then place both hands in the mixed water. That water will feel hot to the hand originally in the cold water but cold to the hand originally in the hot water, even though both hands are now in the same water!

There are a wide variety of things to measure in science, and many ways to make the measurements. For example, the volume of a rectangular box can be calculated by measuring its length, width, and height, and multiplying the values together. The volume of a sphere can be measured by determining its radius and using the equation $V = \frac{4}{3}\pi r^3$. Measuring the radius directly might not be feasible, as for example with a bowling ball, so we might measure the diameter by placing the ball between two parallel boards (Figure 2.2a) and taking half of the distance between them, because the radius is half the diameter. Alternatively, we might measure the circumference and find r from that, using the equation $c = 2\pi r$ (Figure 2.2b). The total volume of a bunch of small pieces of copper can be measured by measuring the volume of a sample of water, placing the copper in the water, and measuring the total volume. The difference between the volumes is the volume of the copper (Figure 2.2c). (This method works only with samples that do not dissolve to form a solution.) Quantities other than volume are measured in a variety of other ways.

Several aspects of measurement will be considered in this chapter. First, Section 2.1 presents the factor label method, which makes calculations with measured quantities easier. This method will be used in the sections that follow and throughout the book. Next, in Section 2.2, we consider how to calculate with extremely large and extremely small numbers, using exponential notation. Section 2.3 introduces the metric system, a system of weights and measures

2.1 ■ Factor Label Method**27****Figure 2.2** Various Measurements

(a) Measuring the diameter of a bowling ball by placing it between two parallel boards and measuring the distance between the boards. (b) Measuring the circumference of a bowling ball, whereby the diameter may be calculated using $c = \pi d$. (c) Measuring the volume of irregularly shaped, insoluble objects by displacement of water. The volume of the copper shot is the total volume (shown) minus the volume of the water before the shot was added.



(a)



(b)



(c)

designed to make calculations as easy as possible. In Section 2.4, we discuss the accuracy and precision of measurements and how the precision should be reported, using the proper number of significant digits. The concept of density, considered in Section 2.5, not only is useful in itself, especially for identifying substances, but also enables us to apply the concepts presented in previous sections. Finally, Section 2.6 briefly discusses temperature scales.

The measurement of energy will be discussed in Section 14.3, and kinetic energy will be treated in Section 12.10.

2.1 Factor Label Method

Use units in reporting all measurements and the results of calculations using them. Always use full spellings or standard abbreviations for all units.

Every measurement results in a number and a **unit**. Reporting the unit is just as important as reporting the number. For example, it makes quite a bit of difference whether a pet is 6 *inches* tall or 6 *feet* tall! The units are an integral part of any measurement, and from the outset, we must get used to stating the units for every measured quantity and for every quantity calculated from measured data. Always use full spellings or standard abbreviations for all units.

In a great many cases, we can use the units as a clue to which operation—multiplication or division—to perform in calculations with measured quantities. The units of measurement can be treated as algebraic quantities in calculations. For example, we can calculate the total wages of a student aide who has earned 9 dollars per hour for 30 hours of work, as follows:

$$\text{Total wages} = (\text{hours worked})(\text{hourly rate})$$

$$= 30 \text{ hours} \left(\frac{9 \text{ dollars}}{1 \text{ hour}} \right) = 270 \text{ dollars}$$

The unit *hours* (h) in the time cancels the unit *hour* in the rate, leaving the unit *dollars* in the answer. Each unit is treated as a whole, no matter how many letters it contains. Moreover, for the units to cancel, it does not matter if the unit is singular (such as hour) or plural (such as hours). If we did not know the equation to calculate the total wages, we could have put down the time with the unit *hours* and multiplied by the rate of pay, which has the unit *hour* in its denominator. The units tell us that we must multiply!

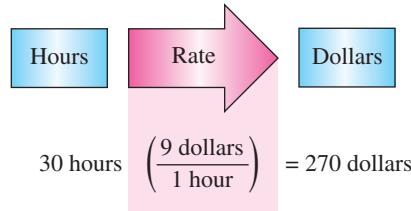
The previous calculation is an example of the use of the **factor label method**, also called **dimensional analysis**, in which a quantity is multiplied by a factor equal or equivalent to 1. The units included in the factor are the labels. In the previous example, \$9 is equivalent to 1 hour (h), and the calculation changes the number of hours worked to the equivalent number of dollars. To use the factor label method, first put down the given quantity, then multiply by a **conversion factor** (a rate or ratio) that will change the units given to the units desired for the answer. The factor may be a known constant or a value given in the problem.

To summarize the steps of the factor label method:

1. Put down the *quantity* given (or, occasionally, a ratio to be converted).
2. Multiply the quantity by one or more factors—rates or ratios—which will change the units *given* to those *required* for the answer. The conversion factors may be given in the problems, or they may be constants of known value.

To use the factor label method effectively, we must know the units of all the quantities involved.

Small diagrams that show the initial units and the final units connected by the conversion factor are used in many places in this book to show how to change a quantity from one of the units to the other. For example, for calculating the student aide's total wages, we can use the following diagram:



Diagrams like this will accompany many of the solutions to the in-text examples. To solve the practice problems and the problems at the end of the chapter, make your own diagrams if necessary.

EXAMPLE 2.1

Change 5445 minutes to hours.

Solution

Put down the quantity given and then multiply it by a factor (which in this case is known) that changes minutes to hours. The factor should have the unit

2.1 ■ Factor Label Method**29**

minutes in the denominator to cancel the *minutes* in the quantity given. It should also have the unit *hour* in the numerator so that the answer is in hours:

$$5445 \text{ minutes} \left(\frac{1 \text{ hour}}{60 \text{ minutes}} \right) = 90.75 \text{ hours}$$

Any units in the denominator are divided into units in the numerator, just as any number in the denominator is. Any units and any numbers in the numerator are multiplied. (If a quantity, such as 5445 minutes, is given with no denominator, the quantity is considered to be in a numerator.)

Practice Problem 2.1 Change 5445 minutes to seconds (s).

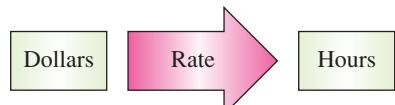
A ratio or rate may be inverted (turned upside down) if the units that need to be canceled call for that.

EXAMPLE 2.2

Calculate the time required for a student aide to earn \$483 at \$11.50 per hour.

Solution

First, put down the quantity given; then multiply it by a factor involving the rate:



$$483 \text{ dollars} \left(\frac{1 \text{ hour}}{11.50 \text{ dollars}} \right) = 42.0 \text{ hours}$$

In this case, the inverse of the rate of pay (the factor used previously to calculate total wages) is employed. Rates or ratios can be used either right side up or upside down; getting the units to cancel properly will indicate which form to use. Just be sure that the number in the rate (such as 11.50) stays with the proper unit (dollars).

Practice Problem 2.2 Calculate the time required to travel 15.0 miles at 60.0 miles per hour (mph).

EXAMPLE 2.3

Explain why the factor label method works, using the conversion of \$2.67 to cents as an example.

Solution

Consider this equality:

$$1 \text{ dollar} = 100 \text{ cents}$$

Dividing both sides of this equation by \$1 yields

$$1 = \frac{100 \text{ cents}}{1 \text{ dollar}}$$

Anything divided by itself is equal to 1, so the left side of this equation is 1. The right side of the equation is thus equal to 1 and therefore may be used to multiply any quantity to change its *form* without changing its *value*.

$$2.67 \text{ dollars} \left(\frac{100 \text{ cents}}{1 \text{ dollar}} \right) = 267 \text{ cents}$$

In any factor, the numerator is equal or equivalent to the denominator, so the value of the number multiplied is not changed, even though the units are.

EXAMPLE 2.4

In the United States, troy weight is used to measure gold and silver and avoirdupois weight is used for most other things. Given that

$$1 \text{ troy pound} = 12 \text{ troy ounces}$$

$$1 \text{ avoirdupois pound} = 16 \text{ avoirdupois ounces}$$

and that ounces in the two systems are *almost* the same weight, calculate the number of (a) troy ounces in 2.50 troy pounds. (b) the number of avoirdupois ounces in 2.50 avoirdupois pounds.

Solution

$$2.50 \text{ troy lb} \left(\frac{12 \text{ troy oz}}{1 \text{ troy lb}} \right) = 30.0 \text{ troy oz}$$

$$2.50 \text{ avoirdupois lb} \left(\frac{16 \text{ avoirdupois oz}}{1 \text{ avoirdupois lb}} \right) = 40.0 \text{ avoirdupois oz}$$

Practice Problem 2.4 (a) Which weighs more, a pound of bricks or a pound of lead. (b) Which weighs more, a pound of gold or a pound of lead.

It may be necessary to use more than one factor to get a desired answer. The factors may be used in separate steps or may be combined in a single step.

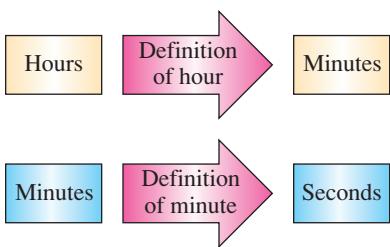
EXAMPLE 2.5

Calculate the number of seconds in 5.175 h.

Solution

$$5.175 \text{ hours} \left(\frac{60 \text{ minutes}}{1 \text{ hour}} \right) = 310.5 \text{ minutes}$$

$$310.5 \text{ minutes} \left(\frac{60 \text{ seconds}}{1 \text{ minute}} \right) = 18,630 \text{ seconds}$$



2.1 ■ Factor Label Method**31**

Alternatively,

The diagram illustrates two equivalent conversion paths from hours to seconds.

Path 1: Hours → Definition of hour → Minutes → Definition of minute → Seconds

$$5.175 \text{ hours} \left(\frac{60 \text{ minutes}}{1 \text{ hour}} \right) = 310.5 \text{ minutes} \left(\frac{60 \text{ seconds}}{1 \text{ minute}} \right) = 18,630 \text{ seconds}$$

Path 2: (Hours → Minutes) → (Minutes → Seconds)

$$5.175 \text{ hours} \left(\frac{60 \text{ minutes}}{1 \text{ hour}} \right) \left(\frac{60 \text{ seconds}}{1 \text{ minute}} \right) = 18,630 \text{ seconds}$$

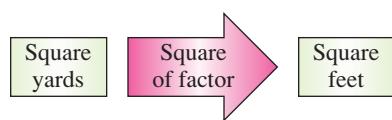
In this particular problem, it does not matter if we press the equal key on the calculator after entering the first 60. Similarly, we can write down the 310.5 min or not write it down, as we please, but the final answer is still the same.

Practice Problem 2.5 Calculate the number of seconds in exactly 7 weeks.

A factor can be raised to a power if the units to be converted require that. Remember that when a ratio in parentheses is raised to a power, *all the numbers and all the units* within the parentheses must be raised to that power.

EXAMPLE 2.6

How many square feet (ft^2) are in 12.0 square yards (yd^2)?

Solution

$$\begin{aligned} & 12.0 \text{ yd}^2 \left(\frac{3 \text{ ft}}{1 \text{ yd}} \right)^2 \\ & = 12.0 \text{ yd}^2 \left(\frac{9 \text{ ft}^2}{1 \text{ yd}^2} \right) = 108 \text{ ft}^2 \end{aligned}$$

The second factor can be derived as follows:

$$\begin{aligned} 3 \text{ ft} &= 1 \text{ yd} \\ (3 \text{ ft})^2 &= (1 \text{ yd})^2 \\ 3^2 \text{ ft}^2 &= 1^2 \text{ yd}^2 \\ 9 \text{ ft}^2 &= 1 \text{ yd}^2 \end{aligned}$$

Note that the number 3 is squared, the unit *feet* is squared, the number 1 is squared, and the unit *yard* is squared. There are 9 ft^2 in 1 yd^2 (Figure 2.3).

Practice Problem 2.6 How many cubic feet (ft^3) of cement can be held in a cement mixer with a capacity of 7.34 cubic yards (yd^3)?

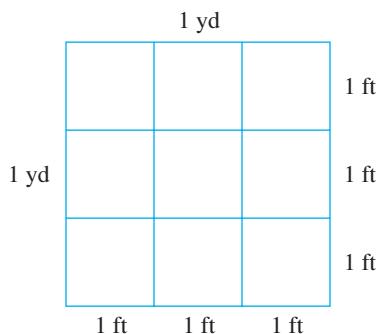
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Figure 2.3 Number of Square Feet in a Square Yard

(not actual size) Each side of the square is 1 yard long or 3 feet long. The area is the square of these, 1 yd^2 or 9 ft^2 .

A ratio may be changed to an equivalent ratio with different units by applying the factor label method.

EXAMPLE 2.7

Change 75 mph to feet per second.

Solution

$$\frac{75 \text{ miles}}{1 \text{ hour}} \left(\frac{5280 \text{ feet}}{1 \text{ mile}} \right) \left(\frac{1 \text{ hour}}{60 \text{ minutes}} \right) \left(\frac{1 \text{ minute}}{60 \text{ seconds}} \right) = \frac{110 \text{ feet}}{\text{second}}$$

Practice Problem 2.7 Calculate the speed in miles per hour of a runner who runs the 100- yd dash in 8.53 s.

The use of percentages as factor labels is presented in Appendix 1.

Many more examples of the use of the factor label method will be presented in the sections that follow, where we will work problems involving quantities that are directly proportional to each other. The method can be expanded to quantities that are equivalent to each other. For example, its use with percentages is presented in Appendix 1 and with moles of substances in Section 7.3.



ChemSkill Builder 2.5

Snapshot Review

- In the factor label method, units may be canceled like variables (x, y) in algebra. Placement of the units so that they cancel to give the desired units is the essence of the method.
- Some factors are constant, such as the number of cents in a dollar; others are variable, such as the number of miles traveled by a car per hour, and these must be given in the statement of a problem.

- A. (a) Calculate the number of quarters (\$0.25) in \$22.75. (b) Calculate the value in dollars of 144 quarters.

2.2 Exponential Numbers

Objects of scientific interest range from incredibly tiny to almost unimaginably large. The number of iron atoms that would fit side by side on a line 1 inch (2.54 cm) in length is about 100 million (Section 13.1). The number that could

2.2 ■ Exponential Numbers**33**

be packed into a volume of 1 inch³ is 100 million cubed—about 1 million billion billion! Each iron atom is almost unimaginably small.

EXAMPLE 2.8

To get an idea of how large a number 1 billion is, calculate the number of years it would take to spend \$1 billion if a person spent \$1000 per day. (Assume that there is no interest or other addition to the \$1 billion.)

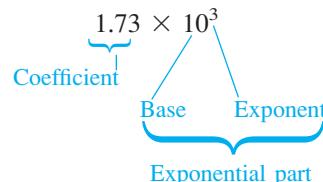
Solution

$$1,000,000,000 \text{ dollars} \left(\frac{1 \text{ day}}{1000 \text{ dollars}} \right) \left(\frac{1 \text{ year}}{365 \text{ days}} \right) = 2740 \text{ years}$$

It would take over 2700 years to spend \$1 billion by spending \$1000 a day! Just think how large the number 100 billion or 1 million billion billion is. Some numbers common in science are even larger than these.

Practice Problem 2.8 Calculate the amount of money that you would have to spend *per second* to use up \$10 billion in 100 years.

Scientists handle large and small numbers using **exponential notation**. A number written in this format has the following parts:



The **coefficient** is an ordinary number that may or may not include a decimal point. It is multiplied by an **exponential part**, consisting of a **base** and an **exponent**. For numbers used in scientific work, the base is usually 10, and the exponent is usually an integer (a whole number). The coefficient is multiplied by the base the number of times given by the exponent. That is, the number in the example is 1.73 multiplied three times by 10:

$$1.73 \times 10^3 = 1.73 \times 10 \times 10 \times 10 = 1730$$

Table 2.1 lists important exponential parts and their meanings. Thus we can write 1 million in exponential notation as follows:

$$1,000,000 = 1 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 = 1 \times 10^6$$

Table 2.1 Important Exponential Parts and Their Meanings

Exponential Part	Value	Meaning
10^{-9}	0.000000001	One-billionth
10^{-6}	0.000001	One-millionth
10^{-3}	0.001	One-thousandth
10^{-2}	0.01	One-hundredth
10^{-1}	0.1	One-tenth
10^0	1	One
10^1	10	Ten
10^2	100	One hundred
10^3	1000	One thousand
10^6	1,000,000	One million
10^9	1,000,000,000	One billion

In standard exponential notation, the coefficient is 1 or more but less than 10.

Scientists generally report numbers in exponential notation with coefficients that have one and only one integer digit, and that digit is not zero. That is, the coefficient is a number that is greater than or equal to 1 and less than 10. Numbers in this format are said to be written in **standard exponential form**, or **scientific notation**. A scientific calculator gives exponential numbers in this form, unless “engineering format” is selected. See Appendix 1 for methods of handling numbers in exponential format with a scientific calculator.

EXAMPLE 2.9

Which one(s) of the following numbers is (are) written in scientific notation?

- (a) 0.131×10^8 (b) 73×10^3 (c) 2.01×10^4 (d) 1.66×10^0
(e) $1.001 \times 10^{2.5}$

Solution

- (a) The number 0.131×10^8 is not in scientific notation because the integer digit of its coefficient is zero.
- (b) The number 73×10^3 is not in scientific notation because its coefficient is a two-digit integer.
- (c) The number 2.01×10^4 is in scientific notation because the coefficient has only one integer digit and the exponent is an integer.
- (d) The number 1.66×10^0 is in scientific notation. The zero exponent is permitted.
- (e) The number $1.001 \times 10^{2.5}$ is not in scientific notation because the exponent is not an integer.

Practice Problem 2.9 Which of the following numbers is in scientific notation?

- (a) $4.000 \times 10^{2.1}$ (b) 0.500×10^3 (c) 6.51×10^{-2}

To enter a number in exponential notation on an electronic calculator, enter the coefficient, press the EXP or EE key, then enter the exponent. *Do not* press the multiplication key \times or the [1] and [0] keys. See Appendix 1. If a number is given in exponential notation without a coefficient, a coefficient of 1 is assumed. Thus, 10^6 is 1 million. (Some electronic calculators require a coefficient of 1 to be entered.)

EXAMPLE 2.10

How many times should the multiplication key be pressed to solve the following problem?

$$(2.9 \times 10^{12})/(1.71 \times 10^7)$$

Solution

None. (Press the EXP or EE key twice.)

Changing the Form of Exponential Numbers

The *form* of an exponential number may be changed without changing its *value*. For example, 1.25×10^4 can be changed to another coefficient times 10^3 or a different coefficient times 10^2 , and so on:

$$\begin{aligned} 1.25 \times 10^4 &= 1.25 \times 10 \times 10 \times 10 \times 10 \\ &= 1.25 \times 10 \times (10 \times 10 \times 10) = 12.5 \times 10^3 \\ &= 1.25 \times 10 \times 10 \times (10 \times 10) = 125 \times 10^2 \\ &= 1.25 \times 10 \times 10 \times 10 \times (10) = 1250 \times 10^1 \\ &= 1.25 \times 10 \times 10 \times 10 \times 10 = 12,500 \times 10^0 = 12,500 \end{aligned}$$

In the first conversion, we multiplied the coefficient by one of the tens and ended up with one fewer ten in the exponential portion of the number. The *values* of all these numbers are the same; only their *format* is different. We may need to change to different formats when we add or subtract exponential numbers, or we can use a scientific calculator.

We can *increase* either the coefficient or the exponential part of a number by any factor without changing the number's overall value if we *reduce* the other part by the same factor. A simple working rule allows changing the format of a number in exponential notation: Move the decimal point in the coefficient *to the right n places and reduce the exponent n units*, or move the decimal point in the coefficient *to the left n places and increase the exponent n units*.

Move the decimal point in the coefficient to the right n places and reduce the exponent n units,
or
move the decimal point in the coefficient to the left n places and increase the exponent n units.

EXAMPLE 2.11

Change the format of each of the following numbers to scientific notation:

- (a) 237×10^4 (b) 0.0141×10^{-1} (c) 300.3×10^0

Read the instruction manual for your calculator to learn to change numbers in decimal format to scientific notation.

Solution

- The decimal point must be moved two places to the *left*, so the exponent is *increased* by 2: 2.37×10^6 .
- The decimal point has to be moved two places to the *right*, so the exponent is *reduced* by 2: 1.41×10^{-3} .
- The coefficient is reduced by a factor of 100 (equal to 10^2), and the exponential part is increased by the same factor: 3.003×10^2 .

Practice Problem 2.11 Change the format of each of the following numbers to scientific notation:

- (a) 0.0110×10^7 (b) 240×10^3 (c) 0.000123×10^1

Multiplication and Division of Exponential Numbers

To multiply numbers in exponential format, we multiply the coefficients and the exponential parts separately. To multiply exponential parts, the exponents are *added*. For example, let's multiply 4.0×10^3 and 1.5×10^4 :

$$\begin{aligned}(4.0 \times 10^3) \times (1.5 \times 10^4) &= (4.0 \times 1.5) \times (10^3 \times 10^4) \\ &= 6.0 \times 10^{3+4} = 6.0 \times 10^7\end{aligned}$$

It's easy to see that if we multiply three tens by four tens, we get seven tens:

$$\begin{aligned}10^3 \times 10^4 &= (10 \times 10 \times 10) \times (10 \times 10 \times 10 \times 10) \\ &= 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 = 10^7\end{aligned}$$

EXAMPLE 2.12

Multiply the following numbers, and express the answers in scientific notation:

- $(2.0 \times 10^3) \times (3.0 \times 10^4)$
- $(4.0 \times 10^3) \times (5.0 \times 10^5)$
- $(6.0 \times 10^7) \times (1.5 \times 10^4)$

Solution

- $(2.0 \times 10^3) \times (3.0 \times 10^4) = 6.0 \times 10^7$
- $(4.0 \times 10^3) \times (5.0 \times 10^5) = 20 \times 10^8 = 2.0 \times 10^9$
- $(6.0 \times 10^7) \times (1.5 \times 10^4) = 9.0 \times 10^{11}$

Practice Problem 2.12 Multiply the following numbers and express the answers in scientific notation:

- $(4.5 \times 10^7) \times (4.0 \times 10^7)$
- $(6.0 \times 10^3) \times (3.5 \times 10^4)$
- $(2.0 \times 10^8) \times (2.7 \times 10^7)$

2.2 ■ Exponential Numbers**37**

To divide exponential numbers, we divide the coefficients and the exponential parts separately. To divide exponential parts, we subtract the exponents.

EXAMPLE 2.13

Divide 7.0×10^6 by 3.5×10^3 .

Solution

$$(7.0 \times 10^6)/(3.5 \times 10^3) = (7.0/3.5) \times 10^{6-3} = 2.0 \times 10^3$$

We can see that this procedure is correct:

$$\begin{aligned}\frac{7.0 \times 10^6}{3.5 \times 10^3} &= \frac{7.0 \times 10 \times 10 \times 10 \times 10 \times 10}{3.5 \times 10 \times 10 \times 10} \\ &= 2.0 \times 10 \times 10 \times 10 = 2.0 \times 10^3\end{aligned}$$

Practice Problem 2.13 Divide 1.6×10^4 by 6.4×10^2 .

We can apply this procedure to calculate the quotient of two exponential numbers even when the denominator has a larger magnitude than the numerator. For example, let's divide 8.0×10^5 by 4.0×10^7 . The rule for dividing exponential numbers gives the following result:

$$(8.0 \times 10^5)/(4.0 \times 10^7) = 2.0 \times 10^{5-7} = 2.0 \times 10^{-2}$$

What does the negative exponent mean? Writing out all the expressions enables us to see:

$$\begin{aligned}\frac{8.0 \times 10^5}{4.0 \times 10^7} &= \frac{8.0 \times 10 \times 10 \times 10 \times 10 \times 10}{2.0 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10} \\ &= 2.0 \times \left(\frac{1}{10 \times 10}\right) = 0.020 = 2.0 \times 10^{-2}\end{aligned}$$

The negative exponent means to *divide* the coefficient by the base a certain number of times.

EXAMPLE 2.14

Calculate the quotient of $(9.5 \times 10^3)/(5.0 \times 10^3)$.

Solution

By the rule for division of exponential numbers:

$$\frac{9.5 \times 10^3}{5.0 \times 10^3} = 1.9 \times 10^0$$

By cancellation:

$$\frac{9.5 \times 10^3}{5.0 \times 10^3} = \frac{9.5 \times 10 \times 10 \times 10}{5.0 \times 10 \times 10 \times 10} = 1.9$$

A positive exponent indicates that the exponential part of the number is greater than 1, a negative exponent indicates that it is less than 1, and a zero exponent indicates that it is equal to 1.

Because $1.9 = 1.9 \times 10^0$, it is apparent that 10^0 is equal to 1.

Practice Problem 2.14 What is the decimal value (the value with no power of 10 shown) of 6.13×10^0 ?

EXAMPLE 2.15

Change the format of each of the following numbers to scientific notation:

(a) 0.0050×10^{-4} (b) 100.0×10^{-2} (c) 30.03×10^{-5}

Solution

- The decimal point has to be moved three places to the *right*, so the exponent is *reduced* by 3: 5.0×10^{-7} .
- The decimal point must be moved two places to the *left*, so the exponent is *increased* by 2: 1.000×10^0 .
- The coefficient is reduced by a factor of 10 (equal to 10^1), and the exponential part is increased by the same factor: 3.003×10^{-4} .

Practice Problem 2.15 Change the format of each of the following numbers to scientific notation:

(a) 0.101×10^{-6} (b) $200,000 \times 10^{-3}$ (c) 0.00300×10^0

The rules for multiplication and division need to be stated slightly differently to allow for negative exponents. To multiply exponential parts, add the exponents *algebraically*. To divide exponential parts, subtract the exponents *algebraically*. The word *algebraically* means “with due regard for the signs.”

EXAMPLE 2.16

Divide 6.0×10^5 by 2.0×10^{-4} .

Solution

$$\frac{6.0 \times 10^5}{2.0 \times 10^{-4}} = 3.0 \times 10^{5-(-4)} = 3.0 \times 10^9$$

Instead of dividing a negative exponent by changing its sign and adding, we may transfer the *exponential part* of a number from numerator to denominator or from denominator to numerator if we simply change the sign of the exponent:

$$\frac{6.0 \times 10^5}{2.0 \times 10^{-4}} = \frac{6.0 \times 10^5 \times 10^{+4}}{2.0} = 3.0 \times 10^9$$

Practice Problem 2.16 Divide 3.0×10^{-5} by 7.5×10^{-3} .

Addition and Subtraction of Exponential Numbers

When we add or subtract numbers in exponential notation, *the exponents must be the same.* (This rule is related to the rule that requires numbers being added or subtracted to have their decimal points aligned.) The answer is then the sum or difference of the coefficients times the same exponential part as in each number being added or subtracted. (The calculator does this operation automatically, but we must know what is happening in order to report the proper number of significant digits [see Section 2.4].)

EXAMPLE 2.17

Add (a) $6.22 \times 10^4 + 2.13 \times 10^4$, (b) $6.00 \times 10^5 + 5.55 \times 10^5$, and (c) $9.13 \times 10^4 + 2.5 \times 10^3$.

Solution

$$\begin{array}{r}
 (a) \quad 6.22 \times 10^4 \\
 + 2.13 \times 10^4 \\
 \hline
 8.35 \times 10^4
 \end{array}$$

Same exponent
 Sum of coefficients

Because the exponents are the same, the coefficients are simply added. The answer has the same exponential part as each number added.

$$\begin{array}{r}
 (b) \quad 6.00 \times 10^5 \\
 + 5.55 \times 10^5 \\
 \hline
 11.55 \times 10^5 = 1.155 \times 10^6
 \end{array}$$

Because the coefficient of the answer has a value greater than 10, the form must be changed to get the answer into scientific notation.

$$\begin{array}{r}
 (c) \quad 9.13 \times 10^4 \\
 + 0.25 \times 10^4 \quad \text{Coefficient and exponent amended to allow addition} \\
 \hline
 9.38 \times 10^4
 \end{array}$$

Because the exponents are not the same, one of them must be changed to equal the other. Of course, we cannot change only the exponent because that would change the value of the number. We can move the decimal point one place to the left in 2.5×10^3 (making the coefficient smaller) and increase the exponent by one (making the exponential part larger). The value of the number is unchanged, but its format is now suitable for the addition we want to do.

Practice Problem 2.17 Subtract (a) $6.11 \times 10^4 - 8.22 \times 10^4$ and (b) $6.43 \times 10^4 - 5.1 \times 10^3$.

Raising an Exponential Number to a Power

To raise an exponential number to a power, we raise both the coefficient and the exponential part to the power. We raise an exponential part to a power by *multiplying* the exponent by the power.

EXAMPLE 2.18

Calculate the cube of 2.0×10^5

Solution

$$\begin{aligned}(2.0 \times 10^5)^3 &= (2.0)^3 \times (10^5)^3 = (2.0)^3 \times 10^{5 \times 3} \\ &= 8.0 \times 10^{15} \\ (2.0 \times 10^5)^3 &= (2.0 \times 10^5)(2.0 \times 10^5)(2.0 \times 10^5) \\ &= 8.0 \times 10^{15}\end{aligned}$$

Practice Problem 2.18 Calculate the value of $(3.0 \times 10^{-3})^2$.

Taking the square root of a number is equivalent to raising the number to the $\frac{1}{2}$ power. In general, the n th root of a number is the number to the $1/n$ power.

EXAMPLE 2.19

Calculate the square root of 2.25×10^{-4} .

Solution

$$\sqrt{2.25 \times 10^{-4}} = 1.50 \times \sqrt{10^{-4}} = 1.50 \times (10^{-4})^{1/2} = 1.50 \times 10^{-2}$$

Practice Problem 2.19 Calculate the cube root of 8.00×10^6 .



Snapshot Review



ChemSkill Builder 2.1

- In addition or subtraction, the units must be the same and the exponents must be the same to merely add the coefficients for the proper result.
- A. Report the following numbers in standard exponential form: (a) 1234, (b) 200.0, and (c) 0.0200.
- B. Do the following calculations
- $1.67 \times 10^3 + 4.2 \times 10^2$
 - $(1.25 \times 10^3)/(8.40 \times 10^2)$
 - $1.6 \times 10^{-3} - 4.20 \times 10^{-2}$

2.3 The Metric System

The **metric system** and its more modern counterpart **SI** (for *Système International d'Unités*) are systems of units designed to make calculations as easy as possible. It was designed to make every word mean one and only one thing. Its subdivisions and multiples of units are powers of 10 times a primary unit. Each of its prefixes means the same thing, no matter what unit it is attached to. The abbreviations for the quantities and prefixes are easy to remember. All these features have been built into the metric system to make it easy. Contrast this lack of ambiguity with the ambiguity in the English system, as illustrated in Example 2.4.

Learning the following six words is essential to understanding the metric system:

- | | |
|----------|-----------|
| 1. meter | 4. centi- |
| 2. gram | 5. milli- |
| 3. liter | 6. kilo- |

(A few more words will be added as we progress.) Meter, gram, and liter are the units of length, mass, and volume, respectively, in the metric system. Just as the English system has subdivisions of its primary units (12 inches [in.] in a foot, for example), so does the metric system. But the metric system uses prefixes that mean the same thing no matter what primary unit they are used with. Centi-, milli-, and kilo- are prefixes that indicate certain multiples or divisions of any primary unit. Other less important prefixes are given along with these in Table 2.2.

The **meter** is the primary unit of length in the metric system. Its abbreviation is m. The meter is defined in such a way that it can be duplicated precisely in any well-equipped laboratory in the world. It had been defined as the distance between two marks on a metal bar kept at the Bureau of Weights and Measures in Paris. (It now has an even more precise definition.) A meter is 39.37 in. long—3.37 in. longer than a yard.

A **standard** is an agreed upon quantity with which like quantities can be compared. For example, the *meter* is the agreed standard of length, to which other lengths can be compared. In the measurement of most quantities, the

Table 2.2 Metric Prefixes*

Prefix	Abbreviation	Meaning	
Giga-	G	One billion	1,000,000,000
Mega-	M	One million	1,000,000
Kilo-	k	One thousand	1000
Deci-	d	One-tenth	0.1
Centi-	c	One-hundredth	0.01
Milli-	m	One-thousandth	0.001
Micro-	μ	One-millionth	0.000001
Nano-	n	One-billionth	0.0000000001
Pico-	p	One-trillionth	0.000000000001

*The most important prefixes for most chemistry courses are given in **boldface** type.

Figure 2.4 One-Kilogram Samples

Note that the same masses of strawberries, water, cubes of sugar, iron, nails, and copper pennies have different volumes.



primary unit is also the standard. With mass, however, the standard is different from the unit. The **gram** is the primary unit of mass in the metric system. The gram, abbreviated g, is such a small mass that the kilogram has been chosen as the legal standard of mass in the United States and as the worldwide standard in SI. Mass is measured by comparison with standard masses. The kilogram (kg) is a mass equivalent to about 2.2 pounds (lb) (Figure 2.4).

The **cubic meter** (m^3) is the primary unit of volume in SI. A smaller unit, the **liter**, is the primary unit of volume in the metric system. The abbreviation for liter is L. We need to know both the cubic meter and the liter. Table 2.3 summarizes the primary metric units of distance, mass, and volume.

The prefix *centi-* means one-hundredth of any primary unit. For example, a centimeter (cm) is 0.01 m, and a centigram (cg) is 0.01 g.

The prefix *milli-* means one-thousandth. No matter which primary unit it is used with, it always means 0.001 times that unit. A millimeter (mm) is 0.001 m, a milliliter (mL) is 0.001 L, and so on.

The prefix *kilo-* means 1000 times the primary unit, no matter which primary unit it is used with. For example, a kilogram (kg) is 1000 g, and a kilometer (km) is 1000 m.

Table 2.3 Primary Metric Units

	Unit	Symbol	Equivalencies
Distance	Meter	m	
Mass	Gram	g	
Volume	Liter	L	
Volume	Cubic meter	m^3	$1000 \text{ L} = 1 \text{ m}^3$
Volume	Cubic centimeter	cm^3	$1000 \text{ cm}^3 = 1 \text{ L}$

EXAMPLE 2.20

Which is bigger—1 Mg or 1 mg?

Solution

$$1 \text{ Mg} = 1,000,000 \text{ g} \text{ (see Table 2.2)}$$

$$1 \text{ mg} = 0.001 \text{ g}$$

A megagram (Mg), equal to a metric ton, is a billion times larger than a milligram (mg).

The metric system is easier to use than the English system.

EXAMPLE 2.21

- (a) How many meters are in 5.200 km?
- (b) How many yards are in 5.200 miles?

Solution

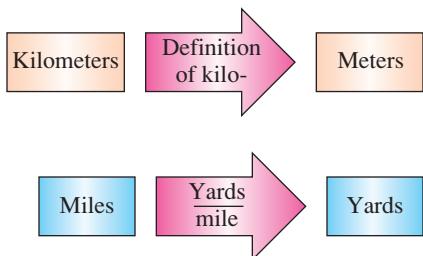
We can use the factor-label method (Section 2.1) to do these metric calculations.

$$(a) 5.200 \text{ km} \left(\frac{1000 \text{ m}}{1 \text{ km}} \right) = 5200 \text{ m}$$

$$(b) 5.200 \text{ miles} \left(\frac{1760 \text{ yards}}{1 \text{ mile}} \right) = 9152 \text{ yards}$$

The metric system problem, part (a), can be solved without paper and pencil—by moving the decimal point in 5.200 three places to the right. The English system conversion, part (b), requires that we remember the number of yards per mile (harder than the 1000 m/km metric conversion factor) and that we use pencil and paper or a calculator to do the arithmetic. The conversion factor 1000 is used for kilograms, kiloliters, kilowatts, and any other factor involving the prefix *kilo-*. The English conversion factor 1760 yd/mile is not used in any other conversion.

Practice Problem 2.21 (a) How many centimeters are in 2.370 m?
 (b) How many inches are in 2.370 ft? (c) For which of these two conversions do we need to use a calculator?



To convert a value expressed in a primary metric unit to its equivalent in a subunit, or vice versa, use a conversion factor with a 1 in front of the sub-unit and the equivalent value in front of the main unit. Note that either the prefix abbreviation or its equivalent is in front of the symbol for the primary unit:

Prefix	Equivalent value
Kilo	1000
Centi	0.01
Milli	0.001

44**CHAPTER 2 ■ Measurement**

For example, either of the following conversion factors is correct:

$$\left(\frac{1 \text{ centimeter}}{0.01 \text{ meter}} \right) \left(\frac{0.01 \text{ meter}}{1 \text{ centimeter}} \right)$$

Thus, to convert 729 cm to meters:

Note that 1 centi- (1 c) means 0.01.

$$729 \text{ cm} \left(\frac{0.01 \text{ m}}{1 \text{ cm}} \right) = 7.29 \text{ m}$$

To convert 1.66 m to centimeters:

$$1.66 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 166 \text{ cm}$$

EXAMPLE 2.22

Convert 75.0 g to (a) kilograms and (b) milligrams.

Solution

$$(a) 75.0 \text{ g} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.0750 \text{ kg}$$

$$(b) 75.0 \text{ g} \left(\frac{1 \text{ mg}}{0.001 \text{ g}} \right) = 75,000 \text{ mg}$$

Practice Problem 2.22 Calculate the number of (a) meters in 6.66 km, (b) liters in 6.66 kL, and (c) grams in 6.66 kg. (d) Highlight the differences among these three problems and comment on the ease of the metric system.

Some conversions between metric and English system units are presented in Table 2.4. Engineers must know how to do such conversions because they still use some English system units. However, scientists rarely use English system units, and therefore, these conversions are less important for them. (The use of a metric unit that is slowly becoming familiar to the general public is shown in Figure 2.5. Note that 80 km/h is about 50 mph.)

Table 2.4 Metric-English Conversions

Length	Mass	Volume
1 m = 39.37 in.	1 kg = 2.2045 lb (avoirdupois)	1 L = 1.059 qt
2.540 cm = 1 in.	453.6 g = 1 lb (avoirdupois)	29.57 mL = 1 fl oz
1.609 km = 1 mile = 1760 yd = 5280 ft	28.35 g = 1 oz (avoirdupois) 31.103 g = 1 oz (troy)* 1 metric ton = 2204.5 lb (avoirdupois)	3.777 L = 1 US gal 0.472 L = 1 US pt

*Troy weight is generally used for gold and silver.

2.3 ■ The Metric System**45**

The units must be the same for the addition or subtraction of numbers that represent measurements.

When we add or subtract measured quantities, we treat the units just as we treat variables (such as x , y , and z) in algebraic manipulations (see Appendix 1). The units must be the same for the addition or subtraction of numbers that represent measurements. A sum or difference will have the same units as the quantities being added or subtracted.



Figure 2.5 English and Metric Usage

The metric system is increasingly being used in everyday life in the United States, as illustrated by the automobile speedometer. Kilometers per hour are shown in smaller yellow digits.

EXAMPLE 2.23

Add (a) $7.13 \text{ m} + 0.45 \text{ m}$ and (b) $7.13 \text{ m} + 45 \text{ cm}$.

Solution

(a) The units are the same, so we simply add:

$$7.13 \text{ m} + 0.45 \text{ m} = 7.58 \text{ m}$$

(b) We must either change 7.13 m to centimeters or 45 cm to meters, and then add:

$$45 \text{ cm} \left(\frac{0.01 \text{ m}}{1 \text{ cm}} \right) = 0.45 \text{ m}$$

$$7.13 \text{ m} + 0.45 \text{ m} = 7.58 \text{ m}$$

Practice Problem 2.23 Add the following algebraic quantities:

- (a) $179x + 22x$ (b) $179x + 33.00y$, where $x = 0.10y$

To multiply or divide measured quantities of the same type, such as two lengths, we may have to convert the units so that they are the same. For quantities of different types, the units cannot be the same.

EXAMPLE 2.24

Multiply (a) $1.08 \text{ cm} \times 6.50 \text{ cm}$ and (b) $4.10 \text{ m} \times 32.5 \text{ cm}$.

Solution

(a) The units are already the same, so we just multiply:

$$1.08 \text{ cm} \times 6.50 \text{ cm} = 7.02 \text{ cm}^2$$

Note that both the numbers and the units are multiplied.

(b) The 4.10 m could be changed to centimeters, or the 32.5 cm could be changed to meters:

$$32.5 \text{ cm} \left(\frac{0.01 \text{ m}}{1 \text{ cm}} \right) = 0.325 \text{ m}$$

$$4.10 \text{ m} \times 0.325 \text{ m} = 1.33 \text{ m}^2$$



Practice Problem 2.24 Multiply the following algebraic quantities:

$$(1.08x)(6.50x)$$

How does the x in this problem resemble the unit in Example 2.24(a)?

EXAMPLE 2.25

The cost of a certain 75.00-cm gold chain is \$975.00. What is the cost per centimeter?

Solution

$$\frac{\$975.00}{75.00 \text{ cm}} = \$13.00/\text{cm}$$

Practice Problem 2.25 Divide the algebraic quantities: $(195x)/(15y^3)$.

Length or Distance

The primary unit of **length** in the metric system is the meter, which is 3.37 in. longer than a yard. The same prefixes are used with the meter as with all other metric units.

EXAMPLE 2.26

Olympic divers use 3.00-m boards and 10.00-m boards. Calculate these heights in centimeters.

Solution

A centimeter is 0.01 m, just as a cent is 0.01 dollar. There are 100 cm in 1 m, so in exactly 3 m, there are 300 cm:

$$3.00 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 300 \text{ cm}$$

In exactly 10 m, there are 1000 cm:

$$10.00 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 1000 \text{ cm}$$



Practice Problem 2.26 Calculate the heights of these Olympic diving boards in millimeters.

EXAMPLE 2.27

How many kilometers are in 206 m?

Solution

There are 1000 m in 1 km, by definition.

$$206 \text{ m} \left(\frac{1 \text{ km}}{1000 \text{ m}} \right) = 0.206 \text{ km}$$

Practice Problem 2.27 How many millimeters are in 1.04 cm?

**Mass**

As stated earlier, the primary unit of mass in the metric system is the gram. Because the gram is so small, however, the standard mass in SI and the legal standard in the United States is the kilogram.

EXAMPLE 2.28

How many grams are in 1 kg?

Solution

The prefix *kilo-* means 1000 of whatever it is attached to. Therefore, 1 kg is 1000 g.

Practice Problem 2.28 How many grams are in 1 mg?

EXAMPLE 2.29

Airlines usually have a 15-kg free-baggage allowance for overseas travelers.

(a) How many grams does this allowance represent? (b) How many pounds?

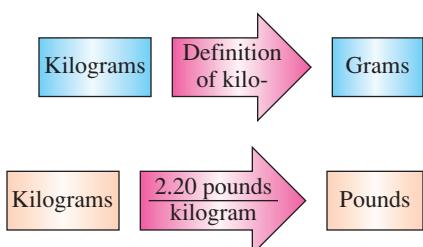
Solution

(a)

$$15 \text{ kg} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) = 15,000 \text{ g}$$

(b) From Table 2.4, we see that 1 kg = 2.20 lb:

$$15 \text{ kg} \left(\frac{2.20 \text{ lb}}{1 \text{ kg}} \right) = 33 \text{ lb}$$



Practice Problem 2.29 Calculate the mass of a 207-lb person in kilograms.

EXAMPLE 2.30

- Using data from Table 2.4, calculate the number of troy ounces in 1.000 kg.
- Using data from Table 2.4, calculate the number of avoirdupois ounces in 1.000 kg.

Solution

$$(a) 1.000 \text{ kg} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ troy ounce}}{31.103 \text{ g}} \right) = 32.15 \text{ troy ounces}$$

$$(b) 1.000 \text{ kg} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ avoirdupois ounce}}{28.35 \text{ g}} \right) = 35.27 \text{ avoirdupois ounces}$$

Practice Problem 2.30 (a) Which is heavier, a pound of lead or a pound of bricks? (b) Which is heavier, a pound of lead or a pound of gold? (c) Calculate the mass of each in grams.

Volume

Volume can be measured in two ways (Figure 2.6): (1) using the capacity of a certain container, and (2) using the space defined by a cube of length l on each side. The second method uses the cube of a length (and thus one possible unit for volume is the cube of a length unit). The volume of a rectangular solid is given by

$$\text{Volume} = \text{length} \times \text{width} \times \text{height}$$

$$V = l \times w \times h$$

A cube is a special case for which $l = w = h$, so the volume of a cube is $V = l^3$.

The metric system unit of volume is the liter (L), originally defined as the volume occupied by a cube exactly 10 cm on each side (see Figure 2.6). In SI, the cubic meter is the standard. Because the cubic meter is a rather large

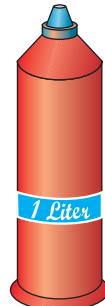
The only metric units that are cubed are units of length—any unit ending in m —to give a unit of volume.

Figure 2.6 Two Methods to Determine Volume

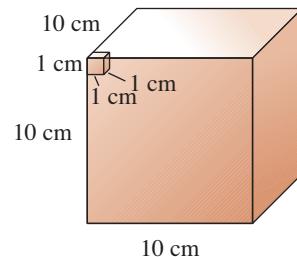
(not drawn to scale)

Note that

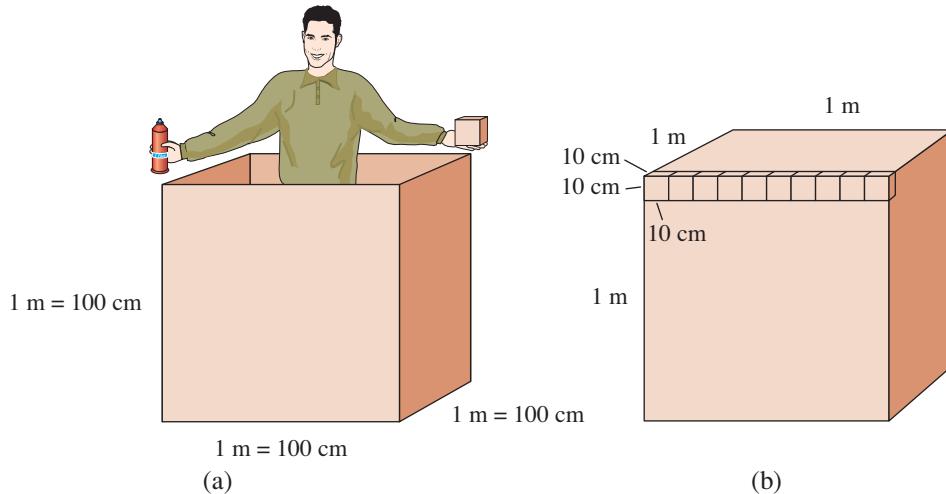
$$10 \text{ cm} \times 10 \text{ cm} \times 10 \text{ cm} = 1000 \text{ cm}^3.$$



1-liter bottle



1-liter cube

2.3 ■ The Metric System**49****Figure 2.7** Cubic Meter and Liter

(a) The man in the cubic meter box is holding two objects, each of which is 1 L in volume. Note the difference in size between 1 L and 1 m³. (b) A cubic meter has edges that are 1 m = 100 cm long. Thus the 1 m³ cube is $(100 \text{ cm})^3 = 1,000,000 \text{ cm}^3$ in volume. Ten boxes with 10-cm edges fit along each such edge. Ten rows of those 10-cm boxes would fit in a layer covering the whole top surface of the cubic meter, and ten layers would fill the whole volume. There is 1000 liters in a cubic meter.

volume (about half the capacity of a small cement truck), the liter is favored by chemists (Figure 2.7).

$$1.00 \text{ L} = (10 \text{ cm})^3 = 1000 \text{ cm}^3 = 1000 \text{ mL}$$

Thus,

$$1.00 \text{ cm}^3 = 1.00 \text{ mL}$$

and

$$1.000 \text{ m}^3 = 1000 \text{ L}$$

EXAMPLE 2.31

- (a) How many 1-L cubes fit along the top front edge of the cubic meter pictured in Figure 2.7?
- (b) How many fit on the front face?
- (c) How many such vertical layers are in the entire cube?
- (d) How many liters are in 1 m³?

Solution

- (a) Ten 1-L cubes fit along the edge.
- (b) One hundred (10×10) 1-L cubes fit in the 10 rows on the front face.
- (c) There are 10 layers from front to back.
- (d) One thousand ($10 \times 10 \times 10$) 1-L cubes fit into 1 m³. Thus,

$$1 \text{ m}^3 = 1000 \text{ L} = 1 \text{ kL}$$

Practice Problem 2.31 How many cubic centimeters are in 1 L?

EXAMPLE 2.32

Calculate the number of centimeters in 7.13×10^{-2} km.

Solution

$$7.13 \times 10^{-2} \text{ km} \left(\frac{1000 \text{ m}}{1 \text{ km}} \right) \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 7.13 \times 10^3 \text{ cm}$$

Practice Problem 2.32 Calculate the number of kilograms in 1.77×10^3 milligrams.

EXAMPLE 2.33

Calculate the volume of a 0.887 m^3 container in (a) liters and (b) cubic centimeters.

Solution

$$(a) 0.887 \text{ m}^3 \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) = 887 \text{ L}$$

$$(b) 0.887 \text{ m}^3 \left(\frac{1,000,000 \text{ cm}^3}{1 \text{ m}^3} \right) = 887,000 \text{ cm}^3 = 8.87 \times 10^5 \text{ cm}^3$$

Practice Problem 2.33 Calculate the volume of a 623-L container in cubic meters.

EXAMPLE 2.34

A *unit cell* is a small portion of a crystalline solid that, when repeated very many times, builds up an entire sample. A unit cell of a certain solid is cubic, with edge length $2.00 \times 10^{-10} \text{ m}$. How many unit cells does it take to occupy 1.00 cm^3 ?

Solution

The volume of the unit cell is

$$(2.00 \times 10^{-10} \text{ m})^3 = (2.00 \times 10^{-8} \text{ cm})^3 = 8.00 \times 10^{-24} \text{ cm}^3$$

The number of unit cells is therefore

$$1.00 \text{ cm}^3 \left(\frac{1 \text{ unit cell}}{8.00 \times 10^{-24} \text{ cm}^3} \right) = 1.25 \times 10^{23} \text{ unit cells}$$

**Snapshot Review**

ChemSkill Builder 2.4

- The metric system is easy because all the conversions are powers of 10, all the prefixes mean the same thing no matter what unit they are attached to, and all the symbols and abbreviations are meaningful.

- English-metric conversions are most often presented, if at all, to give an idea of the size of the metric unit. They are not used very much in this course.
 - Volume can be presented in liters (or its subdivisions) or in the cube of a unit of length (such as m^3 or cm^3). The *centi-* in cm^3 does *not* mean one-hundredth of $1\ m^3$, because the 0.01 must be cubed.
- A. Complete each of the following parts by inserting the correct metric unit:
- | | |
|---|-------------|
| (a) Volume of a can of soda | 0.366 _____ |
| (b) Height of a professional basketball player | 1.9 _____ |
| (c) Volume of water in a backyard swimming pool | 2.5 _____ |
| (d) Mass of a U.S. quarter (25¢) | 5.7 _____ |
- B. Calculate the number of (a) meters in 1234 mm, (b) liters in 1234 mL, and (c) grams in 1234 mg.
- C. Calculate the number of (a) liters in $0.175\ m^3$ and (b) liters in $315\ cm^3$.

2.4 Significant Digits

Scientific measurements are usually repeated three or more times. The average value of the measurements is probably closer to the true value than any one of them. The **accuracy** is the closeness of the average of a set of measurements to the true value. The **precision** is the closeness of all of a set of measured values to one another. A set of measurements may be precise without being accurate or accurate without being precise (if the measurer is very lucky), but the best measurements are both accurate and precise.

No matter how accurate our measuring tool, the accuracy of our measurements is limited. For example, an automobile odometer has divisions of 0.1 mile (or 0.1 km), and we can estimate to one-tenth of that smallest scale division, but we cannot measure 1 in. or even 1 ft with an odometer. Similarly, we cannot measure the thickness of a piece of paper with a ruler marked in centimeters.

EXAMPLE 2.35

A set of weighings is done with a bathroom scale that registers 2 lb with no load (Figure 2.8). Each weighing results in a reading of 117 lb.

- (a) Are the measurements precise?
- (b) Are the measurements accurate?
- (c) What is the probable true weight of the person?

Solution

- (a) The weighings are precise, because exactly the same answer (to the precision of the device) was obtained each time.
- (b) They are not accurate, because the no-load value was incorrect.
- (c) The true weight is probably 115 lb.

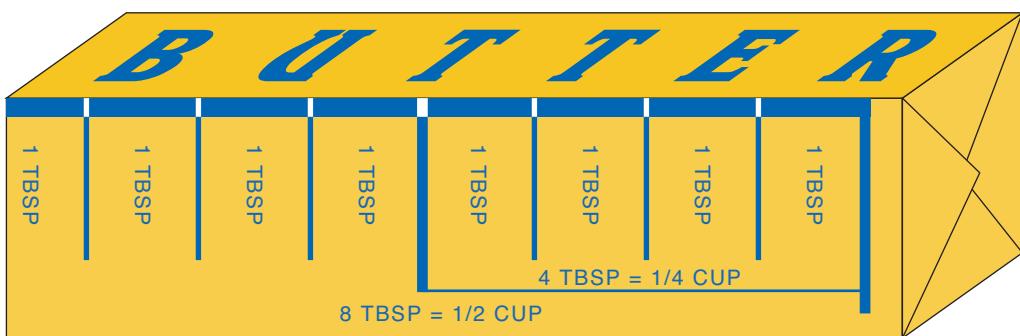
Figure 2.8 Bathroom Scale

If a bathroom scale is not adjusted to read zero when no load is on it, the results it yields with a load may be precise but probably not accurate. For example, if it reads 2 lb with no load, each time a person uses the scale, it will probably read 2 lb heavier than his or her true weight.



Practice Problem 2.35 A machine wraps sticks of butter with paper that is printed with lines marking 1-oz portions. If the machine wraps the butter one-eighth of an inch away from the correct position (Figure 2.9), the first portion might be too small and the last too large. Having 12 sticks of butter all wrapped by the same machine in the same way: (a) Will there be the same mass of butter at the first mark each time? (b) Will each portion be 1 oz in mass? (c) Is the wrapping more precise than accurate or vice versa?

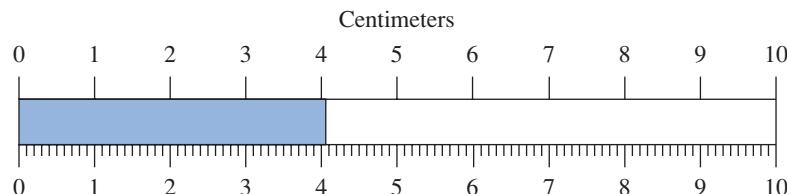
The precision with which we measure must be indicated when we report a measurement. When we use a measuring instrument, we must estimate to one digit beyond the smallest scale division, if possible. For example, see Figure 2.10. If we measure the length of the bar with the top ruler, calibrated in centimeters, we see that the bar is between 4 and 5 cm long and can estimate that it extends 0.1 cm past 4 cm, for a reading of 4.1 cm. In contrast, if we use the bottom ruler, calibrated in tenths of centimeters—that is, millimeters—we see that

**Figure 2.9** Precise but Inaccurate Measurement

If the wrapping machine regularly places the wrapper too close to one end of each stick of butter, the end piece might be the same weight in each stick but still be far from 1 tablespoon (TBSP).

2.4 ■ Significant Digits**53****Figure 2.10** Measurements of Different Precision

The smallest scale divisions on the bottom ruler are millimeters.



the length of the bar is between 4.0 and 4.1 cm. We estimate that it is 4.08 cm. We use the last digit to report that we used a ruler with a millimeter scale.

Suppose that the bar extended exactly to the 4.1 line on the millimeter ruler. How should we report the result? We should report 4.10 cm. If we omit the zero, someone reading the result will think that we used a ruler calibrated only in centimeters. The third digit indicates that the result was obtained on a more precise ruler, but just happened to be a value ending in zero.

EXAMPLE 2.36

About what fraction of measurements reported should be values ending in a zero?

Solution

About one time in 10 the last digit of a reported measurement should be a zero. (There is an equal possibility of each digit, 0–9, being the last, so one-tenth of the time it should be a zero, one-tenth of the time it should be a one, one-tenth of the time a two, and so on.)

Scientists report the precision of their measurements every time they write down a result. The number of digits they use consists of the absolutely certain digits plus one estimated digit. Every digit that reflects the precision of the measurement is called a **significant digit**, or **significant figure**. Note that the word *significant* has a different meaning here than in everyday conversation, where it means “important.”

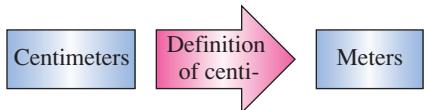
Sometimes, zeros are used merely to indicate the magnitude of a number (how big or small the number is). If the purpose of a zero is *only* to establish the magnitude of the number, that zero is not significant. Determining which zeros are significant in a properly reported measurement is important.

The following rules enable chemists to tell whether zeros in a number are significant or not:

1. Any zeros to the left of all nonzero digits (for example, in 0.03) are not significant.
2. Any zeros between significant digits (for example, in 903) are significant.
3. Any zeros to the right of all nonzero digits in a number with decimal place digits (for example, in 70.00) are significant.
4. Any zeros to the right of all nonzero digits in an integer (for example, in 4000) are uncertain. If they indicate only the magnitude of the measurement, they are not significant. However, if they also show something about the precision of the measurement, they are significant. We cannot tell whether they are significant merely by looking at the number.

EXAMPLE 2.37

A measurement of a bar yields a length of 4.84 cm. How many meters is that? How many significant digits are in the number of meters?

Solution

$$4.84 \text{ cm} \left(\frac{0.01 \text{ m}}{1 \text{ cm}} \right) = 0.0484 \text{ m}$$

Because the number of centimeters has three significant digits, there are three significant digits in the number of meters. The calculation changing the value from centimeters to meters does not change the precision with which the measurement was made. (That 0.01 m equals 1 cm is a *definition*, not a *measurement*.) The zeros in 0.0484 m are not significant; they merely show the magnitude of the number. (If they were not there, the value of the number would be different. They are *important*, but they are not *significant*; they do not tell anything about the precision of the measurement.)

Practice Problem 2.37 How many significant digits does the measurement 2.4 m have? If the measurement is changed to centimeters, how many significant digits will be in that value?

EXAMPLE 2.38

Underline the significant digits in each of the following measurements. If a digit is uncertain, place a question mark under it.

- (a) 0.0020 m (b) 1.200 m (c) 10.002 m (d) 6000 m

Solution

- (a) 0.0020 m

The zeros to the left of the two are not significant (rule 1), but the one to the right is (rule 3).

- (b) 1.200 m

The zeros to the right of the two are significant (rule 3).

- (c) 10.002 m

Zeros between significant digits are significant (rule 2).

- (d) 6000 m

???

The 6 is certainly significant. The zeros to the right of all other digits in an integer are uncertain; they may reflect the precision or just the magnitude of the number. Without further information, it is impossible to tell (rule 4).

Practice Problem 2.38 Underline the significant digits in each of the following measurements. If a digit is uncertain, place a question mark under it.

- (a) 35.00 cm (b) 203.50 cm (c) 30.20 cm (d) 30 cm

2.4 ■ Significant Digits**55****EXAMPLE 2.39**

How many significant digits are in each of the following measurements?

- (a) 3.5 m (b) 3.50 m (c) 3.500 m

Solution

- (a) Two (b) Three (c) Four

The zeros in the numbers of parts (b) and (c) do not affect the magnitude; they must therefore show something about the precision of the measurements (rule 3).

EXAMPLE 2.40

Change each of the measurements given in meters in Example 2.39 to millimeters. How is it possible to tell how many significant digits are in each result?

Solution

- (a) $3.5 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 3500 \text{ mm}$
(b) $3.50 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 3500 \text{ mm}$
(c) $3.500 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 3500 \text{ mm}$

There are two significant digits in the result for part (a), three in the result for part (b), and four in the result for part (c). We know these numbers of significant digits only because we know the numbers of significant digits in the original numbers of meters given in Example 2.39. However, if we just look at the results, they all look the same! We cannot tell just by looking whether the zeros reflect the precision of the measurement or not.

Significant Digits in Calculated Results

In this electronic age, we have come to depend on our electronic calculators for solving arithmetic problems. However, electronic calculators usually do not give the correct number of significant digits. (A calculator may give the correct number of significant digits just by chance.) Each of us is responsible for making sure that the number of significant digits in a calculated answer is correct.

Not only must our recorded data reflect the precision of the measurements, but any results calculated from the data must also reflect that precision. Two rules govern how many significant digits are permitted in calculated results and how to get that many digits.

ADDITION AND SUBTRACTION

In the answers to addition and subtraction problems, the estimated digit that is farthest to the left is the last digit that can be retained. For example, let's add 6.2 cm and 9.203 cm:

$$\begin{array}{r} \text{Estimated digits} \\ | \\ 6.2 \quad \text{cm} \\ + 9.203 \text{ cm} \\ \hline 15.403 \text{ cm} \rightarrow 15.4 \text{ cm} \\ | \end{array}$$

The leftmost estimated digit is the last digit that can be retained in the answer.

The digit 2 in 6.2 cm is an estimated digit; it has some uncertainty in it. Therefore, the digit 4 in the answer is also uncertain, and 0 and 3 are completely unknown. We cannot report the value 15.403 cm, or the reader will believe that 3 is the only uncertain digit. We must reduce the number of digits to leave 4 as the last digit. In general, we increase the last digit retained if the first digit to be dropped is 5 or greater; otherwise we leave that last digit unchanged.

Thus, for addition or subtraction, we retain digits in an answer only as far to the right as the leftmost uncertain digit in any of the numbers being added or subtracted. Note that the *number* of significant digits does not matter for addition or subtraction; what matters is *where the last digits lie*. In the previous calculation, there are two significant digits in the first number and four in the second, but the answer has three.

EXAMPLE 2.41

Calculate the sum of 10.10 cm + 1.332 cm + 6.4 cm.

Solution

$$\begin{array}{r} 10.10 \text{ cm} \\ 1.332 \text{ cm} \\ 6.4 \text{ cm} \\ \hline 17.832 \text{ cm} \rightarrow 17.8 \text{ cm} \end{array}$$

Practice Problem 2.41 Calculate the answer to the proper precision:

$$62.44 \text{ cm} - 7.145 \text{ cm} + 27.7 \text{ cm}$$

MULTIPLICATION AND DIVISION

For multiplication and division, the number of significant digits in the factor with the fewest significant digits limits the number of significant digits in the answer. For example, let's multiply 4.1 cm by 21.07 cm:

$$4.1 \text{ cm} \times 21.07 \text{ cm} = 86.387 \text{ cm}^2 \quad (\text{Incorrect number of significant digits})$$

2.4 ■ Significant Digits**57**

If we just leave the answer the way our electronic calculator gives it to us, anyone could assume that the measurement had been carried out with a precision of 1 part in 86,387, which is not true. We must reduce the number of significant digits in the answer to two because the factor with fewer significant digits has two. Thus, we change the answer to 86 cm^2 .

EXAMPLE 2.42

Do the following calculations, and report the answers to the correct number of significant digits:

(a) $2.171 \text{ cm} \times 4.20 \text{ cm}$ (b) $4.92 \text{ g}/1.64 \text{ cm}^3$

Solution

- (a) The answer is 9.12 cm^2 . We have to reduce the number of digits in 9.1182 cm^2 to three significant digits, because the second factor has only three significant digits.
- (b) The answer is 3.00 g/cm^3 . It must have three significant digits because both the dividend (4.92) and the divisor (1.64) have three significant digits. In this case, *add two zeros* to the answer given by the electronic calculator (3) to get the correct number of significant digits.

Practice Problem 2.42 Perform the following calculations and limit the answers to the correct number of significant digits:

(a) $1.27 \text{ cm} \times 6.220 \text{ cm} \times 4.10 \text{ cm}$
(b) $9.030 \text{ g}/(3.01 \text{ cm} \times 1.414 \text{ cm} \times 7.500 \text{ cm})$

The usual rules for handling significant figures are often not used with sums of money because (1) dollars and cents are counting numbers rather than measurements (for example, a price of \$7.15 means exactly \$7.15 and not a value nearer to \$7.15 than to \$7.14 or \$7.16); and (2) amounts in dollars are customarily stated with two decimal places or none, but not with other numbers of decimal places. Very large or very small costs may be stated using the usual rules for significant digits. Because money calculations are seldom used in chemistry courses (they are used in this chapter to introduce the factor label method with familiar examples), the student need not be concerned with these exceptions from the usual rules.

Numbers that are definitions and not measurements, such as the number of centimeters in a meter (100) or the number of radii in the diameter of a circle (2), are exact numbers. They do not limit the number of significant digits in a calculated result.

EXAMPLE 2.43

The radius of a circle is 13.7 cm. Calculate the diameter of the circle to the correct number of significant digits.

Solution

$$d = 2r = 2(13.7 \text{ cm}) = 27.4 \text{ cm}$$

The *measurement* with the fewest significant digits is 13.7 cm. (It is the only measurement in the problem.)

Practice Problem 2.43 Calculate the number of milligrams in 8.011 g.

Rounding Off

Reducing the number of digits to the number permitted involves a process called *rounding off*, often referred to simply as **rounding**. The process most often involves dropping one or more digits to the right of the decimal point and adjusting the last remaining digit if necessary.

Rule

- If the leftmost digit to be dropped is greater than or equal to 5, we increase the last retained digit by 1 without regard to the sign of the number.
- If the leftmost digit to be dropped is less than 5, we do not change the final digit that is retained.

Example

Round each of the following measurements to two *decimal places*:

- | | |
|----------------|----------|
| (a) 8.5561 cm | 8.56 cm |
| (b) 8.5550 cm | 8.56 cm |
| (c) -8.5561 cm | -8.56 cm |
| (a) 8.5543 cm | 8.55 cm |
| (b) -8.5543 cm | -8.55 cm |

EXAMPLE 2.44

Round off each of the following lengths to retain two significant digits:

- (a) 2.68 m (b) 2.62 m (c) 2.65 m

Solution

- (a) 2.7 m (b) 2.6 m (c) 2.7 m

Where a rounded digit lies in relation to the decimal point is immaterial, as long as it is to the right of the decimal point.

Practice Problem 2.44 Round off each of the following lengths to retain three significant digits:

- (a) 1.177 m (b) 1.173 m (c) 1.175 m

Rounding of integer digits is a little different!

Sometimes integral digits must be dropped. If the digits to be rounded are to the left of the decimal point rather than to the right, they are changed to (non-significant) zeros rather than being dropped. However, quantities greater than 10 are better expressed in scientific notation (Section 2.2).

EXAMPLE 2.45

Round off each of the following values to two significant digits:

- (a) 6742 cm (b) 6773 cm (c) 6750 cm

Solution

- (a) 6700 cm (b) 6800 cm (c) 6800 cm

In each case, the digits rounded are changed to nonsignificant zeros, not dropped.

Practice Problem 2.45 The state of Colorado is essentially a rectangle, measuring 623 km from east to west and 444 km from north to south. Calculate the area of Colorado to three significant digits.

If a problem has both addition or subtraction and multiplication or division, the part that is done first must have its significant digits noted before the next operation is performed, because the rules are different for determining which digits are retained.

If addition or subtraction is done first, the *number* of significant digits in the sum or difference is used to determine the number in the operation to follow. If multiplication or division is done first, the *position* of the last significant digit is noted to help determine the last significant digit in the next answer. In multipart problems in the rest of this text, to avoid excessive round off errors, at least one extra digit will be retained (if it is nonzero) until the final answer. Those digits will be written in *italic* type.

EXAMPLE 2.46

Find the result of each of the following calculations to the proper number of significant digits:

$$(a) \frac{(80.21 \text{ g} - 79.93 \text{ g})}{65.22 \text{ cm}^3} \quad (b) (92.12 \text{ mL})(0.912 \text{ g/mL}) + 223.02 \text{ g}$$

Solution

- (a) The subtraction is done first, yielding an answer that has only two significant digits:

$$\begin{array}{r} 80.21 \text{ g} \\ - 79.93 \text{ g} \\ \hline 0.28 \text{ g} \end{array}$$

That value is divided by 65.22 cm³, yielding an answer with two significant digits: 0.0043 g/cm³.

- (b) The multiplication is done first, yielding a value with one significant digit after the decimal point.

$$\begin{aligned} (92.12 \text{ mL})(0.912 \text{ g/mL}) + 223.02 \text{ g} \\ = 84.01 \text{ g} + 223.02 \text{ g} = 307.0 \text{ g} \end{aligned}$$

The final answer thus is limited to one significant digit after the decimal point.

Practice Problem 2.46 Find the result of the following calculation to the proper number of significant digits:

$$(21.33 \text{ cm})(4.44 \text{ cm})(1.91 \text{ cm}) + 3.12 \text{ cm}^3$$

The rules for significant digits in logarithms are presented in Appendix 1.

Another advantage to scientific notation is that all digits of the coefficient of a number in scientific notation are significant. The exponent determines the magnitude of the number, so any zeros present in the coefficient must be significant.

EXAMPLE 2.47

How can we resolve the difficulty presented in Example 2.40?

Solution

One way to resolve this problem is to report the values in scientific notation, where all digits of the coefficient are significant: (a) 3.5×10^3 mm, (b) 3.50×10^3 mm, (c) 3.500×10^3 mm.

Practice Problem 2.47 Report the number of grams in each of the following quantities in such a way that the proper number of significant digits is obvious:

- (a) 1.2 kg (b) 1.20 kg (c) 1.200 kg

EXAMPLE 2.48

Calculate the result of each of the following problems to the correct number of significant digits:

(a) $1.41 \times 10^7 \text{ g} - 5.98 \times 10^6 \text{ g}$

(b) $\frac{1.41 \times 10^7 \text{ g} - 5.98 \times 10^6 \text{ g}}{6.35 \times 10^4 \text{ cm}^3}$

Solution

(a) $14.1 \times 10^6 \text{ g} - 5.98 \times 10^6 \text{ g} = 8.12 \times 10^6 \text{ g} = 8.1 \times 10^6 \text{ g}$

(b) $\frac{1.41 \times 10^7 \text{ g} - 5.98 \times 10^6 \text{ g}}{6.35 \times 10^4 \text{ cm}^3} = 1.3 \times 10^2 \text{ g/cm}^3$

Because two different rules are used for the subtraction and division, note that the numerator of part (b) has only two significant digits, as shown in part (a). Therefore the quotient has only two significant digits.

Practice Problem 2.48 Calculate the result of each of the following problems to the proper numbers of significant digits:

(a) $3.8 \times 10^4 \text{ cm} - 5.55 \times 10^3 \text{ cm}$

(b) $(3.8 \times 10^4 \text{ cm})(5.55 \times 10^3 \text{ cm})$

(c) $3.8 \times 10^{-4} \text{ cm} - 5.55 \times 10^{-3} \text{ cm}$



Snapshot Review



ChemSkill Builder 2.2

- The precision that was used in a measurement is reflected in the number of significant digits reported.
 - The rules for significant digits in addition and subtraction are different from those in multiplication and division.
 - Significant digits and decimal place digits are not the same. There is no necessary relationship between the two.
 - In general, electronic calculators do not give the proper number of significant digits.
 - All the digits in the coefficient of a number in standard exponential form are significant.
 - Do exponential calculations on the calculator to get the proper magnitude, then redo them mentally to get the proper number of significant digits.
- A. How many significant digits and how many decimal place digits are present in each of the following? (a) 0.041 cm (b) 140.2 cm (c) 20.02 cm (d) 3.110×10^3 cm
- B. Do the following calculations to the proper numbers of significant digits:
 (a) $4.96 \text{ cm} - 0.1919 \text{ cm}$ (b) $(4.96 \text{ cm})(0.1919 \text{ cm})$
 (c) $8.03 \times 10^3 \text{ cm} - 2.42 \times 10^2 \text{ cm}$

2.5 Density

Density is defined as *mass per unit volume*:

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

In symbols,

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

The dimensions (combination of units) of density involve a mass unit divided by a volume unit, such as grams per milliliter (g/mL) or grams per cubic centimeter (g/cm³). Thus, to get the density of an object, we simply divide the mass of the object by its volume. Problems involving density usually involve finding one of the variables—*d*, *m*, or *V*—having been given the other two. Either the equation or the factor label method can be used to solve density problems. The equation is most often used when mass and volume are given. The factor label method is perhaps easier when density and one of the other two variables are given and the third variable is sought.

Densities of some common substances are given in Table 2.5. Note that scientists generally put the units at the heads of the columns when reporting data in a table. The only density to remember is the density of liquid water, about 1.00 g/mL = 1.00 g/cm³.

Table 2.5 Densities of Some Common Substances

Substance	Density (g/mL)
Aluminum	2.702
Copper	8.92
Gold	19.3
Iron	7.86
Lead	11.3
Magnesium	1.74
Mercury	13.6
Platinum	21.45
Silver	10.5
Tin	5.75
Octane	0.7025
Salt (NaCl)	2.165
Sugar (sucrose)	1.56
Water (at 4°C)	1.000

EXAMPLE 2.49

Calculate the density of the wood in a certain desk if its mass is 41.6 kg and its volume is 51.3 L.

Solution

$$d = \frac{m}{V} = \frac{(41.6 \text{ kg})}{(51.3 \text{ L})} = 0.811 \text{ kg/L}$$

Practice Problem 2.49 Calculate the density of a rectangular metal bar that is 7.00 cm long, 4.00 cm wide, and 1.00 cm thick and has a mass of 352 g.

EXAMPLE 2.50

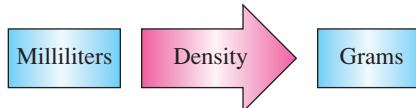
- Two objects have the same volume, but the first has a greater mass. Which is more dense?
- Two objects have the same mass, but the first is larger. Which is more dense?

Solution

- The first is more dense.
- The first is less dense because it has less mass per unit volume.

EXAMPLE 2.51

Calculate the mass of 41.0 mL of mercury (density = 13.6 g/mL).

Solution

$$41.0 \text{ mL} \left(\frac{13.6 \text{ g}}{1 \text{ mL}} \right) = 558 \text{ g}$$

Practice Problem 2.51 Calculate the volume of 12.7 g of mercury (density = 13.6 g/mL).

EXAMPLE 2.52

Calculate the volume in liters of 1719 g of mercury. (*Hint:* see Table 2.5.)

Solution

$$1719 \text{ g} \left(\frac{1 \text{ mL}}{13.6 \text{ g}} \right) \left(\frac{0.001 \text{ L}}{1 \text{ mL}} \right) = 0.126 \text{ L}$$

Practice Problem 2.52 Calculate the mass of 1.000 L of magnesium.

Substances expand when heated, and the resulting change in volume causes some change in density. Within reasonable temperature ranges, the density of a substance is relatively constant. For example, water varies from 0.99979 g/mL at 0°C to 1.0000 g/mL at 4°C to 0.95838 g/mL at 100°C. We will usually ignore such slight differences, especially since we will work most often with densities measured to only three significant digits.

Density is an intensive property, useful in identifying substances. For example, gold can be distinguished from iron pyrite by their greatly differing densities—19.3 g/cm³ for gold and 5.0 g/cm³ for iron pyrite. Iron pyrite is known as “fool’s gold” because of its striking visual resemblance to gold. Many prospectors in the western United States in gold-rush days were terribly disappointed when the test in the assay office showed that they had found iron pyrite rather than gold.

Relative densities determine whether an object will float in a given liquid in which it does not dissolve. An object will float if its density is less than the density of the liquid. For example, the density of liquid water is 1.00 g/mL and that of a particular kind of wood is 0.831 g/mL. The wood will float in water because it has a lower density.

EXAMPLE 2.53

A 7.00 cm × 3.00 cm × 2.50 cm rectangular metal bar has a mass of 593 g. Will the bar float in water or in mercury (density = 13.6 g/mL)?

Solution

The volume of the bar is $l \times w \times h = 52.5 \text{ cm}^3$, and its density is therefore

$$d = \frac{593 \text{ g}}{52.5 \text{ cm}^3} = 11.3 \text{ g/cm}^3$$

The bar will sink in water (density = 1.00 g/cm³), but it will float in mercury.

Practice Problem 2.53 A 5.03 cm × 3.11 cm × 1.22 cm rectangular solid has a mass of 51.5 g. Will the object float in mercury?

EXAMPLE 2.54

Identify the metal in the bar of Example 2.53.

Solution

The density is that of lead (see Table 2.5).

Practice Problem 2.54 Identify the substance in Practice Problem 2.53.

**Snapshot Review**

ChemSkill Builder 2.6

- Density is an important property, useful in identifying substances and other things, but it is used here mainly to tie together and review all the prior sections of this chapter.
- Any units of mass divided by any units of volume are acceptable for density.
- Density may be used as a factor, with either mass units or volume units in the numerator.

- A. Calculate the volume of a 191 g object with density 5.75 g/mL.
- B. Calculate the mass of a 191 mL object with density 5.75 g/mL.

2.6 Temperature Scales

In the United States, it is necessary for scientists to know three different temperature scales. The scale used in everyday American life is the **Fahrenheit scale**, on which the temperature of freezing water is defined as 32°F, and the temperature of water boiling under normal conditions is defined as 212°F. Scientists do not use the Fahrenheit scale (although American engineers sometimes do). Instead, they use the **Celsius scale**, the metric scale for temperature, which was formerly called the **centigrade scale**. On the Celsius scale, the temperature of freezing water is defined as 0°C, and the temperature of water boiling under normal conditions is defined as 100°C. The Celsius scale is used in most other countries of the world for everyday measurements as well as scientific ones. The **Kelvin scale** for measuring temperatures is important for work with gases (Chapter 12) and in other advanced work. On the Kelvin scale, the temperature of freezing water is 273 K, and the temperature of water boiling under normal conditions is 373 K. The degree sign (°) is not used with the Kelvin scale, and the units are called kelvins rather than degrees. The three scales are pictured in Figure 2.11.

To convert from degrees Fahrenheit (t_F) to degrees Celsius (t), or vice versa, we use the following equations:

$$t = \frac{5}{9}(t_F - 32^\circ) \quad \text{and} \quad t_F = \frac{9}{5}t + 32^\circ$$

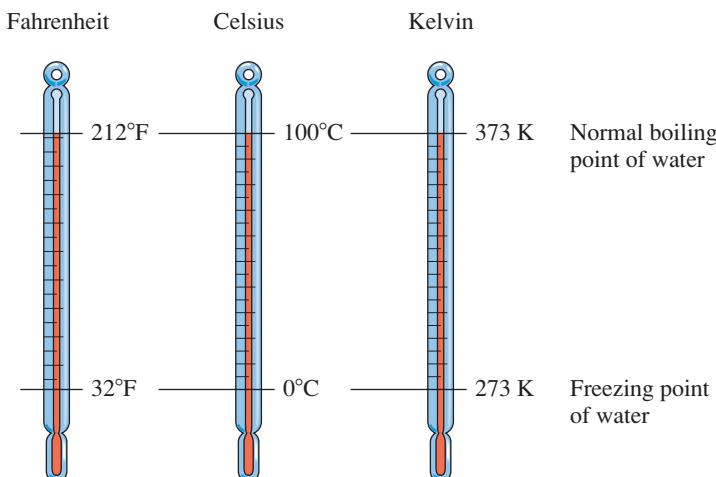
The 32° is a definition and can be expanded to 32.0°, 32.00°, and so on. To convert from degrees Celsius to kelvins (T), we use the following equation:

$$T = t + 273$$

■ Key Terms

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Figure 2.11 Comparison of Temperature Scales



EXAMPLE 2.55

Convert 98.6°F (normal body temperature) to a Celsius temperature.

Solution

$$t = \frac{5}{9}(t_F - 32.0^\circ) = \frac{5}{9}(98.6^\circ - 32.0^\circ) = 37.0^\circ\text{C}$$



ChemSkill Builder 1.6

Snapshot Review



- The symbols for Celsius temperature and Kelvin temperature are lowercase *t* and capital *T*, respectively. Be careful to use the proper one.
- A. What is the normal boiling point of water on the (a) Fahrenheit scale?
 (b) Celsius scale? (c) Kelvin scale?
- B. Convert 30°C (a) to degrees Fahrenheit. (b) to kelvins.

Key Terms

Key terms are defined in the Glossary.

accuracy (2.4)
 base (2.2)
 Celsius scale (2.6)
 centigrade scale (2.6)
 coefficient (2.2)
 conversion factor (2.1)
 cubic meter (2.3)
 density (2.5)
 dimensional analysis (2.1)
 exponent (2.2)

exponential notation (2.2)
 exponential part (2.2)
 factor label method (2.1)
 Fahrenheit scale (2.6)
 gram (2.3)
 Kelvin scale (2.6)
 length (2.3)
 liter (2.3)
 meter (2.3)
 metric system (2.3)

precision (2.4)
 rounding (2.4)
 scientific notation (2.2)
 SI (2.3)
 significant digit (2.4)
 significant figure (2.4)
 standard (2.3)
 standard exponential form (2.2)
 unit (2.1)
 volume (2.3)

Symbols/Abbreviations

c (centi-) (2.3)	L (liter) (2.3)	s (second) (2.1)
d (density) (2.5)	m (mass) (2.3)	t (Celsius temperature) (2.6)
g (gram) (2.3)	m (meter) (2.3)	T (Kelvin temperature) (2.6)
k (kilo-) (2.3)	m (milli-) (2.3)	t_F (Fahrenheit temperature) (2.6)
h (hour) (2.1)	min (minute) (2.1)	V (volume) (2.3)

Summary

Measurement is the key to quantitative physical science. The results of every measurement must include both a numeric value and a unit (or set of units). Be sure to use standard abbreviations for all units. The factor label method is used to convert a quantity from one set of units to another without changing its value. The original quantity is multiplied by a factor equal to 1. (The numerator and denominator of the factor are equal to each other in value but different in form.) To use the factor label method: (1) write down the quantity given, (2) multiply by a factor that will yield the desired units, (3) cancel the units, (4) multiply all numbers in the numerators and divide by the number(s) in the denominator(s). Sometimes, it is necessary to multiply by more than one factor. We may solve for the intermediate answers, but we do not have to. (Section 2.1)

Exponential notation enables easy reporting of extremely large and extremely small numbers. A number in scientific notation consists of a coefficient times 10 to an integral power, where the coefficient is equal to or greater than 1 but less than 10. Learn how to convert numbers from exponential notation to ordinary decimal values, and vice versa, and also how to use exponential numbers in calculations. Also learn to use effectively an electronic calculator with exponential capability (see Appendix 1). (Section 2.2)

The metric system and its newer counterpart, SI, use subunits and multiples of units that are equal to powers of 10, and they also use the same prefixes to mean certain fractions or multiples, no matter what primary unit is being modified. The meter is the primary unit of length; the gram is the primary unit of mass; and the liter (the cubic meter in SI) is the primary unit of volume. The prefixes *centi-* (0.01), *milli-* (0.001), and *kilo-* (1000) are used with any of these or with any other metric unit. Conversions between English and metric units are necessary for American engineers and may help us get familiar with the relative sizes of the metric units. To add, subtract, multiply, or divide measured quantities of the same type, first be sure that they all have the same units as far as possible. (Section 2.3)

The number of digits reported for a measurement or for the result of a calculation involving measurements is a means of showing how precisely the measurement(s) was (were) made. The last digit of reported measurements is usually an estimate based on tenths of the smallest scale division of the measuring instrument. Any digit from 1 through 9 in a properly reported result is significant. (The word *significant* as used here refers to the precision of the measurement and does not mean “important.”) Zeros may or may not be significant; if they merely show the magnitude of the number, they are not significant.

When measurements are added or subtracted, the one that has significant digits least far to the right is the one that limits the number of significant digits in the answer. When measurements are multiplied or divided, the one with the fewest significant digits limits the number of significant digits in the answer. If too many digits are present in a calculated answer, the answer is rounded off: Some digits are dropped if they occur to the right of the decimal point or changed to nonsignificant zeros if they occur to the left of the decimal point. If too few digits are present, significant zeros are added. Note that, although a calculator gives the correct magnitude when used properly, we must understand the calculation processes to be able to determine the number of significant figures to report. All digits in the coefficients of numbers in scientific notation are significant. (Section 2.4)

Density, an intensive property, is defined as mass per unit volume. It can be calculated by dividing the mass of a sample by its volume. If a density is given, it may be used as a factor to solve for mass or volume. Density, may be used to help identify a substance. Samples of lower density float in fluids of higher density. (Section 2.5)

Scientists use two different temperature scales: Celsius and Kelvin. Their relationship to each other and to the more familiar Fahrenheit scale is shown in Figure 2.11. (Section 2.6)

■ Self-Tutorial Problems

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Items for Special Attention

- The metric units used to report volumes may involve liters or the cube of a length unit.
- Adding a positive number to a negative exponent either makes the exponent positive or makes the exponent less negative (gives the exponent a smaller magnitude).
- Do not key in 10 for the base of a number in scientific notation on your electronic calculator. The EXP or EE key means “ $\times 10$ to a power.” See Appendix 1.
- Significant digits and decimal place digits are two different things. Do not confuse them. For example, 4.53 has three significant digits and two decimal place digits.
- The expressions that follow are simplified in the same way. That is, the algebraic quantities x and y and the units such

as meters and seconds (m and s) or miles and hours (h) are treated the same:

$$5y\left(\frac{60x}{y}\right) = 300x \quad 5 \text{ s}\left(\frac{60 \text{ m}}{1 \text{ s}}\right) = 300 \text{ m}$$

$$5 \text{ h}\left(\frac{60 \text{ miles}}{1 \text{ h}}\right) = 300 \text{ miles}$$

- When measurements expressed in exponential notation are added or subtracted, both the units and the exponents must be the same. When such measurements are multiplied or divided, units and exponents can be different.

Answers to Snapshot Reviews

- 2.1 A. (a) $22.75 \text{ dollars} \left(\frac{4 \text{ quarters}}{1 \text{ dollar}} \right) = 91 \text{ quarters}$
 (b) $144 \text{ quarters} \left(\frac{1 \text{ dollar}}{4 \text{ quarters}} \right) = 36.00 \text{ dollars}$
- 2.2 A. (a) 1.234×10^3 (b) 2.000×10^2
 (c) 2.00×10^{-2}
 B. (a) 2.09×10^3 (b) 1.49×10^0
 (c) -4.04×10^{-2}
- 2.3 A. (a) L (b) m (c) m^3 (d) g
 B. (a) $1.234 \text{ mm} \left(\frac{0.001 \text{ m}}{1 \text{ mm}} \right) = 1.234 \text{ m}$
 (b) $1234 \text{ mL} \left(\frac{0.001 \text{ L}}{1 \text{ mL}} \right) = 1.234 \text{ L}$
 (c) $1234 \text{ mg} \left(\frac{0.001 \text{ g}}{1 \text{ mg}} \right) = 1.234 \text{ g}$
 C. (a) $0.175 \text{ m}^3 \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) = 175 \text{ L}$
 (b) $315 \text{ cm}^3 \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) = 0.315 \text{ L}$

- 2.4 A. (a) Two significant digits, three decimal place digits
 (b) Four significant digits, one decimal place digit
 (c) Four significant digits, two decimal place digits
 (d) Four significant digits, three decimal place digits
 B. (a) 4.96 cm

$$\underline{-0.1919 \text{ cm}}$$

$$4.7681 \text{ cm} \rightarrow 4.77 \text{ cm}^2$$

 (b) $(4.96 \text{ cm})(0.1919 \text{ cm}) = 0.952 \text{ cm}^2$
 (c) $8.03 \times 10^3 \text{ cm} - 2.42 \times 10^2 \text{ cm}$

$$= 7.79 \times 10^3 \text{ cm}$$

- 2.5 A. $191 \text{ g} \left(\frac{1 \text{ mL}}{5.75 \text{ g}} \right) = 33.2 \text{ mL}$
 B. $191 \text{ mL} \left(\frac{5.75 \text{ g}}{1 \text{ mL}} \right) = 1100 \text{ g} = 1.10 \text{ kg}$

- 2.6 A. (a) 212°F (b) 100°C (c) 373 K
 B. (a) $t_F = \frac{9}{5}(30^\circ\text{C}) + 32^\circ = 86^\circ\text{F}$ (b) 303 K

Self-Tutorial Problems

- 2.1 Identify each of the following as a quantity or rate or ratio:
 (a) Cost to fill a gas tank (b) Amount of pay
 (c) Number of hours worked (d) Price of gasoline
 (e) Minimum wage
- 2.2 (a) If we multiply a certain number by 1000 and then divide the result by 1000, what is the relationship of the final answer to the original number?
 (b) If we multiply the coefficient of an exponential number by 1000 and divide the exponential part by 1000, what is the effect?
- 2.3 Find the value of this expression on an electronic calculator:

$$2 \times 10^0 + 0$$
- 2.4 Write each of the following numbers in exponential notation:
 (a) 6 thousandths (b) 4.2 million
 (c) 195 billion (d) 12.3 million
 (e) 11 thousand (f) 17 millionths

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- 2.5 Use your electronic calculator to do the following calculation to check your calculator procedure:

$$\frac{12 \times 6}{4 \times 9}$$

- 2.6 Which of the following numbers have values less than zero? Which have magnitudes less than one? Which have values less than one?
- (a) -1.8×10^{-3} (b) 7.5×10^{-2}
(c) 3.2×10^6 (d) -2.3×10^4
- 2.7 What is the exponential equivalent of each of the following metric prefixes?
- (a) kilo- (b) centi- (c) milli-
- 2.8 (a) Which is bigger, a cent or a dollar? Which would you need more of to buy a certain textbook?
(b) Which is bigger, a centimeter or a meter? Which does it take more of to measure the length of a certain textbook?
- 2.9 Which is bigger: 1 kg or 1 mg? Which would there be more of in a measurement of your own mass?
- 2.10 What is the difference between the masses 7 mg and 7 Mg?

- 2.11 Which of the following are units of volume?

L Mg m³ mm³ g m kg mg mL

- 2.12 Which of the following animals is most likely to have a mass of 30 kg?
- (a) Elephant (b) Chicken
(c) Saint Bernard dog (d) Fly

- 2.13 The author of this text is of average build. Fill in the metric units in the following description:

Height: 171 _____

Mass: 64 _____

Total volume of blood in his system: 4 _____

CHAPTER 2 ■ Measurement

- 2.14 What factor is used to convert a measurement in grams to kilograms?
- 2.15 (a) How many square centimeters are in a square measuring 3.0 cm along each edge? (b) How many cubic centimeters are in a cube 3.0 cm on each edge?
- 2.16 Which of the following is the most probable distance between a dormitory room and the chemistry lecture room?
- (a) 0.5 km (b) 0.5 m
(c) 0.5 cm (d) 0.5 mm
- 2.17 The population of New York City is 7 million people. A lottery advertises a \$7 million jackpot. How many significant digits are probably in each number?
- 2.18 Refer to the more precise ruler in Figure 2.10. Count the number of smaller scale divisions in each 1 cm. How many would there be in 1 m (100 cm)? What unit represents the value of each small scale division?
- 2.19 Which metals in Table 2.5 will not float in mercury?
- 2.20 What is the difference in density, if any, among the following?
- 6.73 g in 1.00 mL
6.73 g divided by 1.00 mL
6.73 grams per milliliter
6.73 g/mL
6.73 g in exactly 1 mL
- 2.21 (a) How can we reduce the sweetness of a cup of coffee without taking out any sugar?
(b) How can a company raise the price of coffee at the supermarket without charging more for each can?
(c) What happens to the average speed for a trip if the time spent traveling remains unchanged but the distance is decreased?
(d) What happens to the density of an object if its volume is increased but its mass remains the same?

Problems**2.1 Factor Label Method**

- 2.22 Calculate the number of minutes in 5.150 h.
- 2.23 Assume that donuts are \$5.00 per dozen. Use the factor label method to answer each of the following:
(a) How much do 2.50 dozen cost?
(b) How many dozens can you buy with \$32.50?
(c) How many donuts can you buy with \$32.50?
- 2.24 Determine the cost of 540 pencils if the price is \$1.15 per dozen.
- 2.25 Calculate the pay earned by a student who worked 18 h per week for 32 weeks at \$9.00 per hour.

- 2.26 Calculate the pay received for 1.00 h of work by a junior executive who works 40 h per week and earns \$48,250 per year for 50 weeks of work.
- 2.27 There is 60.0% oxygen by mass in a compound of sulfur and oxygen. Percent by mass is a ratio of the number of grams of a particular component to 100 g of the total sample. How many grams of sulfur are in a 14.6-g sample of the compound?
- 2.28 Calculate the number of hours in 8676 seconds.
- 2.29 Calculate the cost of a rug required to cover a living-room floor that is 15.3 ft wide and 18.3 ft long if the price is \$29.00 yd².

■ Problems

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2.2 Exponential Numbers

- 2.30** Which one(s) of the following is (are) in standard exponential notation?
- $2.5 \times 10^{2.5}$
 - 0.123×10^4
 - 1.23×10^{-4}
 - 62×10^{15}
 - 7.1×10^0
 - 8×10^{-23}
- 2.31** Convert each of the following numbers to standard exponential notation:
- 621
 - 0.1033
 - 100.001
 - 0.011
- 2.32** Convert each of the following numbers to decimal format:
- 2.25×10^2
 - 2.18×10^{-1}
 - 4.56×10^{-2}
 - 6.31×10^0
- 2.33** Write each of the following numbers in scientific notation:
- 103.7
 - 0.00200
 - 602,000,000,000,000,000,000,000
 - 0.0000000080
- 2.34** Express each of the following answers in scientific notation:
- $(4.0 \times 10^4)/(2.50 \times 10^4)$
 - $(3.0 \times 10^2) + (3.72 \times 10^3)$
 - $(2.0 \times 10^{-5}) - (2.0 \times 10^{-4})$
 - $(6.0 \times 10^2)(3.06 \times 10^3)$
 - $(7.0 \times 10^4)(3.5 \times 10^1)$
- 2.35** Subtract:
- $$(7.0 \times 10^{-3}) - (-8.0 \times 10^{-2})$$
- 2.3 The Metric System**
- 2.36** (a) How many milligrams are in 6.21 g?
 (b) How many centimeters are in 6.21 m?
 (c) How many kilograms are in 6.21 g?
- 2.37** How many milligrams are in 12.1 kg?
- 2.38** Convert
- 6.96 m to millimeters
 - 6.96 L to milliliters
 - 6.96 g to milligrams
 - 6.96 watts to milliwatts
- 2.39** Convert:
- 21.3 m to centimeters
 - 21.3 m to millimeters
 - 21.3 m to kilometers
- 2.40** Calculate the number of
- millimeters in 6.03 m
 - milliliters in 6.03 L
 - milligrams in 6.03 g
- 2.41** Calculate the number of
- feet in 6.03 miles
 - English tons (2000 lb per ton) in 6.03 lb
 - fluid ounces in 6.03 gal
 - Compare the difficulty of these calculations to those in the prior problem.
- 2.42** Express each of the following measurements as a decimal value:
- 7.00×10^{-3} L
 - 7.0×10^{-3} L
 - 7×10^{-3} L
- 2.43** Calculate the number of cubic centimeters in a rectangular box 0.0722 m by 3.39 cm by 7.013 mm. Be sure to use the proper units.
- 2.44** Calculate the length of each edge of a cube that has a volume of 2.57 cm^3 .
- 2.45** The edge of a cube is 3.000×10^{-1} cm. What is the volume of the cube in cubic meters?
- 2.46** Which of the following is the smallest container that could hold 1 m^3 of liquid?
- Swimming pool
 - Drinking glass
 - Soda bottle
 - Thimble
- 2.47** Convert
- 1.09×10^{-4} kg to milligrams
 - 6.03×10^{-4} m³ to milliliters, and express the answer in standard exponential notation
- 2.48** Calculate the number of liters in
- 0.0117 m^3
 - 808 cm^3
 - 290.2 mL
 - $1.43 \times 10^3 \text{ mm}^3$
- 2.49** How many liters are in 6.11×10^{-2} m³?
- 2.50** How many cubic millimeters are in 0.117 mL?
- 2.51** What is the volume of a rectangular solid that is 0.0622 m wide, 7.15 cm long, and 0.0000560 km thick?
- 2.52** Calculate the number of liters in 7.05×10^{-2} m³.
- 2.53** Convert each of the following numbers to centimeters, and express the answer in standard exponential notation:
- 6133 mm
 - 1.733 m
 - 20.2 km
 - 6.191×10^4 mm
- 2.54** Change 3.50×10^4 cm to:
- meters
 - millimeters
 - kilometers

70**2.4 Significant Digits**

- 2.55** Underline the significant digits in each of the following measurements. If any digit is uncertain, place a question mark below it.

- (a) 67.00 km (b) 0.0013 kg (c) 690 m
(d) 209 L

- 2.56** Underline the significant digits in each of the following measurements. If a digit is uncertain, place a question mark below it.

- (a) 5.0×10^2 cm (b) 5.02×10^2 cm
(c) 7.00×10^2 cm (d) 5.000×10^{-2} m

- 2.57** Convert each of the following values to ordinary (decimal) notation:

- (a) 6.000×10^3 cm (b) 6.00×10^3 cm
(c) 6.0×10^3 cm (d) 6×10^3 cm

- 2.58** Express each of the following volumes in milliliters:

- (a) 7.00×10^{-3} L (b) 7.0×10^{-3} L
(c) 7×10^{-3} L

- 2.59** Express each of the following measurements in liters:

- (a) 3.00×10^3 mL (b) 3.0×10^3 mL
(c) 3×10^3 mL

- 2.60** Underline the significant digits in each of the following measurements. If a digit is uncertain, place a question mark below it.

- (a) 4.000 mm (b) 0.0040 cm
(c) 4000 m (d) 40.00 km

- 2.61** Round off each of the following measurements to three significant digits:

- (a) 0.0637425 cm
(b) 0.637425 cm
(c) 6.37425 cm
(d) 63.7425 cm
(e) 6374.25 cm

- 2.62** Round off each of the following measurements to three significant digits:

- (a) 0.02316 cm
(b) 0.2316 cm
(c) 23.16 cm
(d) 2316 cm

- 2.63** Do the following calculations to the proper number of significant digits:

- (a) $6.17 \text{ cm} \times 3.722 \text{ cm}$
(b) $3.09 \text{ cm} - 122.7 \text{ cm}$
(c) $7.07 \text{ g}/1.81 \text{ mL}$

CHAPTER 2 ■ Measurement

- 2.64** Express each of the following lengths in centimeters (to the proper number of significant digits):

- (a) 4×10^{-3} m (b) 4.0×10^{-3} m
(c) 4.00×10^{-3} m (d) 4.000×10^{-3} m

- 2.65** Convert each of the following distances to meters, and express the results as ordinary numbers (not in exponential notation).

- (a) 1.00×10^5 mm
(b) 1.00×10^5 cm
(c) 1.00×10^{-3} km

- 2.66** How many significant digits are present in each of the following measurements? How many decimal place digits?

- (a) 127.900 kg (b) 12.88 cm^3
(c) 0.3930 mL (d) 2.002 m

- 2.67** Underline the significant digits in each of the following measurements. If a digit is uncertain, place a question mark under it.

- (a) 1.630 cm (b) 8.090 cm
(c) 0.022 cm (d) 4000 cm

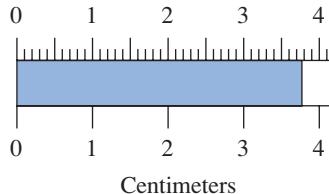
- 2.68** Underline the significant digits in each of the following measurements. If a digit is uncertain, place a question mark below it.

- (a) 41.07 cm (b) 6050 cm
(c) 400.0 cm (d) 0.00120 m
(e) 220 mm

- 2.69** How many significant digits are present in each of the following measurements? How many decimal place digits?

- (a) 0.020 kg (b) 33.0 cm^3
(c) 403 mL (d) 1.0 m

- 2.70** Report the length of the shaded bar, using each of the rulers shown:



- 2.71** Add the following quantities, and report the answers to the proper number of significant digits:

- (a) 219 g + 17.39 g
(b) 6.11 mL + 0.012 mL
(c) 1.102 mL + 0.013 mL
(d) 42.7 km + 61.4 km

■ Problems

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- 2.72** Round off the following measurements to three significant digits:
- 110.9 mL
 - 1109 mL
 - Are the answers the same?
- 2.73** Express each of the following measurements as a decimal value. State how many significant digits are in each result. Could we tell just from looking at the results without knowing the original values?
- $9.00 \times 10^3 \text{ mL}$
 - $9.0 \times 10^3 \text{ mL}$
 - $9 \times 10^3 \text{ mL}$
- 2.74** Divide the following quantities, and report the answers to the proper number of significant digits:
- $(3.08 \times 10^3 \text{ g})/(6.912 \text{ m}^3)$
 - $(9.39 \text{ cm}^2)/(3.13 \times 10^{-1} \text{ cm})$
 - $(6.93 \times 10^3 \text{ cm}^3)/(30.0 \text{ cm})$
 - $(6.66 \times 10^4 \text{ g})/(2.22 \times 10^1 \text{ cm})^3$
- 2.75** Multiply the following quantities, and report the answers to the correct number of significant digits:
- $5.10 \text{ cm} \times (1.40 \times 10^2 \text{ cm})$
 - $0.0115 \text{ cm} \times (9.2 \times 10^{-2} \text{ cm})$
 - $(2.505 \times 10^{-2} \text{ cm}) \times 40.00 \text{ cm}$
 - $(1.03 \times 10^3 \text{ cm})(6.88 \times 10^2 \text{ cm})$
- 2.76** Perform the following additions and explain the results:
- $(4.000 \times 10^{-3} \text{ mm}) + (2.0 \times 10^{-1} \text{ cm})$
 - $(7.44 \times 10^2 \text{ g}) + 9.31 \text{ mg}$
- 2.77** In Problem 2.73, how can we report the proper number of significant digits in the results without using exponential notation?
- 2.78** Add the following quantities, and report the answers to the proper number of significant digits:
- $(3.000 \times 10^{-3} \text{ g}) + (7.0 \times 10^1 \text{ mg})$
 - $(4.00 \times 10^{-1} \text{ g}) + (8.88 \times 10^{-4} \text{ kg})$
- 2.79** In Problem 2.58, can we tell how many significant digits are in each measurement as it is given in exponential form in the problem? Can we tell in decimal form in the answer?
- 2.80** Solve the following problem and state the answer with the proper number of significant digits:
- $$\begin{array}{r} 101.1 \text{ g} - 98.31 \text{ g} \\ \hline 38.92 \text{ mL} - 0.97 \text{ mL} \end{array}$$
- 2.81** Calculate the answer to each of the following problems to the proper number of significant digits:
- $(7.11 \times 10^3 \text{ cm})(23.7 \text{ cm})$
 - $(9.02 \times 10^{-6} \text{ m})(4.9 \times 10^{-3} \text{ mm})$
 - $(6.13 \text{ kg})/(6.8 \times 10^3 \text{ mL})$
 - $(1.627 \text{ g})/(0.1122 \text{ L})$
- 2.82** Calculate the answer to each of the following problems to the proper number of significant digits:
- $(4.66 \times 10^2 \text{ cm}^2)/(23.3 \text{ cm})$
 - $(3.18 \times 10^{-5} \text{ cm}^3)/(6.929 \times 10^{-3} \text{ cm})$
 - $(215 \text{ g})/(3.5 \times 10^2 \text{ mL})$
 - $(19.55 \text{ g})/(21.21 \text{ mL})$
 - $(6.172 \times 10^5 \text{ cm}^2)(7.17 \times 10^2 \text{ cm})$
 - $(6.33 \text{ g}) + (2.3 \times 10^{-2} \text{ g})$
- 2.83** Do the following calculations to the proper number of significant digits:
- $(8.14 \times 10^3 \text{ cm})^3$
 - $3.38 \times 10^{-3} \text{ g} - 1.902 \times 10^{-1} \text{ g}$
 - $1.173 \times 10^6 \text{ cm} - 9.09 \times 10^4 \text{ cm}$
- 2.84** Add the following quantities, and report the answers to the correct number of significant digits:
- $1.72 \text{ kg} + (3.44 \times 10^2 \text{ g})$
 - $0.0115 \text{ kg} + (6.96 \times 10^{-1} \text{ g})$
 - $9.42 \text{ kg} + (3.72 \times 10^5 \text{ g})$
 - $(9.00 \times 10^4 \text{ cm}^2) + (1.14 \times 10^4 \text{ cm})^2$

2.5 Density

- 2.85** What quantity is obtained in each of the following cases?
- Density is multiplied by volume.
 - Mass is divided by density.
 - Mass is divided by volume.
- 2.86** Calculate the number of milliliters of lead (density = 11.3 g/mL) having a mass of 4.145 kg .
- 2.87** Calculate the mass of water that occupies 9.10 L .
- 2.88** Calculate the density of an object that has a volume of 7.05 L and a mass of 52.6 kg .
- 2.89** (a) Calculate the volume of a rectangular box 42.6 cm by 4.41 cm by 1.932 cm .
 (b) Calculate the number of kilograms of mercury (density = 13.6 g/mL) that can fit in that box.
- 2.90** Using the data of Table 2.5, explain why magnesium is preferable to steel (mostly iron) for building airplanes. What other metal might be useful for this purpose?
- 2.91** Using the densities in Table 2.5, identify the metal in a 30.38 cm^3 solid of mass 319 g .
- 2.92** Calculate the number of milliliters of mercury (density = 13.6 g/mL) having a mass of 1.213 kg .
- 2.93** Does lead float in mercury? (Hint: See Table 2.5 if necessary.)

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- 2.94 Explain why gasoline floats on water. Is water good for putting out gasoline fires?
- 2.95 Calculate the density of a rectangular 42.3-g piece of wood 12.2 cm long, 3.05 cm wide, and 1.43 cm thick.
- 2.96 Calculate the density of a rectangular solid of mass 716.0 g and dimensions:
- 20.21 cm × 3.163 cm × 2.321 cm
 - 0.2021 m × 31.63 mm × 23.21 mm
- 2.97 Calculate the mass of mercury (density = 13.6 g/mL) that fills a rectangular box 23.0 cm by 3.06 cm by 1.551 cm.
- 2.98 Calculate the volume in cubic centimeters of an object with a density of 4.15 g/mL and a mass of 673 g.
- 2.99 Express the density 11.7 kg/L in grams per cubic centimeter.
- 2.100 Convert the density 2.05×10^3 kg/m³ to grams per cubic centimeter.
- 2.101 Calculate the number of kilograms of mercury (density = 13.6 g/mL) occupying 747 mL.
- 2.102 An object has a density of 3.55 g/mL. Convert this density to kilograms per cubic meter.

CHAPTER 2 ■ Measurement

- 2.103 Calculate the density in grams per milliliter of an object that has a volume of 7.81 cm³ and a mass of 44.9 g.

2.6 Temperature Scales

- 2.104 Calculate the temperature in degrees Celsius of each of the following:
- 212°F
 - 32.0°F
 - 60°F
 - 98.6°F
 - 0°F
 - 40.0°F
 - 35.0°F
- 2.105 Calculate the temperature in degrees Fahrenheit of each of the following:
- 0°C
 - 100°C
 - 27.0°C
 - 50.0°C
 - 15°C
 - 75°C
 - 273°C
- 2.106 Calculate the temperature in kelvins of each of the following:
- 25°C
 - 19.2°C
 - 273°C
 - 42°C
 - 100°C
- 2.107 Calculate the temperature in degrees Celsius of each of the following:
- 295 K
 - 373 K
 - 273 K
 - 0 K

General Problems

- 2.108 Calculate the answer to each of the following expressions to the correct number of significant digits:
- (6.33 cm + 7.2 cm) × 5.00 cm
 - 1.37 cm × (9.05 cm - 4.782 cm)
 - (6.11 cm × 1.4 cm) + 3.09 cm²
 - (3.89 × 10³ cm) - 4.46 cm
 - 3.34 cm × (6.12 × 10³ cm)
 - 2.10×10^{-3} cm + 6.90×10^{-2} cm
- 2.109 Calculate the answer to each of the following expressions to the correct number of significant digits:
- 6.33 cm × 7.2 cm - 5.00 cm²
 - 137 cm² - 9.05 cm × 4.782 cm
 - 6.11 cm² + 1.4 cm × 3.09 cm
 - $(3.89 \times 10^3 \text{ cm})^2 - 4.46 \times 10^5 \text{ cm}^2$
 - $3.34 \text{ cm} \times (6.12 \times 10^2 \text{ cm})^2$
 - $(2.10 \times 10^{-3} \text{ cm}) \times (6.90 \times 10^{-2} \text{ cm})$
- 2.110 Convert
- 4.82 km to millimeters
 - 4.82 L to cubic meters
 - 4.82 mg to kilograms

- 2.111 Convert
- 6.14 cm to millimeters
 - 6.14 m³ to milliliters
 - 6.14 cm³ to milliliters
- 2.112 Calculate the number of cubic millimeters in 1.00 L.
- 2.113 How many cubic millimeters are there in 5.00 mL?
- 2.114 Convert
- 7.56×10^4 mm to kilometers
 - 2.58×10^{-2} m³ to liters
 - 7.18×10^{-3} L to milliliters
- 2.115 Calculate the sum of 6.90×10^3 cm and 7.10×10^{-3} km.
- 2.116 Calculate the sum of 6.90×10^3 cm and 7.10×10^{-3} cm. Explain your result.
- 2.117 Calculate the price of a 3.00-kg bar of gold if the price of gold is \$600 per troy ounce.
- 2.118 Calculate the cost of a bar of gold 110.0 cm by 10.0 cm by 10.0 cm if the price of gold is \$600 per troy ounce.
- 2.119 Calculate the length of each edge of a 7.440-kg cube of gold.

■ General Problems

- 2.120 Calculate the density of a cube with each edge 3.93 cm and mass 171 g.
- 2.121 Calculate the density of a cube with each edge 0.0393 m and mass 0.171 kg.
- 2.122 Compare the sizes, masses, and densities of the cubes in Problems 2.120 and 2.121.
- 2.123 Calculate the number of particles of volume $2.0 \times 10^{-22} \text{ cm}^3$ that can fit into a cubic box of edge length 1.00 m.
- 2.124 Calculate the density in grams per milliliter of a cubic unit cell (see Example 2.34) of edge $6.63 \times 10^{-8} \text{ cm}$ and mass $5.09 \times 10^{-25} \text{ kg}$.
- 2.125 Calculate the mass of one unit cell (see Example 2.34) of a substance with density 2.50 g/mL if its cubic unit cell has an edge $9.10 \times 10^{-10} \text{ m}$.
- 2.126 A unit cell of a substance has a mass of $1.98 \times 10^{-22} \text{ g}$. One particle of the substance has a mass of $4.94 \times 10^{-25} \text{ g}$. How many particles are in each unit cell?
- 2.127 Calculate the number of cubic centimeters in a rectangular box
 $1.21 \times 10^{-1} \text{ m by } 12.2 \text{ cm by } 6.01 \times 10^2 \text{ mm}$
- 2.128 Calculate the density in grams per milliliter of an object with a volume of 0.6912 L and a mass of 460.7 g.
- 2.129 How many $3.44 \times 10^{-28} \text{ m}^3$ particles will fit into a 4.00-mL vessel?
- 2.130 Explain how it is possible to calculate an answer having five significant digits using two measurements having two significant digits each and two having four significant digits each.
- 2.131 A certain atom is spherical with radius $2.2 \times 10^{-10} \text{ m}$, and its mass is $7.3 \times 10^{-23} \text{ g}$. Calculate its density.
- 2.132 Perform the following calculations, and report the results to the proper number of significant digits:
(a) $(6.53 \text{ cm})(7.113 \text{ cm})(1.9 \text{ cm})$
(b) $(7.19 \text{ kg})/[(6.12 \times 10^2 \text{ cm})(25.7 \text{ cm})(3.3 \text{ cm})]$
(c) $(6.9021 \text{ g} - 0.016 \text{ g})/(5.1274 \text{ cm}^3)$
- 2.133 Using the densities in Table 2.5, identify the metal in a cube with 3.00-cm edges and a mass of 579 g.
- 2.134 A certain road map of Maine shows part of Canada. The distances in Canada are shown in kilometers, and the legend states: "To convert kilometers to miles, multiply by 0.62." What is actually being converted?
- 2.135 Calculate the results of the following calculations to the proper number of significant digits:
(a) $1.36 \times 10^{24} \text{ g} - 6.17 \times 10^{23} \text{ g}$
(b) $\frac{1.36 \times 10^{24} \text{ g} - 6.17 \times 10^{23} \text{ g}}{4.05 \times 10^9 \text{ cm} \times 4.11 \times 10^8 \text{ cm}^2}$

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- 2.136 Calculate the number of
(a) Millimeters in $1.21 \times 10^{-3} \text{ m}$
(b) Milliliters in $5.09 \times 10^{-6} \text{ m}^3$
(c) Milligrams in $3.12 \times 10^{-3} \text{ kg}$
- 2.137 Calculate the results of the following calculations to the proper number of significant digits:
(a) $(9.99 \times 10^7 \text{ mg}) + (3.36 \times 10^3 \text{ g})$
(b) $(2.49 \times 10^{-3} \text{ kg})/(7.31 \times 10^{-1} \text{ cm})^3$
(c) $(50.334 \text{ g} - 49.01 \text{ g})/(39.11 \text{ cm}^3)$
- 2.138 A certain brand of vitamin pill contains 346.0 μg of the vitamin per pill; another brand has 0.3460 mg of the vitamin per pill. Which is the better buy, all other factors being equal?
- 2.139 A nurse who is directed to give a patient a pill that has 0.150 cg of active ingredients has no pills with centigrams as units. What pill labeled in milligrams should the nurse administer?
- 2.140 Under a certain set of conditions, the density of water is 1.00 g/mL and that of oxygen gas is 1.30 g/L. Which will float on the other?
- 2.141 Calculate the number of liters in
(a) 62.1 mL (b) 0.0293 m^3
(c) 703 cm^3 (d) $2.28 \times 10^5 \text{ mm}^3$
- 2.142 Calculate the sum of $1.71 \times 10^8 \text{ cm} + 7.09 \times 10^6 \text{ mm}$.
- 2.143 Calculate the result of the following calculation:

$$\frac{2.103 \times 10^{-22} \text{ g} - 6.18 \times 10^{-23} \text{ g}}{2.11 \times 10^{-9} \text{ cm} \times 8.10 \times 10^{-12} \text{ cm}^2}$$
- 2.144 Convert the density of air in a portion of the upper atmosphere, $2.78 \times 10^{-4} \text{ kg/m}^3$, to grams per milliliter.
- 2.145 Calculate the sum of 2.00 m and 0.200 mm. Attempt to draw a picture of this sum to the proper scale. Explain the effect in terms of significant digits.
- 2.146 Calculate the density of a 25.0% by mass sodium chloride solution in water if 253 g of sodium chloride is used to make 850 mL of the solution.
- 2.147 Explain why a football referee, after two successive defensive offside penalties on a first down, rules *without a measurement* that a new first down has been achieved, but does not do so after a first-down running play for no gain followed by two offside penalties.
- 2.148 The density of a solution 25.0% by mass sodium chloride (table salt) in water is 1.19 g/mL. Calculate the mass of sodium chloride in 842 mL of the solution.
- 2.149 Calculate the approximate height in meters of the man in the cubic meter box (Figure 2.7). Use a ratio

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- of the height of the man to the height of the box in the figure, which is equal to the ratio of the heights in real life.
- Use a metric ruler to measure the figure.
 - Use an inch ruler.
 - State another reason why the metric system is easier to use than the English system of measurement.
- 2.150 Repeat Problem 2.149 but estimate the man's width at his waist instead of his height.
- 2.151 Calculate the value of "72.90 ks" in (a) minutes and (b) hours.
- 2.152 If a patient has a blood count of 835 white corpuscles per cubic millimeter, what is the number of white corpuscles per milliliter?
- 2.153 (a) Draw a figure showing the addition of the lengths of two line segments, 20.0 cm and 0.20 cm.
(b) Can you do the same with 20.0 cm and 0.0020 cm? Explain.
- 2.154 How many grains of sand, each with a volume of 1.0 mm^3 , could be held in a volume approximately equal to that of the Earth? (The Earth's radius is $6.4 \times 10^3 \text{ km}$. For a sphere, $V = \frac{4}{3}\pi r^3$)
- 2.155 (a) A bank usually charges 16.0% interest for a certain type of loan. If the bank advertises a special 15.0% discount for that type of loan, what is the actual rate?
(b) The percentage of a certain ore in the rock from a mine is 19%. The percentage of iron in the ore is 69%. What is the percentage of iron in the rock?
- 2.156 Calculate the length in meters of each side of a cube that has a volume of $6.92 \times 10^7 \text{ cm}^3$.
- 2.157 Calculate the radius of a sphere of volume 9.02 cm^3 .
- 2.158 Equal volumes of water (density 1.00 g/mL) and ethyl alcohol (density 0.789 g/mL) are combined. If the total volume is 190% of the volume of each component, what is the density of the solution?
- 2.159 Calculate the length of each side of a cube that has a volume of 74.3 cm^3 . (Be sure to use the proper units and the proper number of significant digits.)
- 2.160 Calculate the temperature in kelvins of each of the following:
(a) 98.6°F (b) -40°F
(c) 37°F (d) 212°F
- 2.161 Calculate the mass of gold in a bracelet that contains 66.7% gold by mass and that has a volume of 17.9 mL and a density of 14.9 g/mL.
- 2.162 How many significant digits are in the value 0°F ? (The zero is not left of all other digits, right of all other digits, or between all other digits.) How many are there in its Celsius equivalent?

CHAPTER 2 ■ Measurement

- 2.163 Calculate the depth of water in centimeters in a cubic box (not full) with 40.0-cm edges if the mass of the contents is 25.6 kg.
- 2.164 Calculate the length of a rectangular solid if its density is 6.12 g/cm^3 , its mass is 512 g, its width is 9.12 cm, and its thickness is 0.250 cm.
- 2.165 A vitamin pill maker produces pills with a mass of 1.00 g each. If each of the following indicates the mass of active ingredient, what percentage of the pill is active in each case?
(a) 3.00 mg (b) 0.300 mg (c) 300 mg
- 2.166 What is the volume of a cube whose edge measures:
(a) 4.99 cm (b) $6.13 \times 10^{-8} \text{ cm}$
- 2.167 Using the densities in Table 2.5, identify the substance in a sphere with a 3.00-cm radius and a mass of 177 g. ($V = \frac{4}{3}\pi r^3$)
- 2.168 Calculate the average density of the Earth, assuming it to be spherical with radius 6400 km and mass $6.1 \times 10^{24} \text{ kg}$. ($V = \frac{4}{3}\pi r^3$)
- 2.169 Calculate the temperature in degrees Fahrenheit of each of the following:
(a) 250 K (b) 0 K (c) 273 K (d) 329 K
- 2.170 Which of the following amounts of money would more likely be rounded by a merchant to the nearest \$10?
(a) \$1303.22 or (b) \$13.22
- 2.171 (a) Calculate the price of an average grain of a certain type of rice if a pound of this rice costs \$2.12 and there are 4.1×10^4 grains of rice per pound.
(b) How many significant digits should be reported in this calculation?
- 2.172 Calculate the mass of a sphere of radius 2.75 cm and density 0.382 g/cm^3 . ($V = \frac{4}{3}\pi r^3$)
- 2.173 Calculate the density of a sphere of radius 5.12 cm and mass 441 g. ($V = \frac{4}{3}\pi r^3$)
- 2.174 Calculate the density in grams per cubic centimeter of an average chlorine atom, which has a radius of $1.05 \times 10^{-10} \text{ m}$ and a mass of $5.89 \times 10^{-23} \text{ g}$. ($V = \frac{4}{3}\pi r^3$)
- 2.175 Equal volumes of water (density 1.00 g/mL) and ethyl alcohol (density 0.789 g/mL) are combined. If the density of the resulting solution is 0.942 g/mL, what is the volume of the solution compared to that of the water?
- 2.176 Calculate the volume of a (spherical) atom of chlorine, which has a radius of $1.05 \times 10^{-10} \text{ m}$. ($V = \frac{4}{3}\pi r^3$)
- 2.177 Calculate the temperature in Celsius of each of the following: (a) 19°F , (b) 19.0°F , and (c) 0.0°F . How many significant digits should be reported for each?

■ General Problems

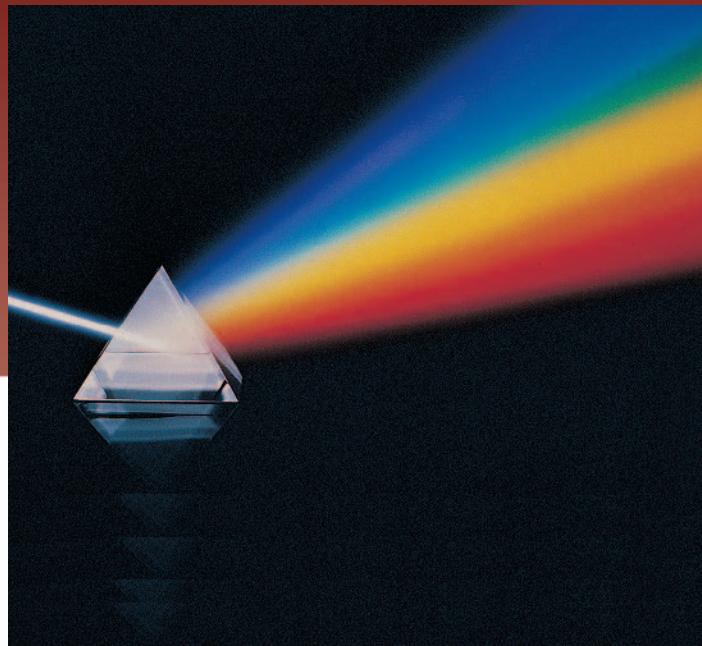
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- 2.178 Calculate the reduction in volume after 99.00 g of sulfuric acid is added to 1.000 g of water. The density of water is 1.000 g/mL, that of sulfuric acid is 1.8305 g/mL, and that of 99.00% sulfuric acid in water is 1.8342 g/mL.
- 2.179 Calculate the density of a solution prepared with 54.08 mL of sulfuric acid and 1.00 mL of water. The density of water is 1.00 g/mL and that of sulfuric acid is 1.8305 g/mL. The volume of the solution is 54.52 mL.
- 2.180 Calculate the reduction in volume after 30.00 g of sulfuric acid is added to 70.00 g of water. Assume that the density of water is 1.000 g/mL, that of sulfuric acid is 1.8305 g/mL, and that of 30.00% by mass sulfuric acid in water is 1.2185 g/mL.
- 2.181 Calculate the density of a solution prepared with 16.39 mL of sulfuric acid and 70.00 mL of water. Assume that the density of water is 1.000 g/mL and that of sulfuric acid is 1.8305 g/mL. The volume of the solution is 82.068 mL.
- 2.182 In light of the answers to the Problems 2.178–2.181, state why the method of determining volume of irregularly shaped objects in Figure 2.2 would not work for sugar crystals.
- 2.183 Calculate the number of microliters in $2.55 \times 10^{-2} \text{ m}^3$.

3

Atoms and Atomic Masses

- 3.1 Laws of Chemical Combination
- 3.2 Dalton's Atomic Theory
- 3.3 Subatomic Particles
- 3.4 Atomic Mass
- 3.5 Development of the Periodic Table



White light broken into its spectrum of colors by a prism

Review Clues

- Section 3.1 Section 1.1, Chapter 2
- Section 3.2 Section 1.6
- Section 3.3 Sections 1.4, 1.5
- Section 3.5 Section 1.5

Objectives

- 3.1 To calculate some of the quantities involved in chemical combinations of elements, using the classical laws known at Dalton's time
- 3.2 To interpret the classical laws of chemical combination using Dalton's atomic theory
- 3.3 To use the properties of subatomic particles—protons, electrons, and neutrons—to determine atomic structure
- 3.4 To calculate the atomic mass of any element—the average mass of its atoms on a relative scale—two ways: (1) from the ratios of masses of equal numbers of atoms, as was done historically, and (2) from masses and abundances of its naturally occurring mixture of isotopes, the more modern method
- 3.5 To repeat the thought processes of Mendeleyev and Meyer in the development of the periodic table

3.1 ■ Laws of Chemical Combination**77**

The theory of the atom has had a long history. The ancient Greeks postulated that matter exists in the form of atoms, but they did not base their theory on experiments, nor did they use it to develop additional ideas about atoms. In 1803, John Dalton proposed the first modern theory of the atom, which was based on the experimentally determined laws of conservation of mass, definite proportions, and multiple proportions. Dalton suggested for the first time that atoms of different elements are different from each other. His theory generated a great deal of research activity, which brought forth additional laws and knowledge about atoms, and he is recognized as the father of the atomic theory.

Section 3.1 takes up the experimental laws on which Dalton based his atomic theory, and Section 3.2 discusses that theory itself. Some modern extensions of the theory, including subatomic particles and isotopes, are presented in Section 3.3. The concept of the masses of atoms of the individual elements is presented in Section 3.4, and the development of the periodic table is traced in Section 3.5. A much more sophisticated theory of the atom will be presented in Chapter 4.

3.1 Laws of Chemical Combination

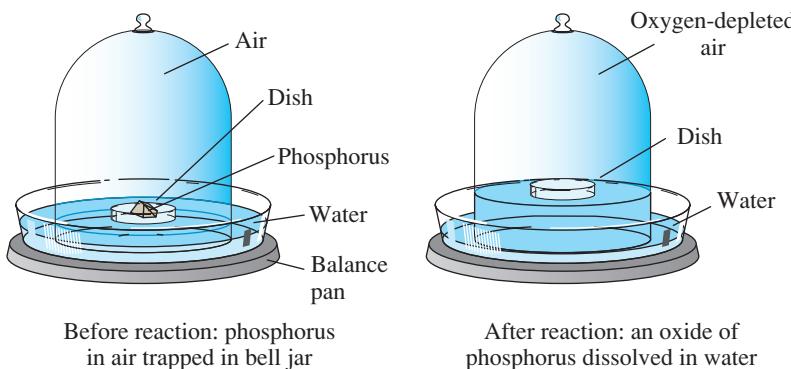
Antoine Lavoisier (1743–1794), called the father of modern chemistry, discovered the law of conservation of mass (Section 1.6) by showing that during a chemical reaction, mass is neither gained nor lost. His quantitative work (work involving measurements) enabled him to conclude that the mass of the products generated during a chemical reaction is the same as the mass of the reactants used up (Figure 3.1). This was not an easy conclusion because “anyone could see that the ashes left after a large log burned did not weigh as much as the log itself.” However, when the oxygen from the air (also a reactant in the burning of wood) and the carbon dioxide, water vapor, and other products formed (in addition to the ash) were considered, the total mass of the reactants and the total mass of the products were found to be equal. Lavoisier’s work led other chemists to measure their reactants and products to confirm his conclusions and to see if they could make other quantitative observations.

The **proportion** of an element in a compound is the ratio of the mass of the element to the total mass of the compound. The **percent** of the element in the compound is just the proportion of the element times 100%.

The **law of definite proportions**, also known as the **law of constant composition**, emerged after careful work by many investigators. This law states that any given compound is composed of definite proportions by mass of its elements. For example, every sample of sucrose (table sugar) contains 6.55 times the mass of carbon as hydrogen and 8.00 times the mass of oxygen as hydrogen. This law was difficult to prove because many samples of compounds contain impurities of other compounds that have the same elements. For example, dinitrogen monoxide (N_2O), known as laughing gas, and nitrogen monoxide (NO), an air pollutant, are two different compounds, but each is composed of only nitrogen and oxygen. The two compounds can form a homogeneous mixture in any proportions. Analysis of an impure sample of either gas could lead to a percentage of nitrogen anywhere between that in pure dinitrogen monoxide and that in pure nitrogen monoxide. A pure sample of dinitrogen monoxide or nitrogen monoxide, not an arbitrary mixture of the two, is necessary to insure a definite percent composition. Once chemists isolated and worked on pure compounds, it was apparent that the law of definite proportions was valid (Section 1.6).

Figure 3.1 Illustration of the Law of Conservation of Mass

In an eighteenth-century experiment, phosphorus in air is ignited by sunlight focused with a magnifying glass. The phosphorus reacts with the oxygen present in the air to produce an oxide of phosphorus, which dissolves in the water. The mass of the system after the reaction is the same as it was before, but the volume of gas trapped in the bell jar has obviously been reduced.



EXAMPLE 3.1

A 4.33-g sample of dinitrogen monoxide is composed of 63.65% nitrogen and 36.35% oxygen by mass. What is the percent composition of a 14.9-g sample of dinitrogen monoxide?

Solution

The 14.9-g sample is 63.65% nitrogen and 36.35% oxygen also. All samples of dinitrogen monoxide have the same percent composition, as required by the law of definite proportions.

Practice Problem 3.1 Nitrogen monoxide has a percent composition of 46.68% nitrogen and 53.32% oxygen. What possible percentages of nitrogen could be in a *mixture* of dinitrogen monoxide and nitrogen monoxide?

EXAMPLE 3.2

Calculate the mass of nitrogen in a 4.75-g sample of nitrogen monoxide, using the percentages in Practice Problem 3.1.

Solution

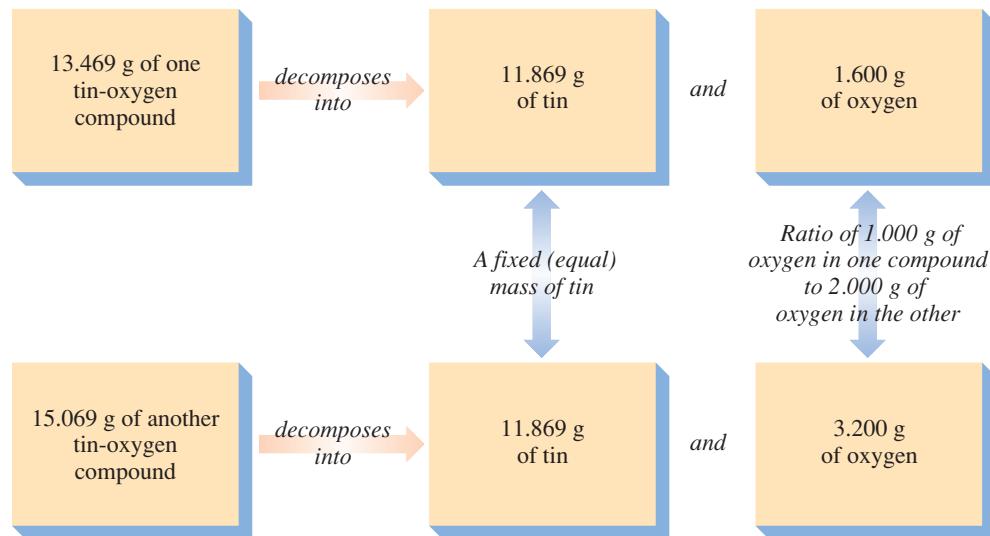
$$4.75 \text{ g NO} \left(\frac{46.68 \text{ g N}}{100.0 \text{ g NO}} \right) = 2.22 \text{ g N}$$

From the
percent composition

Practice Problem 3.2 Calculate the mass of nitrogen monoxide that contains 100.0 g of nitrogen.



The **law of multiple proportions** states that for two (or more) compounds composed of the same elements, for a given mass of one of the elements, the ratio of masses of any other element in the compounds is a small, whole-number

3.1 ■ Laws of Chemical Combination**Figure 3.2** Example Illustrating the Law of Multiple Proportions

ratio (Figure 3.2). For example, hydrogen peroxide contains 0.06300 g of hydrogen for each gram of oxygen present. Water contains 0.1260 g of hydrogen for each gram of oxygen present. For the fixed mass of oxygen (1 g in each case), the ratio of masses of hydrogen is $(0.1260 \text{ g})/(0.06300 \text{ g}) = 2/1$.

Sometimes, the ratio does not appear to be integral at first, but it can be converted to an integral ratio while keeping the value the same by multiplying both numerator and denominator by the same small integer. For example, a compound of chromium and oxygen contains 3.2499 g of chromium per gram of oxygen, while a second compound of these elements contains 2.1666 g of chromium per gram of oxygen. Per gram of oxygen, the ratio of masses of chromium is $(3.2499 \text{ g})/(2.1666 \text{ g}) = 1.5000/1$. We can convert that ratio to an integral ratio by multiplying both numerator and denominator by 2:

$$\frac{1.5000 \times 2}{1 \times 2} = \frac{3}{2}$$

Converting ratios to integral ratios is discussed further in Appendix 1.

EXAMPLE 3.3

The percent compositions of nitrogen dioxide and dinitrogen trioxide are as follows:

Nitrogen dioxide	Dinitrogen trioxide
30.45% nitrogen	36.85% nitrogen
69.55% oxygen	63.15% oxygen

Show that these data follow the law of multiple proportions.

Solution

Per gram of nitrogen, the following mass of oxygen is present in each of the two compounds:

$$\begin{array}{ll} \text{In nitrogen dioxide} & \text{In dinitrogen trioxide} \\ \frac{69.55 \text{ g O}}{30.45 \text{ g N}} = \frac{2.284 \text{ g O}}{1 \text{ g N}} & \frac{63.15 \text{ g O}}{36.85 \text{ g N}} = \frac{1.714 \text{ g O}}{1 \text{ g N}} \end{array}$$

The ratio of grams of oxygen in nitrogen dioxide (per gram of nitrogen) to grams of oxygen in dinitrogen trioxide (per gram of nitrogen) is

$$\frac{2.284 \text{ g O}}{1.714 \text{ g O}} = \frac{1.333}{1.000} = \frac{3.999}{3.000} = \frac{4}{3}$$

This ratio is, within limits of experimental error, equal to a small, whole-number ratio.

Note that it is *not* the ratio of mass of nitrogen to mass of oxygen that must be an integral ratio, according to the law of multiple proportions, but the ratio of the mass of oxygen in one compound to the mass of oxygen in the other compound (for the same mass of nitrogen in the two compounds).

Practice Problem 3.3 The percent compositions of two oxides of iron are 77.73% Fe and 22.27% O for one oxide and 69.94% Fe and 30.06% O for the other. Show that these compounds obey the law of multiple proportions.

How did the chemists of 1800 explain *why* compounds obeyed the law of definite proportions and the law of multiple proportions? They didn't. A theory to explain these and many other phenomena was just about to be proposed.

**Snapshot Review**

- The empirical laws governing the masses of reactants and products of chemical reactions formed the basis for the theoretical development of chemistry.
- A. What is the total mass of the mercury and oxygen produced from the decomposition of 25.0 g of HgO?
 - B. Barium and chlorine combine in a ratio of 137.3 g of barium to 70.90 g of chlorine. What is the percent chlorine in (a) a 5.00-g sample of the compound? (b) a 10.0-g sample of the compound?
 - C. One compound of iron and chlorine contains 1.269 g of chlorine for each gram of iron. A second compound of these elements contains 1.907 g of chlorine for each gram of iron. Calculate the mass of iron per gram of chlorine in each compound, and show that the masses obey the law of multiple proportions.

3.2 Dalton's Atomic Theory



Figure 3.3 John Dalton

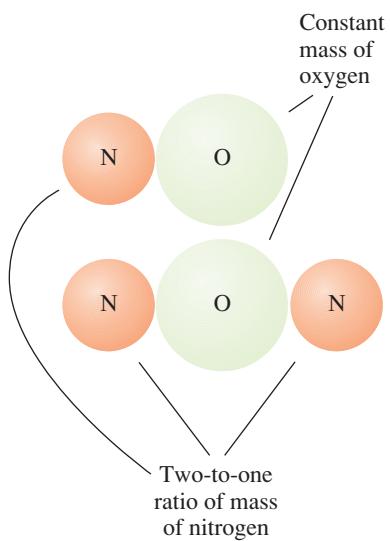


Figure 3.4 Dalton's Explanation of the Law of Multiple Proportions

Because the atoms of each element have a given mass, the fact that the atomic ratio is two atoms of nitrogen in one compound to one atom of nitrogen in the other (for one atom of oxygen in each) means that there is a 2 : 1 ratio of masses of nitrogen in the two compounds (for a given mass of oxygen).

In 1803, John Dalton (1766–1844) (Figure 3.3) proposed his atomic theory, including the following **postulates**, to explain the laws of chemical combination discussed in Section 3.1:

1. Matter is made up of very tiny, indivisible particles called **atoms**.
2. The atoms of each element all have the same mass, but the mass of the atoms of one element is different from the mass of the atoms of every other element.
3. Atoms combine to form **molecules**. When they do so, they combine in small, whole-number ratios.
4. Atoms of some pairs of elements can combine with each other in different small, whole-number ratios to form different compounds.
5. If atoms of two elements can combine to form more than one compound, the most stable compound has the atoms in a 1 : 1 ratio. (This postulate was quickly shown to be incorrect.)

The first three postulates have had to be amended, and the fifth was quickly abandoned altogether. But the postulates explained the laws of chemical combination known at the time, and they caused great activity among chemists, which led to more generalizations and further advances in chemistry.

The postulates of **Dalton's atomic theory** explained the laws of chemical combination very readily.

1. The law of conservation of mass is explained as follows: Because atoms merely exchange “partners” during a chemical reaction and are not created or destroyed, their mass is also neither created nor destroyed. Thus, mass is conserved during a chemical reaction.
2. The law of definite proportions is explained as follows: Because *atoms* react in definite integral ratios (postulate 3), and atoms of each element have a definite *mass* (postulate 2), the *mass* ratio of one element to the other(s) must also be definite.
3. The law of multiple proportions is explained as follows: Because atoms combine in different ratios of small whole numbers (postulate 4), for a given number of atoms of one element, the number of atoms of the other element is in a small, whole-number ratio. A given number of atoms of the first element implies a given mass of that element, and a small, whole-number ratio for the atoms of the second element (each of the same mass) implies a small, whole-number ratio of masses of the second element (Figure 3.4). For example, consider water (H_2O) and hydrogen peroxide (H_2O_2), two compounds of hydrogen and oxygen. For a given number of hydrogen atoms (2), the numbers of oxygen atoms in the two compounds are 1 and 2. Stated another way, for a given mass of hydrogen (2.0160 g), the ratio of masses of oxygen in the two compounds is 15.9994 g to 31.9988 g, a ratio of 1 to 2—a small, whole-number ratio.

We will discuss the ways in which the first three of Dalton's postulates have had to be amended after we learn more about the atom.



Snapshot Review

- Dalton's theory explained why the classical laws of chemical combination worked and provided the theoretical background for the entire future development of chemistry.
- A. If elements A and B react in a 1-to-2 atom ratio, yielding a compound with 4.80 g of B per gram of A, what is the mass ratio in a compound with a ratio of two atoms of A to three atoms of B?

3.3 Subatomic Particles

Since Dalton proposed his atomic theory, many types of experiments have been performed and many discoveries made that have led to the inescapable conclusion that the atom is *not* indivisible. Experiments with electricity in the 1850s showed that chemical reactions can be caused by the passage of electricity (a process called electrolysis) and that electricity can be generated by chemical reactions (as in batteries). (See Chapter 17.) The discovery of radioactivity, in which atoms of an element are changed into atoms of other elements, was another source of evidence (see Chapter 21). The fact that the placement of three pairs of elements in the periodic table are not in order of atomic mass (Sections 3.4 and 3.5) throws doubt on Dalton's theory. The interaction of light with matter gives further evidence that the atom is not indivisible. Absorption of specific wavelengths of light, meaning specific energies of light, led to the conclusion that atoms have certain energy levels in them. (See the following enrichment section.) Many other discoveries have been made that are beyond the scope of this text. If atoms are not indivisible, then what are the particles that constitute them?

The atom is composed of many types of **subatomic particles**, but only three types will be important in this course. **Protons** and **neutrons** exist in the atom's **nucleus**, and **electrons** exist outside the nucleus. The nucleus (plural, *nuclei*) is incredibly small, with a radius about one ten-thousandth of the radius of the atom itself. (If the atom were the size of a car, the nucleus would be about the size of the period at the end of this sentence.) The nucleus does not change during any ordinary chemical reaction. (Nuclear reactions are described in Chapter 21.) The protons, neutrons, and electrons have the properties listed in Table 3.1. These properties are independent of the atom of which the subatomic particles are a part. Thus, the atom is the smallest unit that has the characteristic composition of an element, and in that sense, it is the smallest particle of an element.

An uncombined atom is neither positive nor negative but electrically **neutral**, and thus the number of protons (*p*) must equal the number of electrons:

$$\text{Number of protons} = \text{number of electrons} \quad (\text{For a neutral atom})$$

The nucleus does not change during any ordinary chemical reaction.

Because neutrons are neutral (see Table 3.1), the number of neutrons (*n*) does not affect the charge on the atom. The number of protons in an atom determines the element's identity. All atoms having the same number of protons are atoms of the same element. Atoms with different numbers of protons are atoms of different elements. The number of protons in an atom is what



ENRICHMENT

Visible light (in fact all portions of the electromagnetic spectrum—microwaves, infrared radiation, visible light, ultraviolet light, X-rays, gamma rays) can be described in terms of wave motion. Each wavelength of visible light has a particular color, and a suitable combination of all the wavelengths of visible light produces white light. White light can be broken into its *spectrum* (a rainbow) by passing it through a prism (Figure 3.5).

When white light is passed through a sample of *gaseous* atoms, the atoms absorb some of the wavelengths of light. A given wavelength implies a given energy. Different elements absorb different sets of wavelengths, so an element can be identified by the wavelengths of white light that it absorbs. Helium was first discovered in the Sun because sunlight has a set of absorbed wavelengths that did not match the set of any element known on Earth (Figure 3.6). It was found on Earth shortly afterward.

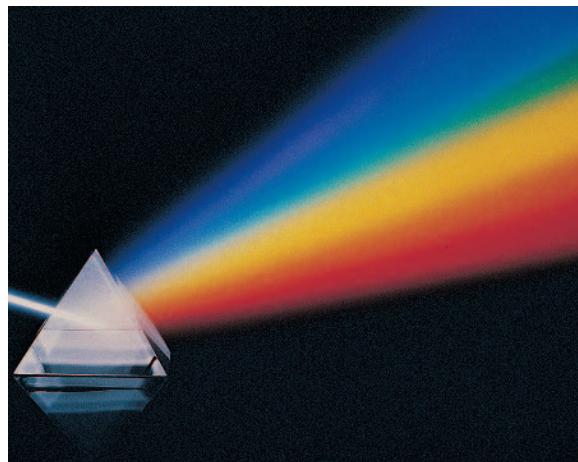


Figure 3.5 Components of White Light

Visible light is broken up into all the colors of the rainbow by passing it through a prism.

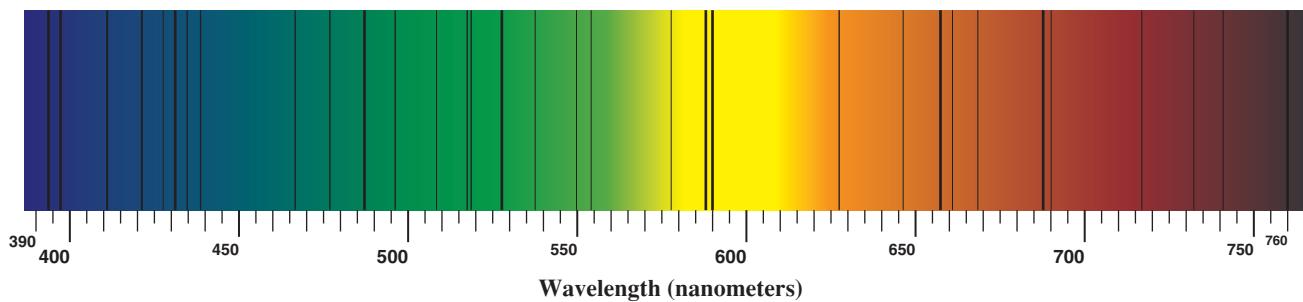


Figure 3.6 Spectral Lines in Sunlight

The dark lines on the visible spectrum of sunlight are due to energies of precise wavelengths of light being absorbed by atoms of elements in the outer layers of the Sun. Bright lines of the same wavelengths are emitted when gaseous samples of those elements are excited electrically.

Table 3.1 Properties of Subatomic Particles

Particle	Charge (e)*	Mass (amu) [†]	Location in the Atom
Proton	1 +	1.0073	In the nucleus
Neutron	0	1.0087	In the nucleus
Electron	1 -	0.000549	Outside the nucleus

*The charges given are relative charges, based on the charge on the electron, e , as the fundamental unit of charge ($1 e = 1.60 \times 10^{-19}$ coulomb).

[†]The masses are given in atomic mass units (amu), described in Section 3.4.

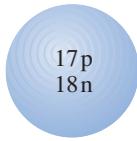
84**CHAPTER 3 ■ Atoms and Atomic Masses**

The atomic number (Z) is equal to the number of protons (p) in the atom, and determines its identity.

The mass number (A) is equal to the sum of the numbers of protons (p) and neutrons (n) in the atom. The number of neutrons is thus the difference between the mass number and the atomic number:

$$n = A - Z$$

$$\begin{array}{c} p + n = A \\ \text{(Optional)} \quad p = Z \end{array}$$



differentiates each element from all others. It is called the **atomic number** (Z) of the element:

$$Z = p$$

The number of neutrons in the nuclei of atoms of the same element can differ. If two atoms have the same number of protons and different numbers of neutrons, they are atoms of the same element (they have the same atomic number). However, they have different masses because of the different numbers of neutrons. Such atoms are said to be **isotopes** of each other. Each isotope of an element is usually identified by its **mass number** (A), which is defined as the sum of the number of protons and the number of neutrons in the atom:

$$A = p + n = Z + n$$

Generally, the mass number for the isotopes rises as the atomic number rises, but the two are *not* directly proportional.

Symbols for the elements were introduced in Chapter 1. In addition, each of those symbols can be used to represent an atom of the element. Moreover, an isotope is identified by the symbol of the element, with the mass number added as a superscript on the left side. For example, the isotope of hydrogen with mass number of 1 is designated as ^1H . (Its name is hydrogen-1.) Note that the number of neutrons is not given; the mass number is. The number of protons (the atomic number) may be shown as a subscript on the left, if desired, as in ^1H . However, because the element's identity determines the atomic number, and vice versa, giving both the symbol and the atomic number is redundant—it identifies the element twice. Except for ^1H , the number of neutrons equals or exceeds the number of protons in the nucleus of every isotope.

EXAMPLE 3.4

Two atoms have 17 protons each, but the first atom contains 18 neutrons and the second contains 20 neutrons. Show that their atomic numbers are the same but that their mass numbers differ.

Solution

The atomic numbers are the numbers of protons, in each case 17, so the atoms are both atoms of the same element—chlorine. (See the periodic table inside the front cover.) The mass number of the first atom is $17 + 18 = 35$, and the mass number of the second is $17 + 20 = 37$. Thus, the atoms have the same atomic number but different mass numbers. Their properties are essentially the same because they are the same element, but their masses are somewhat different. They are isotopes of each other: ^{35}Cl and ^{37}Cl .

Practice Problem 3.4 Two atoms have mass number 119, but one has 69 neutrons and the other 70 neutrons. Are they isotopes of each other?

EXAMPLE 3.5

How many electrons are associated with each of the uncombined atoms in Example 3.4?

Solution

Each atom has 17 protons in its nucleus, so there is a 17+ charge on each nucleus. Because uncombined atoms are neutral, there must be 17 electrons, each with a 1– charge, to exactly balance the nuclear charge.

Practice Problem 3.5 How many electrons does each of the atoms in Practice Problem 3.4 have?

Dalton's first three postulates have had to be amended in light of information discovered after his work. The existence of subatomic particles means that atoms are not indivisible (postulate 1). Dalton thought that the mass differentiated the atoms of one element from those of another (postulate 2) because he believed that atoms were indivisible. However, atoms of *different* elements can have the *same mass number*. Atoms of each element have a distinctive atomic number—the number of protons in the nucleus—to distinguish them from atoms of other elements. In Chapter 5, postulate 3 will be shown to be only partially true. Only some combinations of atoms form molecules; other combinations form ionic compounds.

**Snapshot Review**

ChemSkill Builder 9.1

- The atom is not indivisible, but consists of protons and neutrons within a nucleus and electrons outside the nucleus.
 - Atoms with different numbers of neutrons but the same number of protons are isotopes of each other.
 - The atomic number determines the element of which the atom is a part.
- A. How many protons are in an atom X that is an isotope of an atom Q that has 16 protons and 18 neutrons?
 - B. What are the atomic number and the mass number of atom Q of Problem A?
 - C. For what isotope is the mass number less than double the atomic number?

3.4 Atomic Mass

Atoms are so tiny that, until recently, the masses of individual atoms could not be measured directly (Figure 3.7). However, because mass was so important in Dalton's theory, some measure of atomic masses was necessary. Therefore, a **relative scale**—the **atomic mass scale**—is used. This scale is sometimes called the **atomic weight scale**. On this scale, an average of the masses of all the atoms of the naturally occurring mixture of isotopes of a given element is measured relative to the mass of an atom of a *standard*.



Figure 3.7 The Problem with Weighing Atoms

If we try to weigh one grain of rice on a bathroom scale, we get an inkling of the very much more difficult task of weighing atoms. (The ratio of the mass of an atom to that of the smallest mass weighable on any balance is about 10^{-22} g/ 10^{-6} g, or 10^{-16} . This is much lower than the ratio of the mass of a grain of rice to that of a person, which is about 10^{-3} g/ 10^5 g, or 10^{-8} .)

Historic Determination of Atomic Mass

The early pioneers of chemistry, trying to verify Dalton's atomic theory, could not measure the mass of individual atoms. The best they could do was to measure the masses of equal numbers of atoms (or other known ratios of atoms) of two (or more) elements at a time, to determine their relative masses. They established one element as a standard, gave it an arbitrary value of atomic mass, and used that value to establish the atomic mass scale. The last naturally occurring mixture of isotopes that was used as a standard was oxygen, defined as having an atomic mass of exactly 16 **atomic mass units** (amu). That standard has been replaced; see the next subsection. The atomic mass unit is tiny; it takes 6.02×10^{23} amu to make 1.00 g. We can see how **atomic masses**, sometimes called **atomic weights**, were determined historically by using the analogy presented in Example 3.6.

EXAMPLE 3.6

A student buys beverages for a party. He buys an equal number of bottles of two sizes. The total volume of all the bottles of the first size is 27.5 L and the total volume of the second size is 16.5 L. What is the ratio of volumes of the first size of beverage to the second?

Solution

Let x equal the number of bottles of each size. The volume of each bottle of the first size is thus $(27.5 \text{ L})/x$. The volume of a bottle of the second size is $(16.5 \text{ L})/x$. The ratio of the two is thus

$$\frac{(27.5 \text{ L})/x}{(16.5 \text{ L})/x} = 1.67$$

Practice Problem 3.6 A student buys twice the number of bottles of one size of beverage than bottles of a second for a party for his group. The total volume of all the bottles of the first size is 6.50 L, and the total volume of the second size is 13.0 L. What is the ratio of volumes of each bottle of the first size of beverage to that of each bottle of the second?

This method is illustrated for elements in Example 3.7.

EXAMPLE 3.7

A compound contains equal numbers of nickel atoms and oxygen atoms. A sample of this compound contains 8.15 g of nickel and 2.22 g of oxygen. Calculate the atomic mass of nickel from this information.

Solution

Let x = the number of atoms of each element

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Then

$$\frac{(8.15 \text{ g})}{x} = \text{the mass of each nickel atom, and}$$

$$\frac{(2.22 \text{ g})}{x} = \text{the mass of each oxygen atom}$$

Thus the ratio of masses is

$$\frac{(8.15 \text{ g})/x}{(2.22 \text{ g})/x} = 3.67$$

Since the atomic mass of oxygen is 16.0 amu, the atomic mass of nickel is $3.67(16.0 \text{ amu}) = 58.7 \text{ amu}$.

After it has been determined as shown, the atomic mass of nickel can be used to determine the atomic masses of other elements.

Practice Problem 3.7 Oxygen and selenium form a compound containing twice as many oxygen atoms as selenium atoms. In a sample of the compound, the ratio of masses of selenium to oxygen is 2.47 to 1.00. Calculate the atomic mass of selenium.

How could the early chemists be sure that their samples of two elements had equal numbers of atoms? They made a compound of the elements in which the atomic ratio was 1 : 1. They did not need to know the exact number of atoms of each element, only that the atoms were present in a 1 : 1 ratio.

Modern Determination of Atomic Mass

The modern method of determining atomic mass uses the ^{12}C isotope as the standard, with a mass defined as exactly 12 amu. (The atomic mass of carbon on this scale is 12.011 amu, and that of oxygen is 15.9994 amu.) The atomic mass of an element is defined as the **weighted average** of the actual masses of its naturally occurring isotopes (not the mass numbers of the isotopes). A weighted average is the average taking into account the relative numbers of atoms of each type of isotope. The concept of weighted average may be understood using an analogy to a situation in everyday life, presented in Examples 3.8 and 3.9.

EXAMPLE 3.8

A supermarket is having a special, selling a package of seven 2.00-L bottles of soda at regular price and including three 1.00-L bottles free. (a) What is the average volume of two bottles—one bottle of each size? (b) What is the average volume of all 10 bottles together? (c) Explain the meaning of the term **weighted average**.

Solution

- (a) The average of one bottle of each size is

$$\frac{2.00 \text{ L} + 1.00 \text{ L}}{2} = 1.50 \text{ L}$$

- (b) The average of all the bottles is

$$\frac{7(2.00 \text{ L}) + 3(1.00 \text{ L})}{10} = 1.70 \text{ L}$$

- (c) This weighted average calculated in part (b) takes into account the number of each size bottle.

EXAMPLE 3.9

- (a) Calculate the percentage of 2-L bottles in Example 3.8. (b) Calculate the percentage of 1-L bottles in Example 3.8. (c) Determine the weighted average using the percentages rather than the actual numbers of bottles.

Solution

(a) $\frac{7 \text{ two-liter bottles}}{10 \text{ bottles total}} = 70\%$

(b) $\frac{3 \text{ one-liter bottles}}{10 \text{ bottles total}} = 30\%$

(c) $\frac{70\%(2.00 \text{ L}) + 30\%(1.00 \text{ L})}{100\%} = 1.7 \text{ L}$

EXAMPLE 3.10

Naturally occurring copper consists of 69.17% ^{63}Cu , which has a mass of 62.9396 amu, and 30.83% ^{65}Cu , which has a mass of 64.9278 amu. Calculate the atomic mass of copper.

Solution

The weighted average is given by the sum of the fraction of ^{63}Cu times its mass and the fraction of ^{65}Cu times its mass:

$$(0.6917)(62.9396 \text{ amu}) + (0.3083)(64.9278 \text{ amu}) = 63.55 \text{ amu}$$

Practice Problem 3.10 Naturally occurring gallium consists of 60.108% ^{69}Ga , with a mass of 68.9256 amu, and 39.892% ^{71}Ga , with a mass of 70.9247 amu. Calculate the atomic mass of gallium.

Atomic masses of naturally occurring elements are listed in the periodic table. (Because atomic mass is the weighted average of *naturally occurring* isotopes, artificial elements by definition do not have atomic masses. The mass

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number of the most stable isotope of each artificial element is placed in parentheses in the box for the element in the table.) Naturally occurring samples of an element have almost exactly the same mixture of isotopes, no matter what the source. For example, water from the rain forest of the Amazon, from an iceberg in the Arctic Ocean, or from the combustion of an oak tree in New York contains oxygen that is 99.759% ^{16}O , 0.037% ^{17}O , and 0.204% ^{18}O . Because the relative percentages of the isotopes in any naturally occurring element are remarkably constant, the average of the isotopic masses is also constant (to four, five, or even six significant digits). Thus, Dalton's postulate of a constant mass for the atoms of an element explained the laws of chemical combination because there is a constant *average* mass.

***Snapshot Review***

- Atomic mass is *defined* as the weighted average of the masses of the naturally occurring mixture of isotopes of an element. Be careful to distinguish it from *mass number* and the *mass of a particular atom*.
 - Historically, atomic mass was determined from mass ratios, such as were used to develop the law of definite proportions. Now, the mass and percentage of each isotope is used.
- A. In a compound containing one atom of X for every atom of oxygen, the ratio of masses is 8.58 g X per gram of oxygen. Identify element X.
 - B. Element X consists of 78.99% of atoms with mass 23.985 amu, 10.00% of atoms with mass 24.986 amu, and the rest of the atoms of mass 25.983 amu. Identify element X.

3.5 Development of the Periodic Table



Many atomic masses were determined as a direct result of Dalton's postulates and the work that they stimulated, and scientists attempted to relate the atomic masses of the elements to the elements' properties. This work culminated in the development of the periodic table by Dmitri Mendeleyev (1834-1907) (Figure 3.8) and independently by Lothar Meyer (1830-1895). Because Mendeleyev did more with his periodic table, he is often given sole credit for its development.

Mendeleyev put the elements known in the 1860s in ascending order according to their atomic masses (atomic numbers had not yet been defined) and noticed that the properties of every seventh known element were similar. He arranged the elements in a table, with elements having similar properties in the same group. At several points where an element did not seem to fit well in the position its atomic mass called for, he postulated that there was an undiscovered element for that position. For example, the next known element after zinc (Zn) by atomic mass was arsenic (As). However, because arsenic's properties were much more similar to those of phosphorus (P) than to those of aluminum (Al) or silicon (Si), Mendeleyev predicted that two elements that fit the positions under aluminum and silicon in the periodic table had not yet been discovered. (Figure 3.9). He described their expected properties from those of the elements above and below them in the table. His predictions helped other chemists discover these elements, now known as gallium (Ga) and germanium (Ge).

Figure 3.8 Dmitri Mendeleyev

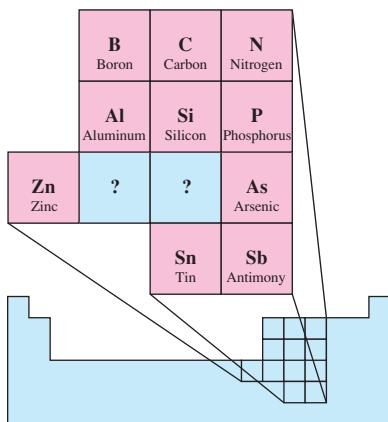


Figure 3.9 A Portion of Mendeleev's Periodic Table

The periodic table is based on the atomic numbers of the elements, not the atomic masses.

Several other elements seemed out of order. For example, their atomic masses placed iodine (I) before tellurium (Te), but their chemical properties required the opposite order. Mendeleev concluded that the atomic masses must have been determined incorrectly and put these two elements in positions reflecting their properties. We now know that the periodic properties of the elements are based on their atomic numbers, not their atomic masses, which explains Mendeleev's difficulty with the placement of certain elements.

EXAMPLE 3.11

In the periodic table, locate two pairs of elements besides iodine and tellurium that are out of order, based on their atomic masses.

Solution

The elements argon and potassium and the elements cobalt and nickel are in reverse order with respect to their atomic masses.

Practice Problem 3.11 Are any elements in the periodic table out of order according to their atomic numbers?

An entire group of elements—the noble gases—was discovered after the periodic table was first formulated. These elements are colorless, odorless gases and almost totally inert. Their lack of combining capacity means that they are not found in any naturally occurring compound. If some compound had had a percentage of its mass unaccounted for, chemists would have known to look for the missing elements, but because the noble gases do not combine spontaneously with substances that they come into contact with in nature, there was no clue to their existence.

That each element fits properly into place in a vertical column proves the fundamental correctness of arranging the elements according to their atomic numbers and chemical properties. Henry Moseley (1887-1915) discovered a quantitative relationship between the wavelength of X-rays emitted by an element and the atomic number of the element. Every atomic number between 1 and 92 was accounted for, which means that there are no more “undiscovered” elements except possibly artificial elements with very high atomic numbers yet to be synthesized.

Atomic numbers and atomic masses are usually included in the boxes with the chemical symbols in the periodic table. The atomic number is the integer. (The mass number, also an integer, is given in parentheses for the most stable isotope of the synthetic elements.)

The periodic table is a tremendous source of information for students who learn to use it well. In Chapter 4, we will learn to use the periodic table to predict the electronic configuration of each of the elements, and in Chapter 5, we will use it to predict outermost electron shell occupancy. The table's numeric data are used in later chapters on formula calculations and stoichiometry, and its information on chemical trends is applied in the chapters on bonding and molecular structure.

■ Summary

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***Snapshot Review***

- The periodic table was originally developed using atomic masses and chemical and physical properties of the elements, but it is now known that the atomic number is the real basis of the periodic table.
- A. How did Mendeleev know to leave spaces in his periodic table for gallium and germanium?

Key Terms

Key terms are defined in the Glossary.

atom (3.2)
 atomic mass (3.3, 3.4)
 atomic mass scale (3.4)
 atomic mass unit (3.4)
 atomic number (3.3)
 atomic weight (3.4)
 atomic weight scale (3.4)
 Dalton's atomic theory (3.2)
 electron (3.3)

isotope (3.3)
 law of constant composition (3.1)
 law of definite proportions (3.1)
 law of multiple proportions (3.1)
 mass number (3.3)
 molecule (3.2)
 neutral (3.3)
 neutron (3.3)

nucleus (3.3)
 percent (3.1)
 postulate (3.2)
 proportion (3.1)
 proton (3.3)
 relative scale (3.4)
 subatomic particle (3.3)
 weighted average (3.4)

Symbols/Abbreviations

A (mass number) (3.3)

p (number of protons) (3.3)

amu (atomic mass unit) (3.4)

n (number of neutrons) (3.3)

Z (atomic number) (3.3)

Summary

Lavoisier discovered the law of conservation of matter, which states that matter cannot be created or destroyed during chemical reactions or physical changes. This generalization increased chemists' efforts to measure the masses of elements in compounds and resulted in two more laws. The law of definite proportions states that the percentage of each element in any sample of a pure compound is always the same. According to the law of multiple proportions, if the mass of one of the elements in two or more compounds of the same elements is held constant, the masses of each other element form a small, whole-number ratio. (Section 3.1)

Dalton suggested that the elements are composed of indivisible atoms and that the atoms of each element have a characteristic mass, different from the mass of any other element. He stated that the atoms combine to form molecules when the elements combine to form compounds. These postulates explained the laws of chemical combination known at that time, but most of them have been

amended in light of later discoveries. However, the atom is still considered to be the fundamental particle of an element. (Section 3.2)

In the past 200 years, numerous experiments have shown that the atom is not indivisible but is composed of electrons plus a nucleus containing protons and neutrons. The nucleus does not change in any chemical reaction. The characteristics of the subatomic particles (Table 3.1) should be memorized. The number of protons, called the atomic number, governs the number of electrons in the neutral atom. The sum of the numbers of protons and neutrons is called the mass number. All atoms of a given element have the same atomic number, which differs from the atomic numbers of other elements. Different atoms of the same element may have different numbers of neutrons and thus different mass numbers. Such atoms are *isotopes* of each other. An isotope is identified by the symbol of the element, with the mass number as a superscript to the left. (Section 3.3)

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The naturally occurring mixture of isotopes in any sample of a given element has almost exactly the same percentage of each isotope as any other sample. Therefore, the average mass of all the atoms in any sample of the element is constant (to four or more significant digits). That weighted average is called the atomic mass (which is not the same as the mass number or the mass of an atom). Atomic masses are reported on a relative scale, with an atom of the ^{12}C isotope being defined as having a mass of exactly 12 amu. (Section 3.4)

CHAPTER 3 ■ Atoms and Atomic Masses

When arranged in order of increasing atomic mass, the various elements, with a few exceptions, have periodically recurring properties. Mendeleyev produced a periodic table based on this ordering. Later, it was learned that the atomic number is the basis for the chemical properties of an element, so the modern periodic table arranges the elements in order of increasing atomic number, with elements having similar properties arranged in vertical groups. The periodic table has many uses in the study of chemistry. (Section 3.5)

Items for Special Attention

■ Atomic mass and mass number are not the same. Atomic mass refers to the naturally occurring mixture of isotopes; mass number refers to an individual isotope. Atomic mass is an average and is never an exact integer; mass number is a sum (of the number of protons plus the number of neutrons) and is always an integer. Except for the artificial elements, mass numbers are not given in the periodic table.

■ Atoms have masses between 1 and 250 atomic mass units, nowhere near as large as 1 g. Be careful to use the correct units for the masses of individual atoms and for the masses of weighable samples.

■ In the periodic table, the elements are arranged so that their atomic numbers are in increasing order and grouped vertically so that elements with similar chemical properties are in the same group (vertical column).

Answers to Snapshot Reviews

- 3.1 A. 25.0 g (from the law of conservation of mass)
B. In the given sample:

$$\frac{70.90 \text{ g Cl}}{208.2 \text{ g total}} \times 100\% = 34.05\% \text{ Cl}$$

Therefore 34.05% in each of the others. (Percent composition is intensive; it does not depend on the sample size.)

C. $\frac{1.269 \text{ g Fe}}{1.000 \text{ g Cl}}$ means $\frac{1.000 \text{ g Cl}}{1.269 \text{ g Fe}} = \frac{0.7880 \text{ g Cl}}{1.000 \text{ g Fe}}$
 $\frac{1.907 \text{ g Fe}}{1.000 \text{ g Cl}}$ means $\frac{1.000 \text{ g Cl}}{1.907 \text{ g Fe}} = \frac{0.5244 \text{ g Cl}}{1.000 \text{ g Fe}}$
 $\frac{0.7880 \text{ g Cl}}{0.5244 \text{ g Cl}} = \frac{1.50}{1} = \frac{3}{2}$ ratio

- 3.2 A. The first compound has 4 atoms of B for every 2 atoms of A, the second has 3 atoms of B for every 2 atoms of A. Per 2 atoms of A, the ratio of B is 4 atoms in the first

compound to 3 atoms in the second, and therefore 4 g to 3 g. The mass of B in the second compound is

$$4.80 \text{ g in compound 1} \left(\frac{3 \text{ g in compound 2}}{4 \text{ g in compound 1}} \right) \\ = 3.60 \text{ g in compound 2}$$

- 3.3 A. 16 protons
B. Atomic number 16, mass number 34
C. ^1H
3.4 A. The atomic mass of oxygen is 16.0 amu, so the atomic mass of X is
 $(16.0 \text{ amu})(8.58) = 137 \text{ amu}$
The element is barium.
B. $(0.7899)(23.985 \text{ amu}) + (0.1000)(24.986 \text{ amu}) + (0.1101)(25.983 \text{ amu}) = 24.31 \text{ amu}$
The element is magnesium.
3.5 A. He knew that arsenic, the next known element, was similar to phosphorus and not to aluminum or silicon.

Self-Tutorial Problems

- 3.1 At a racetrack, the winning horse paid "5 to 2." How much does a gambler win for each dollar bet on that horse? Is that ratio an integral ratio?
- 3.2 Two compounds are each composed of elements X and Z. The first contains 6.10 g of Z for every gram of X. Of

the following possibilities, which ones could be the correct number of grams of Z per gram of X in the second compound?

- (a) 6.10 g (b) 3.05 g
(c) 12.2 g (d) 6.05 g

■ Problems**93**

- 3.3** On what standard are all atomic masses presently based?
- 3.4** Which of the following are synonyms?
- | | | |
|---------------|---------------|-----------------|
| atomic mass | mass number | mass of an atom |
| atomic number | atomic weight | |
- 3.5** (a) How many protons are in a potassium atom?
 (b) What is the atomic number of potassium?
 (c) What is the number of positive charges on a potassium nucleus?
- 3.6** Which of the three following numbers, each of which appears on the periodic table inside the front cover, is an atomic number, which is an atomic mass, and which is a mass number?
 (a) 65 (b) 101.07 (c) (242)
- 3.7** (a) What is the unit of electric charge used at the atomic level?
 (b) What is the unit of atomic mass?
- 3.8** What is the weighted average of three masses of 4.21 g, seven masses of 5.55 g, and two masses of 6.42 g?
- 3.9** What characteristic of an atom did Dalton think was the most important?
- 3.10** What is the difference between the symbol for an element and the symbol for an isotope of that element?
- 3.11** Of atomic number, atomic mass, and mass number, which two appear with most of the symbols for the elements in the periodic table?
- 3.12** What is the difference between the mass of an atom and the mass number of the atom?
- 3.13** Potassium and iodine react to form one compound only. In a certain reaction, 20.0 g of potassium reacts completely with 64.9 g of iodine to produce potassium iodide.
- (a) How much potassium iodide is produced?
 (b) How much iodine would react with 4.00 g of potassium?
 (c) How much iodine would react with 7.29 g of potassium?

Problems**3.1 Laws of Chemical Combination**

- 3.23** If 31.9 mg of a compound containing only carbon and hydrogen is burned completely in oxygen and yields 87.7 mg of carbon dioxide and 71.8 mg of water, how much oxygen is used up?
- 3.24** When 7.80 mg of a compound containing only carbon and hydrogen was burned completely in 28.3 mg of oxygen, 23.3 mg of carbon dioxide and some water were formed. Calculate the mass of the water.

- 3.14** A 29.7-g sample of a certain compound contains 85.63% carbon and 14.37% hydrogen.
- (a) How much carbon is in a 9.08-g portion of this sample?
 (b) How much carbon is in 9.08 g of a different sample of this compound?
- 3.15** A 4.73-g sample of element A combines completely with a 12.11-g sample of element B. What is the total mass of the product?
- 3.16** A 4.22-g sample of magnesium was burned, yielding 7.00 g of magnesium oxide. How many grams of oxygen was taken up in the reaction?
- 3.17** A 6.73-g sample of an element combines completely with another element to make 12.14 g of a compound. What mass of the second element reacted?
- 3.18** Which two types of subatomic particles must be present in equal numbers for an atom to be neutral?
- 3.19** (a) Which element has atomic number 23?
 (b) Which element has an atomic mass of 23.0 amu (to three significant figures)?
 (c) Locate the elements of part (a) and part (b) on the periodic table.
- 3.20** (a) What is the average of a 30.0-g mass and a 46.0-g mass?
 (b) What is the weighted average of eight 30.0-g masses and twelve 46.0-g masses?
 (c) What is the weighted average mass of three chlorine atoms with mass 35.0 amu each and one chlorine atom with mass 37.0 amu?
- 3.21** Why did Mendeleyev not use atomic numbers instead of atomic masses as the basis for his periodic table?
- 3.22** In the periodic table (inside front cover), locate five elements for which mass numbers rather than atomic masses are given.

- 3.25** A 7.33-g sample of mercury(I) oxide was decomposed into mercury and oxygen, yielding 7.05 g of mercury.
- (a) What mass of oxygen was obtained?
 (b) What fraction of the compound was oxygen?
 (c) What percentage of the compound was oxygen?
- 3.26** A 18.6-g sample of a compound contains 39.35% sodium and 60.65% chlorine.
- (a) Calculate the mass of chlorine present.
 (b) Calculate the mass of chlorine present in a 30.0-g sample of the same compound.

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- 3.27** Sodium and chlorine react to form one compound only. In a certain reaction, 2.241 g of sodium reacts completely with 3.454 g of chlorine to produce sodium chloride.
- How much chlorine would react with 15.44 g of sodium?
 - How much sodium would react with 0.7206 g of chlorine?
- 3.28** Sodium and chlorine react to form one compound only. In a certain reaction, 20.0 g of sodium and 30.8 g of chlorine react completely. How much chlorine would remain unreacted if 20.0 g of sodium and 50.0 g of chlorine were allowed to react?
- 3.29** A compound is formed between elements A and B in which two atoms of B combine with each atom of A. Each atom of B has a mass of 127 amu, and each atom of A has a mass of 24.3 amu.
- Calculate the mass ratio.
 - Which ratio is integral, the ratio of atoms or masses or both?
- 3.30** The ratio of masses of sulfur and oxygen in sulfur dioxide is 1.0 g to 1.0 g. Is this fact a proof of the law of multiple proportions?
- 3.31** The ratio of the mass of carbon to the mass of oxygen in carbon monoxide is about 3 g to 4 g. Does this fact confirm the law of multiple proportions?
- 3.32** Solve Example 3.3 (p. 79) again, this time using 1 g of oxygen in each compound. Is the law of multiple proportions still valid?
- 3.33** A sample of a compound composed of only carbon and hydrogen contains 79.89% carbon. Show that this compound and the one in Problem 3.14 obey the law of multiple proportions.
- 3.34** Show that each of the following sets of data obeys the law of multiple proportions:
- | (a) | First Compound | Second Compound |
|-----------|----------------|-----------------|
| Element 1 | 92.26% | 85.63% |
| Element 2 | 7.74% | 14.37% |
- | (b) | Element 1 | Element 2 |
|-----------------|-----------|-----------|
| First compound | 92.26% | 7.74% |
| Second compound | 85.63% | 14.37% |
- 3.35** Show that the following data obey the law of multiple proportions:
- | | Compound 1 | Compound 2 |
|-----------|------------|------------|
| Element X | 103.1 g | 96.23 g |
| Element Y | 7.96 g | 14.87 g |
- 3.36** Two compounds are each composed of elements A and B. The first contains 2.468 g of B for every gram of A. Of the following possibilities, which ones could be the

CHAPTER 3 ■ Atoms and Atomic Masses

correct number of grams of B per gram of A in the second compound?

- (a) 1.234 g (b) 4.936 g
(c) 2.512 g (d) 2.468 g

3.2 Dalton's Atomic Theory

- 3.37** (a) What happens to a scientific hypothesis if experiments show it to be incorrect?
(b) To which of Dalton's postulates did this first happen?
- 3.38** The formula for water is H_2O , signifying that there are two atoms of hydrogen for every atom of oxygen. If Dalton's fifth postulate had been true, what would the formula for water have been?
- 3.39** According to Dalton's atomic theory, all atoms of the same element have the same mass. If an atom of zinc has a mass of 65.4 amu and an atom of sulfur has a mass of 32.1 amu:
- What is the mass ratio of one atom of zinc to one atom of sulfur?
 - What is the total mass of 100 atoms of zinc? What is the total mass of 100 atoms of sulfur?
 - What is the ratio of masses of 100 atoms of zinc to 100 atoms of sulfur?
 - Choose an arbitrary, large number of atoms of zinc. Then calculate the mass of that number and the mass of an equal number of sulfur atoms. Calculate the ratio of the total masses.
 - What can you conclude about the ratio of masses of equal numbers of zinc and sulfur atoms?
- 3.40** Would it make any difference in the prior problem if average masses had been used? Explain.
- 3.41** Draw a figure like that of Figure 3.4 for potassium oxide, K_2O , and potassium peroxide, K_2O_2 . For a given number of oxygen atoms, what is the ratio of potassium atoms in the two compounds?
- 3.42** All naturally occurring samples of boron trifluoride, when purified, contain the same percentage of boron and the same percentage of fluorine. Naturally occurring fluorine consists of only one isotope. What do the constant percentages say about the two naturally occurring isotopes of boron?
- 3.43** The atoms of element Z each have about 12 times the mass of a ${}^9\text{Be}$ atom. Another element, X, has atoms whose mass is about one-fourth the mass of Z atoms. A third element, Q, has atoms with $1\frac{1}{3}$ the mass of X atoms.
- Make a table of relative atomic masses based on ${}^9\text{Be}$ as 9 amu.
 - Identify the elements Z, X, and Q.
- 3.44** Sulfur dioxide (SO_2) has two atoms of oxygen per atom of sulfur, and sulfur trioxide (SO_3) has three atoms of oxygen per atom of sulfur. The mass ratio of sulfur to

■ Problems

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oxygen in SO_2 is 1.0 : 1.0. What is the mass ratio of sulfur to oxygen in SO_3 ?

- 3.45 Naturally occurring silicon consists of 92.21% ^{28}Si , which has a mass of 27.97693 amu, 4.70% ^{29}Si , which has a mass of 28.97649 amu, and 3.09% of ^{30}Si , which has a mass of 29.97376 amu. Calculate the atomic mass of silicon.
- 3.46 A compound is formed between elements A, B, and C in which two atoms of A combine with each atom of B and four atoms of C. Each atom of A has a mass of 39.1 units, each atom of B has a mass of 32.0 units, and each atom of C has a mass of 16.0 units.
- Is there a definite ratio of masses of one element to the other?
 - Calculate the mass ratio of A to B and of C to B.
- 3.47 Plot the mass number versus the atomic number for the last seven actinide elements. Is there any relationship between the mass numbers and atomic numbers (for these elements that have very similar atomic numbers)?

3.3 Subatomic Particles

- 3.48 Identify the only stable isotope that contains no neutrons.
- 3.49 Restate Dalton's first three postulates in amended form, based on modern information.
- 3.50 Isotopes of which element have:
- The smallest mass number
 - The smallest atomic number
 - The largest number of protons
- 3.51 Which transition metal isotopes whose mass numbers are given in the periodic table on the inside front cover of the text have the greatest number of neutrons?
- 3.52 Identify the elements in the periodic table that are *not* naturally occurring.
- 3.53 Complete the following table for neutral atoms of specific isotopes:

Isotopic Symbol	Atomic Number	Mass Number	No. of Protons	No. of Neutrons	No. of Electrons
(a) ^{112}Cd	_____	_____	_____	_____	_____
(b)	49	115	_____	_____	_____
(c)	81	_____	_____	122	_____
(d)	_____	80	34	_____	_____
(e) $^{128}_{52}\text{Xe}$	_____	_____	_____	_____	_____
(f)	_____	_____	_____	54	42
(g)	_____	_____	45	58	_____

- 3.54 Write the symbol for an isotope:

- Containing one proton and two neutrons
- For which the atomic number is 1 and there is one neutron

(c) For which the atomic number is 1 and the mass number is 1

- (d) With a mass number of 3 and containing one neutron
- (e) With a mass number of 3 and containing two neutrons

- 3.55 In the table in Problem 3.53, two pieces of quantitative information are given in each part.

- What two pieces of information are given in part (a)?
- Why would the atomic number and the number of electrons not be sufficient to complete any part?
- Why would the number of protons and the number of electrons not be sufficient to complete any part?

- 3.56 Complete the following table, concerning uncombined atoms:

Isotopic Symbol	Atomic Number	Mass Number	No. of Protons	No. of Electrons	No. of Neutrons
_____	_____	_____	50	_____	66
_____	44	_____	_____	_____	56
_____	_____	174	70	_____	_____
_____	56	138	_____	_____	_____

- 3.57 Complete the following table for neutral atoms of specific isotopes:

Isotopic Symbol	Atomic Number	Mass Number	No. of Protons	No. of Neutrons	No. of Electrons
(a) ^{134}Xe	_____	_____	_____	_____	_____
(b)	27	60	_____	_____	_____
(c)	_____	144	_____	84	_____
(d)	22	_____	_____	26	_____
(e)	_____	_____	_____	106	72
(f)	_____	126	52	_____	_____
(g)	_____	_____	16	18	_____

- 3.58 Deuterium (symbol: ^2D) is a special name for the isotope that contains one proton and one neutron.

- Of what element is deuterium a part?
- Write the more familiar symbol for this isotope.

- 3.59 Which isotope whose mass number is given in the periodic table on the inside front cover of the text has the

- Largest mass number
- Largest number of neutrons
- Smallest mass number
- Smallest number of neutrons

3.4 Atomic Mass

- 3.60 Which element has atoms with average mass about 10 times those of the fluorine atom?

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- 3.61 Which element has atoms with average mass about 35 times those of the average helium atom?
- 3.62 (a) If 37.4% of the people in a Weight Watchers graduating class weigh 185.0 pounds each and the rest weigh 187.0 pounds each, what is the average weight of the class?
(b) If 37.40% of naturally occurring rhenium atoms have an atomic mass of 184.953 amu and the rest have an atomic mass of 186.956 amu, what is the atomic mass of rhenium?
- 3.63 After a calculation, a student reported the atomic mass of an element as 2.2×10^{-3} amu. The student later changed the value to $2.2 \times 10^{+3}$ amu. Which value, if either, is more probably correct?
- 3.64 One can guess the mass number of the predominant isotope for many elements from the atomic mass of the element, but not in all cases. The mass numbers of the isotopes of selenium are 74, 76, 77, 78, 80, and 82. Explain why the atomic mass is so close to 79 amu.
- 3.65 ^{80}Br does not occur naturally. Explain how bromine gets its atomic mass of 79.909 amu.
- 3.66 ^{108}Ag does not occur naturally. Explain how silver gets its atomic mass of 107.87 amu.
- 3.67 Calculate the atomic mass of rubidium if 72.17% of naturally occurring rubidium atoms have a mass of 84.9118 amu and 27.83% have a mass of 86.9092 amu.
- 3.68 Which of the following represent(s) the mass of one atom (to three significant figures)?
(a) 0.500 amu (b) 12.0 g
(c) 6.02×10^{23} amu (d) 2.11×10^3 amu
(e) 74.9 amu
- 3.69 A compound contains almost equal masses of fluorine and selenium. Using their atomic masses, determine the formula of the compound.

General Problems

- 3.76 Could you use the average number of neutrons, instead of atomic number, to build a periodic table as good as that of Mendeleyev?
- 3.77 At a racetrack, the winning horse paid \$1.75 for each dollar bet. What odds were posted?
- 3.78 What factors limit the number of significant digits in the atomic mass of an element with two naturally occurring isotopes?
- 3.79 Two compounds of carbon, hydrogen, and oxygen have the following percent compositions. Show that these compounds obey the law of multiple proportions.
(a) 62.1% C, 10.3% H, 27.6% O
(b) 52.2% C, 13.0% H, 34.8% O

CHAPTER 3 ■ Atoms and Atomic Masses

- 3.70 The mass of iodine in a certain compound is almost exactly twice that of the only other element—copper. Using their atomic masses, determine the formula of the compound.
- 3.71 Round off the atomic masses of the first 18 elements to two decimal places each.

3.5 Development of the Periodic Table

- 3.72 How important was it to the work of Mendeleyev that atomic mass and atomic number rise somewhat proportionally? Explain.
- 3.73 The following are the formulas for some oxides of seven fourth-period elements:



Predict the formula for an oxide of each of the elements directly above these in the periodic table.

- 3.74 The following are the formulas for certain fluorides of fourth-period elements:



Predict the formula for a fluoride of each of the elements directly above these in the periodic table.

- 3.75 From the following properties of chlorine and iodine, predict the corresponding properties of bromine:

Chlorine	Iodine	Bromine
Gas under normal conditions	Solid under normal conditions	_____
Light yellow	Deep violet	_____
Reacts with metals	Reacts with metals	_____
Reacts with oxygen	Reacts with oxygen	_____
Does not conduct electricity	Does not conduct electricity	_____

- 3.80 The radius of an average nucleus is one ten-thousandth of the radius of the atom as a whole.
- (a) What is the ratio of the *volume* of the atom as a whole to the volume of the nucleus? ($V = \frac{4}{3}\pi r^3$)
- (b) Does the result justify the assertion that the volume of the atom is mostly empty space (with some electrons in it)?
- 3.81 Is there any possibility that the sulfur in the head of a match can combine with *all* the oxygen in the atmosphere of the Earth to form a compound? Explain, using a law studied in this chapter.
- 3.82 In a certain compound, 8.761 g of element B is combined with 15.55 g of element A. In another compound of A

■ General Problems

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and B, 15.55 g of A could possibly be combined with which ones of the following masses of B?

- (a) 4.381 g (b) 2.920 g (c) 17.52 g
 (d) 5.841 g (e) 8.761 g

- 3.83** The law of multiple proportions applies to two or more compounds of the same two or more elements. Show that the following data support the law:

	% H	% S	% O
Compound 1	2.44	39.02	58.54
Compound 2	5.88	94.12	
Compound 3	2.04	32.65	65.31

- 3.84** The law of multiple proportions applies to two or more compounds of the same two or more elements. Show that the following data support the law:

	% C	% H	% O
Compound 1	52.2	13.0	34.8
Compound 2	74.9	25.1	

- 3.85** A 14.9-g sample of element A reacts incompletely with a 7.11-g sample of element B. What is the total mass of the product plus the portion of A that did not react?

- 3.86** Explain why Mendeleev could predict the existence of germanium but missed the entire group of noble gases.

- 3.87** A typical atom has a radius of about 10^{-10} m. Estimate the radius of a typical nucleus.

- 3.88** Naturally occurring sulfur consists of 95.0% ^{32}S , which has a mass of 31.97207 amu, 0.76% ^{33}S , which has a mass of 32.97146 amu, and 4.22% ^{34}S , which has a mass of 33.96786 amu. Calculate the atomic mass of sulfur. How many significant digits are there in the final value?

- 3.89** Calculate the atomic mass of selenium from the following data:

Isotope	Natural Abundance (%)	Relative Mass (amu)
^{74}Se	0.87	73.9205
^{76}Se	9.02	75.9192
^{77}Se	7.58	76.9199
^{78}Se	23.52	77.9173
^{80}Se	49.82	79.9165
^{82}Se	9.19	81.9167

- 3.90** (a) Calculate the mass of oxygen in a 4.75-g sample of nitrogen monoxide, using the answer to Example 3.2.

- (b) How much oxygen should be combined with the same mass of nitrogen as in Example 3.2 to form the compound nitrogen dioxide, assuming that there is twice the mass of oxygen per gram of nitrogen in nitrogen dioxide as there is in nitrogen monoxide?

- (c) What is the percent composition of nitrogen dioxide?

- 3.91** The atomic mass of chlorine is 35.453 amu. Does any atom of any isotope of chlorine have a mass of 35.453 amu? Explain.

- 3.92** The atomic mass of fluorine is 18.9984 amu. Explain why the answer to the prior problem would not be correct for this problem.

- 3.93** (a) Plot mass number versus atomic number for ^1H , ^{16}O , ^{56}Fe , ^{96}Mo , ^{138}Ba , ^{197}Au , and ^{238}U .

- (b) Are atomic number and mass number directly proportional?

- (c) What can you say about the relationship of these two quantities?

- 3.94** The masses of the atoms of the only two stable isotopes of boron are 10.013 amu and 11.009 amu, and its atomic mass is 10.811 amu. Calculate the percentage of each isotope. [Hint: Let x equal the fraction of one of the isotopes, and $(1 - x)$ equal the fraction of the other.]

- 3.95** Calculate the atomic mass of lithium from the following data:

Isotope	Natural Abundance (%)	Relative Mass (amu)
^6Li	7.5	6.0151
^7Li	92.5	7.0160

- 3.96** Sodium and iodine react to form one compound only. In a certain reaction, 10.00 g of sodium and 55.17 g of iodine react completely.

- (a) How much sodium iodide is produced?

- (b) How much iodine would react if 10.00 g of sodium and 75.00 g of iodine were allowed to react?

- (c) How much sodium iodide would be produced?

- (d) What law allowed you to answer each of the prior parts of this problem?

- 3.97** Naturally occurring silicon consists of 92.2% ^{28}Si , which has a mass of 27.9769 amu, 4.67% ^{29}Si , which has a mass of 28.9765 amu, and 3.18% ^{30}Si , which has a mass of 29.9738 amu. Calculate the atomic mass of silicon.

4

Electronic Configuration of the Atom

- 4.1 A Brief Exploration of Light
- 4.2 Bohr Theory
- 4.3 Quantum Numbers
- 4.4 Relative Energies of Electrons
- 4.5 Shells, Subshells, and Orbitals
- 4.6 Shapes of Orbitals
- 4.7 Energy Level Diagrams
- 4.8 Periodic Variation of Electronic Configuration



Fireworks. Energy, input from a chemical reaction, is emitted as light

Review Clues

- Section 4.2 Section 3.3
Section 4.8 Section 3.5

Objectives

- 4.1 To understand the dual nature of light and the relationships among its energy, frequency, and wavelength
- 4.2 To use the Bohr theory of energy levels in atoms to explain light emission and absorption by gaseous atoms
- 4.3 To use quantum numbers to write the electronic structures of the atoms in their most stable states
- 4.4 To write detailed electronic configurations for the elements, using the permitted values for the individual quantum numbers, the $n + \ell$ rule, and the Pauli exclusion principle
- 4.5 To write electronic configurations in a shorter notation, using the concepts of shells, subshells, and orbitals
- 4.6 To understand the spatial orientation of the most common orbitals and the uncertain nature of locating the electron in the atom
- 4.7 To represent pictorially the energies of the subshells in atoms and of the electrons that occupy those subshells
- 4.8 To relate each element's position in the periodic table to the electronic configuration of its atoms, and to deduce electronic structures using the periodic table

4.1 ■ A Brief Exploration of Light**99**

In Chapter 3, we learned that atoms owe their characteristics to their subatomic particles—protons, neutrons, and electrons. Electrons occur in regions of space outside the nucleus, and the electronic structure is responsible for all of the atom's chemical properties and many of its physical properties. The number of electrons in a neutral atom is equal to the number of protons in the nucleus. That simple description enables us to deduce much about atoms, especially concerning their interactions with one another (Chapter 5). However, a more detailed model of the atom enables even fuller explanations, including the reason for the differences between main group elements and elements of the transition and inner transition series.

Many details presented in this chapter are based on mathematics beyond the scope of this course, so some postulates must be accepted as “rules of the game.” When the rules are followed, the explanations that result match the actual properties of the elements, which is assurance that the postulates are valid.

Section 4.1 briefly describes some of the physical properties of light, especially the relationship of its wavelength to the energy of its particles. Section 4.2 describes how Niels Bohr deduced that electrons occur in shells having distinct energies. His theory was a milestone, but it does not explain the properties of atoms other than hydrogen. Section 4.3 introduces the quantum numbers, which provide a more satisfactory picture of electronic structure for atoms with more than one electron. The dependence of the energy of an electron on its quantum numbers is discussed in Section 4.4, and shells, subshells, and orbitals are covered in Section 4.5. The shapes of orbitals are described in Section 4.6, and diagrams depicting the energy levels of subshells are presented in Section 4.7. The electronic configuration of the atom is responsible for the chemical and physical properties of an element. The relationship between electronic configuration and position on the periodic table is developed in Section 4.8.

4.1 A Brief Exploration of Light

We saw in Chapter 3 that light from the Sun was broken into a spectrum and that a new element—helium—was discovered, identified by the dark lines in that spectrum. It is essential to learn at least a little about the physical nature of light in order to understand how the lines in the spectrum can tell us about energy levels in the atoms.

Visible light is a tiny fraction of the **electromagnetic spectrum**, which includes gamma rays, X-rays, ultraviolet light, visible light, infrared light, microwaves, and radio waves (Figure 4.1). The word **light** is sometimes used to mean only visible light (the portion of the electromagnetic spectrum detectable by the human eye) and sometimes to mean the entire electromagnetic spectrum. In this text, light will be used to mean the entire electromagnetic spectrum, and when visible light is meant, the word *visible* will be included.

Light can be described as a wave motion because it can be refracted by a prism (see Figure 3.5) and diffracted by a grating. These phenomena can be explained only by light possessing wave properties. The **wavelength** (λ) is the distance between two successive crests (Figure 4.2). The amplitude (A) is the maximum displacement from the mean position. The **frequency** (ν) is the number of crests that pass any point, such as point X , per second.

Be sure to distinguish between the words *photon* and *proton*.

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CHAPTER 4 ■ Electronic Configuration of the Atom

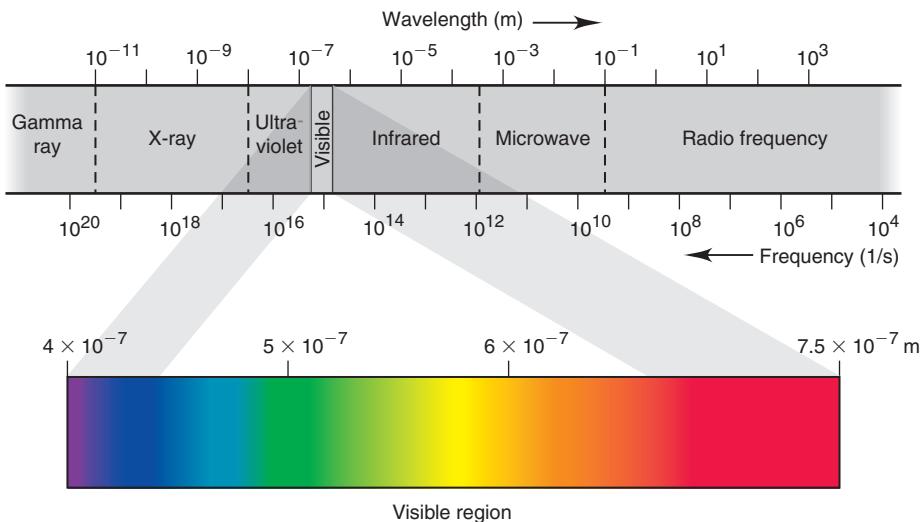


Figure 4.1 The Electromagnetic Spectrum

Light also has a particle nature—it can best be described as a stream of particles called **photons**. The properties of light emitted by glowing (red hot) objects and the photoelectric effect can be explained only with light as a stream of particles. The energy of the photons (E) is related to the frequency of the waves (represented by ν , Greek nu):

$$E = h\nu$$

where h is a constant known as Planck's constant with a value of 6.63×10^{-34} J·s. The frequency of any wave is inversely proportional to its wavelength (λ). In the case of light, the proportionality constant is the velocity of light (c), equal to 3.00×10^8 m/s. (That value is equal to 186,000 miles per second!)

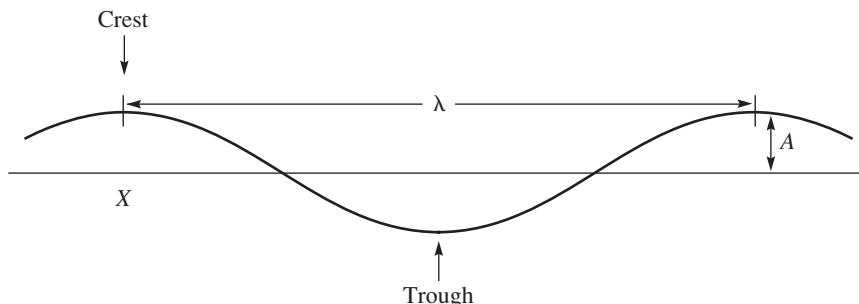
$$\nu = \frac{c}{\lambda}$$

Note that E and ν are directly proportional, and both are inversely proportional to λ . Once any of these values is known for light, the other two can be calculated.

EXAMPLE 4.1

The energy of a photon is 7.50×10^{-16} J. Calculate the frequency and the wavelength of the light.

Figure 4.2 Properties of Wave Motion



Notice the units of h and ν :
joules times seconds for h and
the reciprocal of seconds for ν .

Solution

$$E = h\nu$$

$$7.50 \times 10^{-16} \text{ J} = (6.63 \times 10^{-34} \text{ J}\cdot\text{s})\nu$$

$$\nu = 1.131 \times 10^{18}/\text{s} = 1.13 \times 10^{18}/\text{s}$$

$$\lambda = c/\nu = (3.00 \times 10^8 \text{ m/s})/(1.131 \times 10^{18}/\text{s}) = 2.65 \times 10^{-18} \text{ m.}$$

This photon is in the X-ray portion of the spectrum.

Practice Problem 4.1 Calculate the energy of the photons in green light having wavelength $5.00 \times 10^{-7} \text{ m}$.

A most important concept that we will learn is that distinct wavelengths of light emitted from gaseous atoms result from electronic transitions between definite energy states within the atoms (Sections 4.2 and 4.4).



Snapshot Review



ChemSkill Builder 9.2

- Light has both wave and particle properties. Its wavelength (λ) is inversely proportional to its frequency (ν) and also to the energy of its photons: $E = h\nu = hc/\lambda$.

- A. Calculate the energy of a photon of light if $\lambda = 1.73 \times 10^{-8} \text{ m}$.
- B. If the frequency of light decreases from violet light to red light, what happens to the (a) energy of the photons? (b) wavelength?

4.2 Bohr Theory



When gaseous atoms of a given element are heated, they emit light of only specific energies. When gaseous atoms of that same element absorb light, they absorb those same energies (see Figure 3.6). To explain these phenomena of **light emission** and **light absorption**, Niels Bohr (1885–1962) (Figure 4.3) postulated that the electrons in atoms are arranged in **orbits**, each with a definite energy. The **Bohr theory** was the first to include the explanation that electrons in atoms have **discrete energy levels**; that is, electrons may be found only in orbits with specific energies.

When an atom absorbs energy, an electron is “promoted” to a higher energy level. Because each orbit has a discrete energy level, the *difference* in energy between the orbits is also definite. After an electron has been promoted to a higher energy level, it falls back to a lower energy level (Figure 4.4). When it falls back, light of energy equal to the difference in energy between the orbits is emitted from the atom. In a different experiment, when light is absorbed by the atom, the electron is raised from one orbit to another one. Because there is the same energy difference between the orbits, the same energy of light is absorbed. An example of these effects is shown in Figure 4.5. Some of the possible electron transitions in a hydrogen atom are diagrammed in Figure 4.6.

Figure 4.3 Niels Bohr

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CHAPTER 4 ■ Electronic Configuration of the Atom

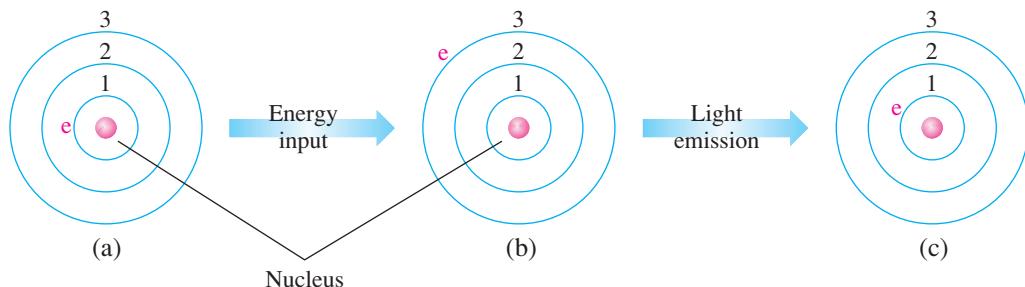


Figure 4.4 Schematic Diagram of Light Emission from an Excited Hydrogen Atom

The first three Bohr orbits, or energy levels, are labeled 1–3. The electron in part (a) is in the lowest energy orbit, so the atom is in the ground state. Energy is put into the atom, most often as heat, electrical energy, or light, and the electron is promoted to a higher energy level, as shown in part (b) where the electron happens to be in the third orbit. This is an excited state of the hydrogen atom, and is unstable. The electron falls spontaneously to the first orbit (either directly or through the second orbit), giving off light energy corresponding to the energy difference between the orbits between which it falls.

EXAMPLE 4.2

How many photons of light will be emitted when the electron in Figure 4.4(b) falls (1) directly to the first orbit? (2) to the second and then to the first orbit as shown in the transition from part (b) of the figure to part (c)?

Solution

- (1) One
- (2) Two, one for each transition

Practice Problem 4.2 Compare the energy of the one photon of Example 4.2(a) to the sum of the energies of the two photons of part (b).



(a)

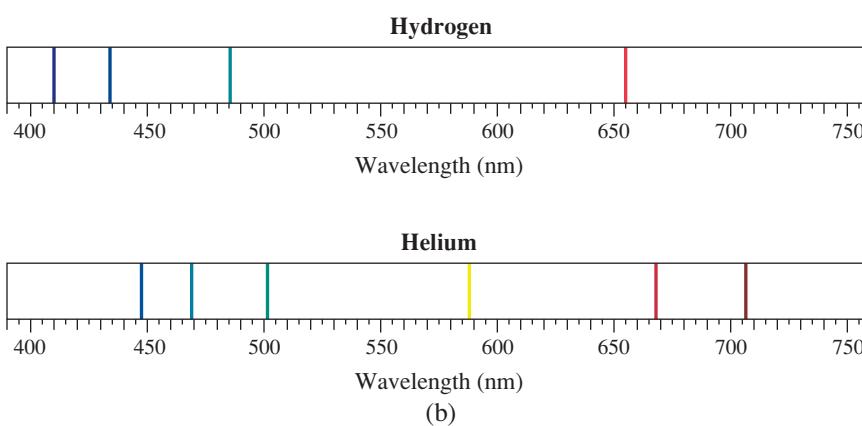
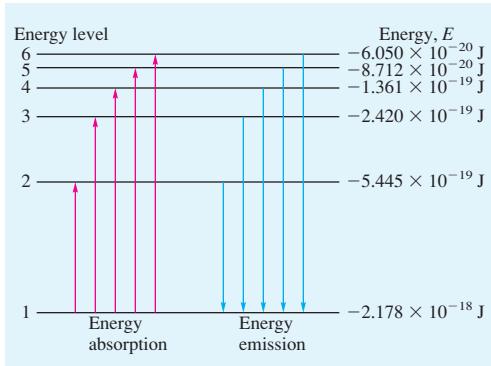


Figure 4.5 Emission of Light by Gaseous Atoms

(a) When neon atoms are excited by electrical energy, electron transitions between their energy levels yield wavelengths of light that produce the familiar red color of a neon sign. Wavelengths corresponding to a large number of different transitions combine to yield that color. Other gases are used to produce other colors, although we refer to all such signs in everyday conversation as “neon” signs. (b) When hydrogen and helium, with fewer electrons than neon, are similarly excited, fewer transitions occur. These emission spectra are relatively simple. Hydrogen and helium are the major components in our Sun.

4.2 ■ Bohr Theory**103**

Figure 4.6 Energy Levels and Some Possible Electron Transitions in the Hydrogen Atom
(not drawn to scale)



EXAMPLE 4.3

The energy of the first orbit of the hydrogen atom is -2.178×10^{-18} J, and that of the second orbit is -5.445×10^{-19} J. (A negative value means that the electron in the atom has a lower energy than a free electron has.)

- What energy change takes place when an electron in a hydrogen atom moves from the first to the second orbit?
- What energy change takes place when an electron moves from the second to the first orbit?

Solution

- The difference in energy between the orbits is 1.634×10^{-18} J. That much energy must be *absorbed* (for example, in the form of light, heat, or electricity) to get the electron promoted to the second orbit. If light is absorbed, light of that particular energy and no other energy is involved.
- The difference in energy between the two orbits is still 1.634×10^{-18} J. In this case, the energy is *emitted* (given off) in the form of light. The energy of the light emitted in this case is equal to the energy of the light absorbed in part (a).

Practice Problem 4.3 The energy of the third orbit of the hydrogen atom is -2.420×10^{-19} J. How much energy is emitted when an electron moves from (a) the third to the first orbit and (b) the third to the second orbit?

Bohr postulated circular orbits for the electrons in an atom and developed a mathematical model to represent the energies of the orbits, as well as their distances from the atom's nucleus. His model worked very well for the hydrogen atom. It could be used to calculate the energy of the emitted and absorbed light, as well as the radius of the atom. However, the intensity of the various wavelengths of light involved was not explained well. Moreover, no other atom was explained well at all. Bohr's theory has since been replaced by a quantum mechanical model, but it was a milestone because Bohr was the first to postulate energy levels in atoms.



Snapshot Review

- Bohr postulated that the electrons in an atom revolved about the nucleus in circular orbits and absorbed or emitted light only when they changed from one orbit to another.
 - Bohr's postulate that electrons have distinct energy levels in atoms was a milestone in the understanding of the nature of the atom.
- A. If Bohr's theory applies only to the hydrogen atom and it doesn't explain the intensities of its spectral lines well, why is it important enough for us to study?
- B. How many different paths can the electron use to go from the fourth orbit to the first?

4.3 Quantum Numbers

Each electron in an atom is associated with a set of four **quantum numbers**. The names of the quantum numbers, along with their symbols and permitted values, are given in Table 4.1.

The **principal quantum number** (n) can have any positive integral value, but the electrons in atoms in their most stable states have principal quantum numbers with values from 1 through 7 only. The most stable electronic state of an atom is called its **ground state**. Any higher energy state is called an **excited state**. (Unless “excited state” is specified in later discussions, ground state is implied.) The principal quantum number has the largest role in determining the energy of the electron, and it is also the main factor in determining how far the electron is, on average, from the nucleus. Thus, it is the most important quantum number.

For each value of n , the **angular momentum quantum number** (ℓ) for an electron can have integral values from zero to $(n - 1)$; it cannot be as large as n . The angular momentum quantum number has a small role in determining the energy of the electron, and it determines the shape of the volume of space that the electron can occupy (see Section 4.6).

EXAMPLE 4.4

What values for ℓ are permitted for an electron with (a) $n = 4$ and (b) $n = 2$?

Table 4.1 The Quantum Numbers

Name	Symbol	Permitted Values	Examples
Principal quantum number	n	Any positive integer	1, 2, 3, ...
Angular momentum quantum number	ℓ	Any integer from zero to $(n - 1)$	0, ..., $(n - 1)$
Magnetic quantum number	m_ℓ	Any integer from $-\ell$ to $+\ell$	$-\ell, \dots, 0, \dots, +\ell$
Spin quantum number	m_s	$-\frac{1}{2}$ or $+\frac{1}{2}$	$-\frac{1}{2}, +\frac{1}{2}$

Solution

- (a) $\ell = 0, 1, 2,$ or $3,$ but no higher (b) $\ell = 0$ or 1 (ℓ cannot be as high as n)

Note that the value of ℓ is not necessarily equal to $(n - 1)$ but can vary from zero up to $(n - 1).$

Practice Problem 4.4 How many different values of ℓ are permitted for an electron with (a) $n = 4$ and (b) $n = 2?$

For each value of the angular momentum quantum number (ℓ), the **magnetic quantum number** (m_ℓ) has values ranging from $-\ell$ through zero to $+\ell$ in integral steps. The value of m_ℓ does not ordinarily affect the energy of an electron, but it does determine the orientation in space of the volume that can contain the electron (Section 4.6).

EXAMPLE 4.5

What values of m_ℓ are permitted for an electron with (a) $\ell = 2$ and (b) $\ell = 0?$

Solution

- (a) $m_\ell = -2, -1, 0, 1,$ or 2 (b) $m_\ell = 0$

Practice Problem 4.5 How many different values of m_ℓ are permitted for an electron with (a) $\ell = 2$ and (b) $\ell = 0?$

EXAMPLE 4.6

Can we tell what values of m_ℓ are permitted for an electron with $n = 3?$

Solution

The permitted values of m_ℓ depend on the value of ℓ , not on the value of $n.$ The most we can say in this case is that ℓ is limited to $0, 1,$ or $2,$ so m_ℓ must be 0 if $\ell = 0,$ it may be $-1, 0,$ or $+1$ if $\ell = 1,$ and it may be $-2, -1, 0, 1,$ or 2 if $\ell = 2.$

Practice Problem 4.6 What is the lowest value of m_ℓ permitted for any electron with $n = 4?$

The **spin quantum number** (m_s) may have values of $-\frac{1}{2}$ or $+\frac{1}{2}$ only. The value of m_s does not depend on the value of any other quantum number. The spin value gives the orientation of the magnetic field associated with the electron.

Another important limitation on the quantum numbers of electrons in atoms, in addition to those listed in Table 4.1, is the **Pauli exclusion principle.** This principle states that no two electrons in an atom can have the same set of four quantum numbers. This is like the business law that states that no two tickets to a rock concert can have the same set of date and section, row, and seat numbers (Figure 4.7). The row number may depend on the section number, and the



Figure 4.7 Ticket to Rock Concert

No two tickets from the same concert hall can have the same set of section designation, row number, seat number, and date.

seat number may depend on the row number, but the date does not depend on any of the other three. Similarly, the spin quantum number is independent of the other three quantum numbers.

Together with the $n + \ell$ rule, discussed in the next section, the Pauli exclusion principle determines the number of electrons in each of the shells in an atom.



Snapshot Review



ChemSkill Builder 9.6

- Each electron in an atom has four quantum numbers, which govern its energy and average distance from the nucleus, among other things. The permitted values for the quantum numbers are critical.

- A. What are the permitted values for the principal quantum number, n ?
- B. What are the permitted values of m_s for an electron with $n = 2$ and $\ell = 0$?
- C. How many different values of m_ℓ are permitted for an electron with an ℓ value of 3?

4.4 Relative Energies of Electrons

The energies of the electrons in an atom are of paramount importance to the atom's properties. Electrons increase in energy as the sum $n + \ell$ increases. We call this the **$n + \ell$ rule**. Thus, we can make a list of sets of quantum numbers in order of their increasing energies by ordering the electrons according to increasing values of $n + \ell$. As a corollary, if two electrons have the same value of $n + \ell$, then the one with the lower n value is lower in energy. If the two n values are the same and the two ℓ values are the same, then the electrons are equal in energy. In an atom, electrons with the same energy are said to be **degenerate**.

EXAMPLE 4.7

Suppose that we must choose two integers with the lowest sum in the following ranges: For the first, we may choose any integer between 1 and 7. For the second, we may choose any nonnegative integer below the first. What integers must we select?

Solution

The lowest sum will come from the lowest possible first integer (1) and the lowest possible (and only possible) second integer (0).

Let's determine sets of four quantum numbers for the electrons of the ground states of the atoms of the first 10 elements. Hydrogen has only one electron. For that electron to be in its lowest energy state, it needs the lowest possible sum of n and ℓ , so we will choose the lowest value of n : $n = 1$.

4.4 ■ Relative Energies of Electrons**107**

Then, referring to Table 4.1, we determine values for the other three quantum numbers:

With $n = 1$, the only permitted value of ℓ is 0.

With $\ell = 0$, the only permitted value of m_ℓ is 0.

The value of m_s can be either $-\frac{1}{2}$ or $+\frac{1}{2}$.

The set of quantum numbers for hydrogen in its ground state can therefore be either of these:

$$\begin{array}{ll} n = 1 & \text{or} \\ \ell = 0 & \\ m_\ell = 0 & \\ m_s = -\frac{1}{2} & \end{array} \quad \begin{array}{ll} n = 1 \\ \ell = 0 \\ m_\ell = 0 \\ m_s = +\frac{1}{2} \end{array}$$

Since the n values and the ℓ values are the same in these two sets of quantum numbers, these possible configurations represent the same energy. Thus, either set of quantum numbers could represent the electron of hydrogen.

A helium atom has two electrons, so we need two sets of quantum numbers. To represent the atom in its lowest energy state, we want each electron to have the lowest energy possible. If we let the first electron have the value of 1 for its principal quantum number, its set of quantum numbers will be the same as one of those given previously for the one electron of hydrogen. The other electron of helium can then have the other set of quantum numbers.

$$\begin{array}{ll} \text{One electron} & \text{The other electron} \\ \text{of helium} & \text{of helium} \\ n = 1 & n = 1 \\ \ell = 0 & \ell = 0 \\ m_\ell = 0 & m_\ell = 0 \\ m_s = -\frac{1}{2} & m_s = +\frac{1}{2} \end{array}$$

Both of these electrons have the same energy because they have the same n value and the same ℓ value. Thus, either one could have been chosen as the first electron.

EXAMPLE 4.8

Could both electrons of helium have the value $m_s = +\frac{1}{2}$ with $n = 1$?

Solution

No. If n is 1, then ℓ and m_ℓ must both have values of 0 (see Table 4.1). If m_s were $+\frac{1}{2}$ for both electrons, they would have the same set of four quantum numbers, which is a violation of the Pauli principle.

Practice Problem 4.8 What is the maximum number of electrons an atom could have if the maximum value of n is 2 and each electron has a value of ℓ equal to 0?

A lithium atom has three electrons. The first two of these can have the same sets of quantum numbers as the two electrons of helium. What should the set of quantum numbers for the third electron be? We cannot choose the lowest permitted value for n , which is 1, because ℓ and m would then both be 0. If we choose $-\frac{1}{2}$ as the value of m_s , the third electron would have a set of quantum numbers exactly the same as that of one of the first two electrons, and if we choose the value $m_s = +\frac{1}{2}$, the third electron would have the same set of quantum numbers as the other. Because neither of these situations is permitted by the Pauli principle, n cannot be 1 for the third electron. We must choose the next higher value, $n = 2$. With $n = 2$, the permitted values of ℓ are 0 and 1. Because $\ell = 0$ will give a lower value for the sum $n + \ell$, we choose that value for ℓ . With $\ell = 0$, m_ℓ must be 0, and we can choose either $-\frac{1}{2}$ or $+\frac{1}{2}$ for m_s . The quantum numbers for the three electrons of the lithium atom can thus be as follows:

<i>First electron of lithium</i>	<i>Second electron of lithium</i>	<i>Third electron of lithium</i>
$n = 1$	$n = 1$	$n = 2$
$\ell = 0$	$\ell = 0$	$\ell = 0$
$m_\ell = 0$	$m_\ell = 0$	$m_\ell = 0$
$m_s = -\frac{1}{2}$	$m_s = +\frac{1}{2}$	$m_s = -\frac{1}{2}$ (or $+\frac{1}{2}$)

We continue deducing quantum numbers for the additional electrons of the first 10 elements. Beryllium (Be) has four electrons. With $m_s = -\frac{1}{2}$ for its third electron, the fourth electron of beryllium will have $n = 2$, $\ell = 0$, $m_\ell = 0$, and $m_s = +\frac{1}{2}$. For the fifth electron of boron (B), we cannot use the combination $n = 2$ and $\ell = 0$ because of the Pauli principle, so we use $n = 2$ and $\ell = 1$. There are three possible values for m_ℓ with $\ell = 1$, and together with the two possible values for m_s , they yield six combinations of quantum numbers with $n = 2$ and $\ell = 1$. The configurations of the first 10 electrons in a multielectron atom are shown in Table 4.2. It must be emphasized that the value of m_ℓ and the sign of the m_s value are arbitrary in some cases but not in others (see Problem 4.10 at the end of the chapter).

We can continue in this manner, building up the configuration of each element by adding a set of quantum numbers for one “last” electron to the configuration of the element before it. This process of adding one electron to those of the preceding element is called the **build-up principle**.

EXAMPLE 4.9

Write the sets of quantum numbers for the last eight electrons of argon, along with the sets given in Table 4.2 for the first 10 electrons.

Table 4.2 Possible Sets of Quantum Numbers for the Ten Electrons of Neon

Quantum Number	First Electron	Second Electron	Third Electron	Fourth Electron	Fifth Electron	Sixth Electron	Seventh Electron	Eighth Electron	Ninth Electron	Tenth Electron
n	1	1	2	2	2	2	2	2	2	2
ℓ	0	0	0	0	1	1	1	1	1	1
m_ℓ	0	0	0	0	-1	0	+1	-1	0	+1
m_s	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

4.4 ■ Relative Energies of Electrons**109****Table 4.3** Possible Sets of Quantum Numbers for the Last Eight Electrons of Argon

Quantum Number	Eleventh Electron	Twelfth Electron	Thirteenth Electron	Fourteenth Electron	Fifteenth Electron	Sixteenth Electron	Seventeenth Electron	Eighteenth Electron
n	3	3	3	3	3	3	3	3
ℓ	0	0	1	1	1	1	1	1
m_ℓ	0	0	-1	0	+1	-1	0	+1
m_s	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

Solution

The sets are shown in Table 4.3. Note that the combination $n = 3, \ell = 1$ has the same sum of n and ℓ as $n = 4, \ell = 0$. Because the sum is the same, the combination with the lower n value is used for each of the thirteenth through eighteenth electrons because it is lower in energy.

When we try to add the nineteenth electron to write the configuration for potassium (K), we encounter a new situation. The combination with the next lowest sum of n and ℓ is $n = 4, \ell = 0$. The combination $n = 3, \ell = 2$ is higher in energy. The nineteenth through twenty-first electrons can have the following sets of quantum numbers:

Quantum number	Nineteenth electron	Twentieth electron	Twenty-first electron
n	4	4	3
ℓ	0	0	2
m_ℓ	0	0	-2
m_s	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$
$n + \ell$	4	4	5

The fact that electrons having quantum number values $n = 4$ and $\ell = 0$ are lower in energy than electrons with $n = 3$ and $\ell = 2$ is of extreme importance; it explains the existence and position on the periodic table of the transition metals. This point will be explained later.

EXAMPLE 4.10

Arrange the following electrons, identified only by their n and ℓ quantum numbers, in order of increasing energy from lowest to highest.

- | | |
|-----------------------|-----------------------|
| (a) $n = 3, \ell = 2$ | (b) $n = 5, \ell = 0$ |
| (c) $n = 4, \ell = 2$ | (d) $n = 4, \ell = 1$ |
| (e) $n = 5, \ell = 1$ | |

Solution

Calculate the sum $n + \ell$ for each electron:

- | | |
|---|---|
| (a) $n = 3, \ell = 2$, so $n + \ell = 5$ | (b) $n = 5, \ell = 0$, so $n + \ell = 5$ |
| (c) $n = 4, \ell = 2$, so $n + \ell = 6$ | (d) $n = 4, \ell = 1$, so $n + \ell = 5$ |
| (e) $n = 5, \ell = 1$, so $n + \ell = 6$ | |

The ones with lower values of $n + \ell$ are lower in energy, so electrons (a), (b), and (d) are lower in energy than (c) and (e). The sum $n + \ell$ is the same for (a), (b), and (d), so (a), the one with the lowest n value, is lowest in energy and (d) is next. The sum $n + \ell$ is the same for (c) and (e), so (c), the one with the lower n value, is lower in energy. Thus, the order of increasing energy is (a) < (d) < (b) < (c) < (e).

Practice Problem 4.10 Arrange the following electrons, identified only by their n and ℓ quantum numbers, in order of increasing energy from lowest to highest.

- (a) $n = 4, \ell = 1$ (b) $n = 5, \ell = 2$ (c) $n = 5, \ell = 0$
(d) $n = 6, \ell = 0$ (e) $n = 5, \ell = 1$



Snapshot Review

- The $n + \ell$ rule, the Pauli exclusion principle, and the permitted values of the quantum numbers enable us to determine the order of the electrons in an atom in increasing energy.
- Atoms in their ground states have all their electrons with the lowest possible values of $n + \ell$.
- If two electrons have the same sum $n + \ell$ but have different n values, the one with the lower n value is lower in energy.

A. In each part, determine which electron, labeled X or Y, has the lower energy:

- | | |
|--------------------------|----------------------|
| (a) X: $n = 4, \ell = 0$ | Y: $n = 3, \ell = 2$ |
| (b) X: $n = 3, \ell = 1$ | Y: $n = 4, \ell = 0$ |
| (c) X: $n = 5, \ell = 2$ | Y: $n = 5, \ell = 1$ |

4.5 Shells, Subshells, and Orbitals

A **shell** is defined as a group of electrons in an atom all having the same principal quantum number. A **subshell** is defined as a group of electrons in an atom all having the same principal quantum number and also the same angular momentum quantum number. If two electrons in an atom have the same principal quantum number, the same angular momentum quantum number, and the same magnetic quantum number, the electrons are said to be in the same **orbital**.

EXAMPLE 4.11

Show that a maximum of two electrons can occupy a given orbital.

Solution

By definition, the electrons in a given orbital have the same n value, the same ℓ value, and the same m_ℓ value. According to the Pauli exclusion principle, they must therefore have different values for their spin quantum numbers (m_s).

4.5 ■ Shells, Subshells, and Orbitals**111**

Because only two m_s values ($-\frac{1}{2}$ and $+\frac{1}{2}$) are permitted, the maximum number of electrons in a given orbital is two.

Practice Problem 4.11 What is the maximum number of electrons that will fit into the first subshell of the second shell of an atom?

Even though the m_ℓ and m_s values do not affect the energy of the electron, it is still important to learn about them. The number of combinations of permitted values of these quantum numbers determines the maximum number of electrons in a given type of subshell. For example, in a subshell for which $\ell = 2$, m_ℓ can have five different values ($-2, -1, 0, +1$, and $+2$), and m_s can have two different values ($-\frac{1}{2}$ and $+\frac{1}{2}$). The ten different combinations of m_ℓ and m_s allow a maximum of ten electrons in any subshell for which $\ell = 2$.

EXAMPLE 4.12

How many electrons are permitted in a subshell for which (a) $\ell = 0$? (b) for $\ell = 3$?

Solution

- When $\ell = 0$, $m_\ell = 0$. Because m_ℓ has only one permitted value and m_s has two, there are two different combinations of m_ℓ and m_s for this subshell. Thus, it can be occupied by a maximum of two electrons.
- Seven permitted m_ℓ values ($-3, -2, -1, 0, +1, +2$, and $+3$) times two permitted m_s values ($-\frac{1}{2}$ and $+\frac{1}{2}$) makes 14 combinations. A maximum of 14 electrons can occupy this subshell.

Writing out each quantum number value for every electron in an atom is very time-consuming. A more efficient method is to group all the electrons in a given subshell. In this method, the following four lowercase letters represent the possible ℓ values:

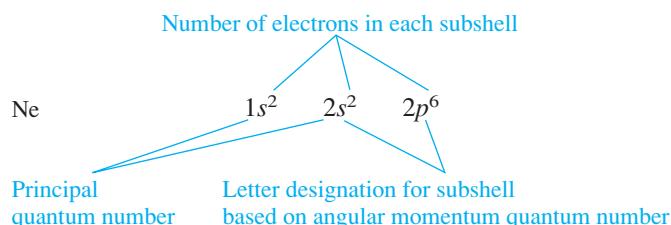
Value of ℓ	Letter
0	<i>s</i>
1	<i>p</i>
2	<i>d</i>
3	<i>f</i>

Because only n and ℓ values affect the energies of electrons, the electrons with the same n value and the same ℓ value all have the same energy. In other words, all the electrons in a given subshell are degenerate. Each subshell is denoted by its principal quantum number and the letter designation for ℓ . For example, for neon, with atomic number 10, the sets of quantum numbers for the 10 electrons are listed in Table 4.2. We can group them as follows:

Value of n	Value of ℓ	Number of electrons	Subshell designation
1	0	2	1s
2	0	2	2s
2	1	6	2p

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We write the **electronic configuration** by listing each subshell in order of increasing energy, with a superscript giving the number of electrons in that subshell. That is, the detailed electronic configuration for a neon atom is



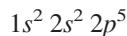
This configuration is read aloud as follows: “one ess two, two ess two, two pee six.” (The superscripts are not exponents, so words such as *square* are not used.) The sum of the superscripts is the total number of electrons in the atom.

EXAMPLE 4.13

Using sets of quantum numbers from Table 4.2, write the detailed electronic configuration of fluorine.

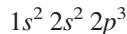
Solution

Fluorine, with atomic number 9, has 9 electrons. The first 9 electrons shown in the table will fit into three subshells, as follows:

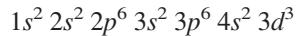


Note that the $2p$ subshell can hold a maximum of 6 electrons, but in fluorine, only 5 electrons are left for that subshell.

Practice Problem 4.13 What element has the following electronic configuration?

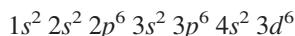
**EXAMPLE 4.14**

Write the detailed electronic structure of vanadium (V). Comment on the relative energies of the “last” 5 electrons.

Solution

Because the “last” 3 electrons are added to an inner shell (following the $n + \ell$ rule) instead of the outermost shell, the $3d$ subshell of a vanadium atom must be higher in energy than the $4s$ subshell.

Practice Problem 4.14 What element has the following electronic configuration?



In Section 4.8, we will learn to use the periodic table as a memory device to aid us in writing electronic configurations.



Snapshot Review

- Electrons in a given shell all have the same n value; electrons in a given subshell all have the same n value and the same ℓ value; electrons in a given orbital all have the same n value, the same ℓ value, and the same m_ℓ value.
- Detailed electronic configurations of elements give the subshells in increasing order of energies with the number of electrons occupying each subshell as a right superscript.

- A. Give the detailed electronic configuration of (a) O, (b) S.
- B. Give the detailed electronic configuration of Mn.

4.6 Shapes of Orbitals

An orbital is an allowed energy state in an atom. Each orbital is designated by the three quantum numbers n , ℓ , and m_ℓ . Because m_s is not specified, either value of m_s can be used, and a maximum of two electrons can occupy any given orbital in an atom.

Knowing exactly both the location and the momentum of an electron in an atom at the same time is impossible. This fact is known as the **Heisenberg uncertainty principle**. Therefore, scientists describe the *probable* locations of electrons. These locations describe the **orbital shapes**, which are important when the atom forms bonds with other atoms, because the orbital shapes are the basis of the geometry of the resulting molecule.

It is equally probable that s orbital electrons will be located in any direction about the nucleus. We say that an s orbital is spherically symmetrical. The $1s$ orbital is pictured in Figure 4.8(a). Because an electron with $\ell = 1$ has three possible m_ℓ values, any p subshell has three orbitals. Each one lies along one of the coordinate axes— x , y , or z —as shown in Figure 4.8(b). Each p orbital consists of two 3-dimensional **lobes** centered on one of the axes. An atom has five $3d$ orbitals, corresponding to the five possible m_ℓ values (-2 , -1 , 0 , $+1$, and $+2$) for a subshell with $\ell = 2$. Their orientations are shown in Figure 4.8(c).

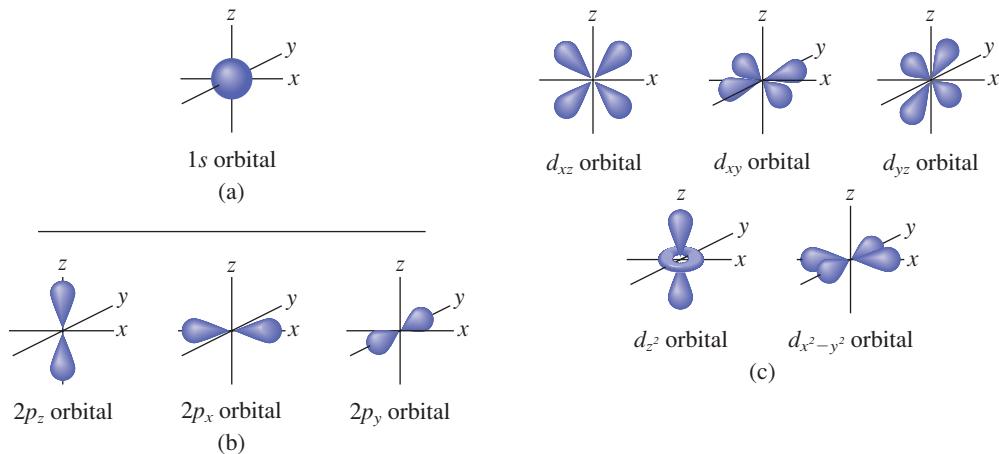


Snapshot Review

- The s orbitals are spherically symmetrical, and the p and d orbitals are oriented as shown in Figure 4.8. Do not mistake the individual lobes of the p and d orbitals as separate orbitals.

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CHAPTER 4 ■ Electronic Configuration of the Atom

**Figure 4.8** Shapes of Orbitals

- (a) The 1s orbital.
 (b) The three 2p orbitals.
 (c) The five 3d orbitals.

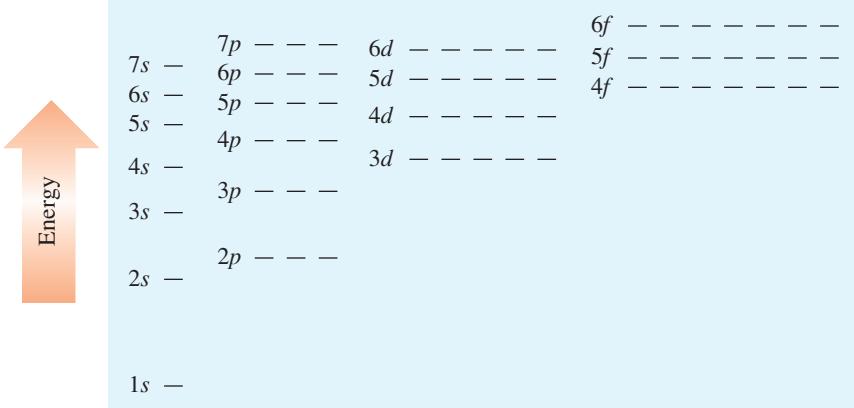
- A. (a) Along what axis does the p_y orbital lie? (b) Along what axis does the d_{z^2} orbital lie? (c) Along what axes does the $d_{x^2-y^2}$ orbital lie?

4.7 Energy Level Diagrams

Energy level diagrams are models for portraying electrons' occupancy of an atom's orbitals. They help chemists predict how many electrons occupy each orbital of a subshell. Electron occupancy of the individual orbitals is important in determining an atom's magnetic properties. A line or a box or a circle is used to represent each orbital. An energy level diagram that could hold the electrons of any known atom is shown in Figure 4.9. The energy level diagram is like a graph in one dimension: The higher a subshell is placed, the higher the energy of that subshell. The lines are spaced horizontally from left to right only to prevent crowding so that the diagram is easier to read.

The lowest line on the energy level diagram represents the orbital in the 1s subshell of the atom. Much higher in the diagram, indicating a much higher

Figure 4.9 Energy level
Diagram
(not drawn to scale)



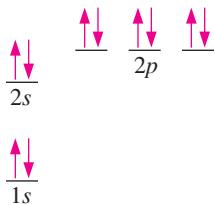
4.7 ■ Energy Level Diagrams**115**

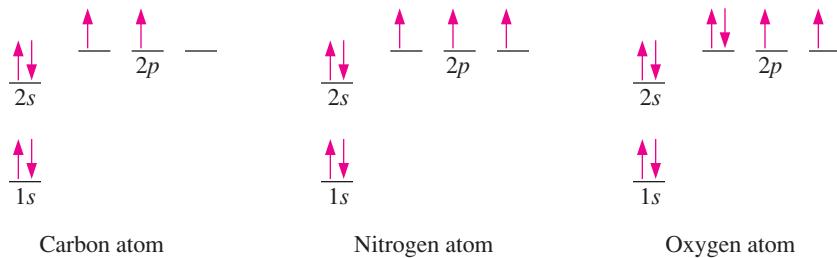
Figure 4.10 Electron Occupancy of the Neon Atom

energy, lies the line for the $2s$ orbital. Somewhat higher than that are the three lines for the orbitals of the $2p$ subshell. The third shell lies at even higher energies and consists of an s subshell, a p subshell, and a d subshell. Note that the $3d$ subshell lies at a slightly higher energy than the $4s$ subshell. The order of energy in the diagram is the same as that given by the $n + \ell$ rule.

We will most often focus our attention on the portion of the energy level diagram containing the last electron added, in which we are most interested. The orbitals that lie above that portion are assumed to be empty, and any orbitals that lie below those pictured are almost always completely filled when the atom is in its ground state.

We represent each electron with an arrow. Different electron spins (m_s value of $-\frac{1}{2}$ or $+\frac{1}{2}$) are indicated by arrows pointing downward or upward. Because each line represents one orbital, each line may hold a maximum of two arrows. If two arrows are present, they must be pointing in opposite directions. The energy level diagram representing the neon atom is shown in Figure 4.10.

Hund's rule states that the electrons *within a given subshell* remain as *unpaired as possible*. Moreover, if there are two or more unpaired electrons in a given subshell, they all must occupy different orbitals and have the same electron spin (all arrows representing unpaired electrons in a subshell point up or all point down). The energy level diagrams for the carbon, nitrogen, and oxygen atoms illustrate these rules:

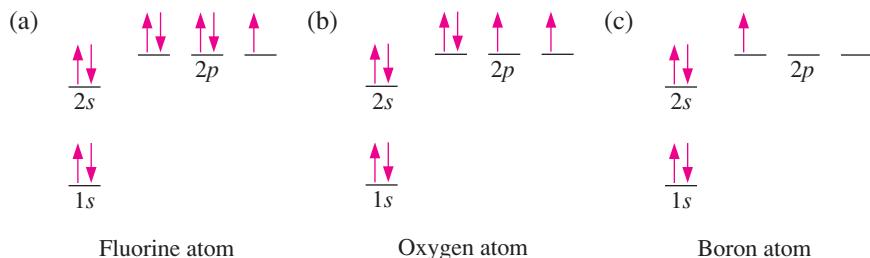


In the carbon atom, the lowest two subshells are filled; all electrons are paired in filled subshells. The $2p$ subshell has two electrons in the three orbitals, so each electron occupies a separate orbital. Moreover, both electrons have the same spin—both arrows point upward (alternatively, both could point downward). They are said to have parallel spin. In the nitrogen atom, the $2p$ subshell is half filled. Each electron occupies a different orbital, and all arrows point in the same direction. In the oxygen atom, the $2p$ subshell is again partially filled. To get four electrons into the three orbitals requires the pairing of two electrons in one orbital. In the other two orbitals, the electrons are unpaired and have the same spin.

The **magnetic properties** of atoms enable us to tell experimentally if all the electrons in an atom are paired or, if not, how many electrons are unpaired. Atoms with all their electrons paired are repelled slightly from a magnetic field, and are said to be *diamagnetic*. If at least one electron per atom in a sample is unpaired, the sample tends to be drawn into a magnetic field, and is said to be *paramagnetic*. The greater the number of unpaired electrons, the greater the attraction into the magnetic field. (In elemental iron, cobalt, and nickel, the unpaired electrons in adjacent atoms reinforce one another, and a very much stronger attraction into a magnetic field results. These are the metals of which magnets are made.)

EXAMPLE 4.15

How many unpaired electrons are in (a) a fluorine atom, (b) an oxygen atom, and (c) a boron atom?

Solution

The energy level diagrams show one unpaired electron in a fluorine atom, two in an oxygen atom, and one in a boron atom.

Practice Problem 4.15 How many unpaired electrons are in (a) an argon atom and (b) a carbon atom?

**Snapshot Review**

ChemSkill Builder 9.3

- An energy level diagram shows the individual orbitals graphically with increasing energy toward the top. Because only two electrons fit into any orbital (thus on any line), the electronic configuration of the atom can be deduced using such a diagram.
- Electrons *in a given subshell* occupy the orbitals singly with their spins aligned until the subshell is half full, after which they start to pair up.

- A. How many unpaired electrons are present in the ground state of (a) a phosphorus atom? (b) a selenium atom?

4.8 Periodic Variation of Electronic Configuration

The elements display a **periodicity of electronic configuration**. For example, if we examine the detailed electronic configurations of the alkali metals, we find that the outermost shell (specifically, the *s* subshell) of electrons contains only a single electron in each case. The alkaline earth metals have two outermost *s* electrons. The elements within each other group of the periodic table also have similarities in their outermost electronic configurations. We deduce that the outermost part of the electronic configuration is the main factor that determines the chemical properties of the elements because the periodic table was constructed from data about the properties of the elements.

The outermost part of the electronic configuration is the main factor that determines the chemical properties of the elements.

EXAMPLE 4.16

Write the electronic configurations of O, S, Se, Te. What feature makes them have similar chemical properties?

Solution

O	$1s^2 2s^2 2p^4$
S	$1s^2 2s^2 2p^6 3s^2 3p^4$
Se	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
Te	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$

The $ns^2 np^4$ configuration of the outermost (n th) shell is common to all the group VIA elements and different from the outermost configuration of the other elements. It is the cause of their similar chemical properties.

Practice Problem 4.16 Write the electronic configurations of N, P, As, and Sb. State the feature that makes them have similar chemical properties.

We can use the periodic table to help us write electronic configurations of the atoms of the elements.

We can use the periodic table to help us write electronic configurations of the atoms of the elements. The periodic table can be divided into blocks corresponding to the type of subshell occupied by the last electron added (Figure 4.11). The two groups at the left of the periodic table—the alkali metals and the alkaline earth metals—constitute the *s* block because their last electrons occupy *s* subshells. Hydrogen and helium also are in this block, and we must mentally shift helium to a place beside hydrogen for this purpose. The six periodic groups at the right of the table constitute the *p* block; their last electrons go into *p* subshells. The transition metals belong to the *d* block, and the *f* block consists of the inner transition metals.

Note the similarity between the number of elements in a particular block in each period and the maximum number of electrons permitted in the corresponding type subshell:



The electronic structure of atoms is the basis for the periodic behavior of the elements.

Type of subshell or block	Maximum number of electrons in subshell	Number of elements in a particular block in each period
<i>s</i>	2	2
<i>p</i>	6	6
<i>d</i>	10	10
<i>f</i>	14	14

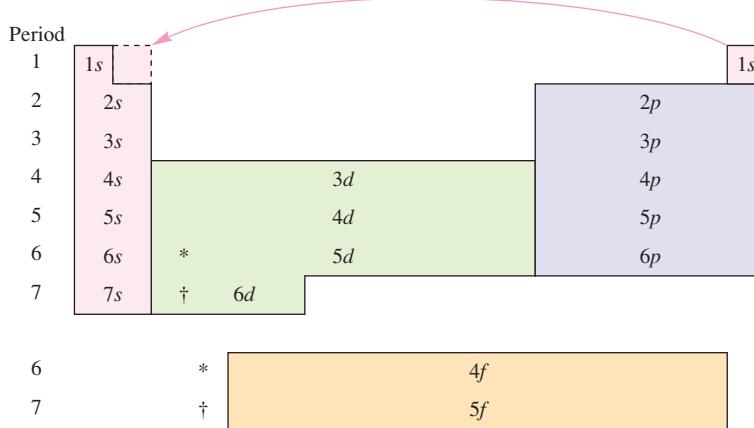
After each noble gas, a new shell of electrons is started, as is a new period of the periodic table. It turns out that electronic structure is the basis for the periodic behavior of the elements.

The four transition metal series arise because, for each of these elements, an electron has been added to the next-to-outermost shell. Addition of 10 electrons to the *3d* subshell *after the completion of the 4s subshell* causes 10 elements to occur after calcium to be the first elements in their periodic groups. The second, third, and fourth transition series occur because the *4d*, *5d*, and *6d* subshells add electrons after the start of the fifth, sixth, and seventh shells,

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Figure 4.11 Using the Periodic Table to Write Electronic Configurations

For the *s* and *p* blocks, the principal quantum number is equal to the period number. For the *d* block, the principal quantum number is equal to the period number minus 1. For the *f* block, the principal quantum number is equal to the period number minus 2.



respectively. The inner transition elements stem from the addition of electrons to *f* subshells two shells lower than the outermost shell of their atoms.

Because the periodic table reflects the electronic structures of the atoms, we can use it to deduce the configuration of any atom. We use the periodic table with its *s*, *p*, *d*, and *f* blocks, as shown in Figure 4.11. We imagine helium to be next to hydrogen in the 1*s* block. To determine the electronic configuration of an element, we start at hydrogen—element 1—and continue *in order of atomic numbers* until we get to the element in question. The subshells come from the blocks in the periodic table, and the numbers of electrons (the superscripts in the configuration) are the numbers of elements in the blocks up to the element in question. Thus, we determine the electronic configuration of phosphorus to be

$$1s^2 2s^2 2p^6 3s^2 3p^3$$

EXAMPLE 4.17

Using the periodic table as an aid, write the detailed electronic configuration for each of the following elements:

- (a) S (b) Fe (c) Lu

Solution

- (a) $1s^2 2s^2 2p^6 3s^2 3p^4$
 (b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 5d^1 4f^1$

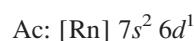
Practice Problem 4.17 Using the periodic table as an aid, write the detailed electronic configuration for each of the following elements:

- (a) V (b) Br (c) Ge

A more compact notation can sometimes be used to reduce the effort of writing long electronic configurations while retaining almost as much information. We are most interested in the outermost shell and the inner subshells having nearly the same energies. We can therefore write the detailed electronic

4.8 ■ Periodic Variation of Electronic Configuration**119**

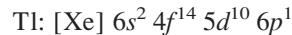
configuration for just that shell and those subshells of the atom, and we use the symbol of the preceding noble gas in square brackets to represent all the other electrons. For example, the electronic configuration of Ac (element 89) is denoted



EXAMPLE 4.18

Write the electronic configuration for thallium (element 81), using the shortened notation.

Solution



The symbol for the preceding noble gas, Xe, is written in square brackets. Then, starting at Cs, the alkali metal in the same period as thallium, we write $6s^2$ for Cs and Ba, $4f^{14}$ for the lanthanide elements, $5d^{10}$ for the elements from La to Hg, and $6p^1$ for Tl. We must be especially careful to follow the atomic numbers after elements 57 (La) and 89 (Ac), where the two inner transition series start. Note that the superscripts in the previous configuration plus the atomic number of Xe (54) add up to the atomic number of Tl (81).

Practice Problem 4.18 Write the electronic configuration for uranium using the shortened notation.

Using the periodic table as a mnemonic device has several advantages over relying on the $n + \ell$ rule and other rules:

1. The periodic table is generally available for reference during examinations.
2. The order of subshells is given “automatically.”
3. The maximum number of electrons in each subshell matches the number of elements in each block.
4. To write a shortened notation for an element, we can start at the alkali metal in the same period.

No matter which “rule” or memory device we use to write configurations, some transition metals and inner transition metals have configurations different from our expected configurations. Some of these occur because of the added stability associated with half-filled or fully filled subshells. For example, chromium and copper have actual configurations with two such outermost subshells instead of only the fully filled $4s$ subshell and $3d$ subshell neither half nor fully filled, as expected:

	<i>Actual configuration</i>	<i>Expected configuration</i>
Cr:	$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^1 \ 3d^5$	$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^4$
Cu:	$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^1 \ 3d^{10}$	$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^9$

Most, but not all, cations formed from atoms of these elements have the same configuration predicted by our “rules” or predicted from their actual configurations, and the compounds containing these cations are of more interest to chemists than the uncombined atoms of these elements anyway. (Section 5.2)

Some transition metals and inner transition metals have configurations different from our expected configurations.



Snapshot Review

- Atoms in a given periodic group have similar outermost electronic configurations.
- The periodic table results from the electronic configurations of the atoms, and so it can be used as a memory device to deduce these configurations.

A. Deduce the outermost electronic configuration of Lr without bothering to assign the inner 86 electrons to subshells.

Key Terms

Key terms are defined in the Glossary.

angular momentum quantum number (4.3)
Bohr theory (4.2)
build-up principle (4.4)
degenerate (4.4)
discrete energy levels (4.2)
electromagnetic spectrum (4.1)
electronic configuration (4.5)
energy level diagram (4.7)
excited state (4.3)
frequency (4.1)
ground state (4.3)

Heisenberg uncertainty principle (4.6)
Hund's rule (4.7)
light (4.1)
light absorption (4.2)
light emission (4.2)
lobe (4.6)
magnetic properties (4.7)
magnetic quantum number (4.3)
 $n + \ell$ rule (4.4)
orbit (4.2)
orbital (4.5)
orbital shape (4.6)

Pauli exclusion principle (4.3)
periodicity of electronic configuration (4.8)
photon (4.1)
principal quantum number (4.3)
quantum numbers (4.3)
shell (4.5)
spin quantum number (4.3)
subshell (4.5)
wavelength (4.1)

Symbols/Abbreviations

c (velocity of light) (4.1)
 d (a subshell) (4.5)
 f (a subshell) (4.5)
 ℓ (angular momentum quantum number) (4.3)

λ (*lambda*, wavelength) (4.1)
 m_ℓ (magnetic quantum number) (4.3)
 m_s (spin quantum number) (4.3)
 n (principal quantum number) (4.3)

v (*nu*, frequency) (4.1)
 p (a subshell) (4.5)
 s (a subshell) (4.5)

Summary

The chemical properties of atoms depend on their electronic structures. The number of electrons in a neutral atom is equal to the number of protons in the nucleus—the atomic number of the element.

Light is electromagnetic radiation that has properties of both wave motion and a stream of particles (photons). The wavelength of light (as a wave) is inversely proportional to the energy of its photons (particles). (Section 4.1)

Bohr first proposed the concept that electrons are arranged in discrete energy levels in the atom, which explained the emission of specific energies of light when gaseous atoms are heated. Although Bohr's theory could

not explain many other details of the behavior of atoms, it was a milestone in relating electronic structure and properties of atoms. (Section 4.2)

The modern theory of electronic structure is based on the assignment of four quantum numbers to each electron in an atom. The principal quantum number, n , governs the energy of the electron and also its probable distance from the nucleus. The angular momentum quantum number, ℓ , also has an effect on the energy and determines the shape of the volume of space that the electron can occupy. The magnetic quantum number, m_ℓ , determines the orientation in space of the volume occupied by the electron, and

■ Answers to Snapshot Reviews

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the spin quantum number, m_s , indicates the spin of the electron on its axis. The limits on the quantum numbers (Table 4.1) must be memorized. The Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers. (Section 4.3)

The $n + \ell$ rule governs the order of increasing energy of the electrons in the atom. Subshells are filled with electrons in the order of increasing $n + \ell$, with due regard for the limitations on the quantum numbers and for the Pauli exclusion principle. In each case, the “last” electron can be added to the configuration of the element before, using a procedure known as the build-up principle. (Section 4.4)

Electrons in a given shell of an atom all have the same n value. Electrons in a given subshell of an atom all have the same n value and the same ℓ value. Electrons in a given orbital of an atom all have the same n value, the same ℓ value, and the same m_ℓ value. By convention, subshells are designated using lowercase letters that correspond to the various ℓ values, and the electronic configuration of an atom is written using superscripts for the numbers of electrons occupying the subshells (for example, $1s^2$ indicates that two electrons occupy the $1s$ subshell). (Section 4.5)

Electrons in the various orbitals occupy portions of space having specified shapes (see Figure 4.8). (These are

important when the shapes of molecules are considered in Section 13.4.) (Section 4.6)

Energy level diagrams portray electrons’ occupation of the orbitals in an atom. Such diagrams are useful for understanding Hund’s rule and atoms’ magnetic properties. Hund’s rule states that in partially filled subshells, the electrons occupy orbitals singly and have the same spins as far as possible. If all the electrons in a substance are paired (two electrons in each occupied orbital), the substance will be repelled slightly from a magnetic field. However, if at least one electron in each formula unit is unpaired, the substance will be drawn into a magnetic field. (Section 4.7)

The properties of the elements stem from their electronic configurations, and the properties place them in their locations in the periodic table. In each group, the elements have a characteristic outermost electronic configuration. The existence of the transition and inner transition elements stems from adding electrons to inner shells after outer shells have been started. Because the periodic table reflects the electronic structures of the atoms, it can be used as a memory device when writing electronic configurations. The ability to write and understand such configurations is a very important skill. (Section 4.8)

Items for Special Attention

- The frequency of light is a number per second, so its unit is the reciprocal of seconds: $1/s$ or s^{-1} . The units of h are joules *times* seconds.
- When electrons undergo transitions to higher shells, energy is *absorbed* by the atom; when electrons undergo transitions to lower shells, energy is *emitted* by the atom.
- There is a difference between the questions “How many m_ℓ values are possible?” and “What are the possible m_ℓ values?” The number of m_ℓ values is the number of orbitals in the subshell.
- We can think of electrons in shells as being similar to small children on a ladder: They can never be between levels and are most stable at the lowest energy level possible.
- The p , d , and f orbitals have more than one lobe each. Do not mistake each lobe for a separate orbital.

Answers to Snapshot Reviews

- 4.1 A. $E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.73 \times 10^{-8} \text{ m}} = 1.15 \times 10^{-17} \text{ J}$
- B. (a) The energy decreases.
(b) The wavelength increases.
- 4.2 A. It was the first postulate of discrete energy levels in atoms, a critical breakthrough.
- B. Four. ($4 \rightarrow 3 \rightarrow 2 \rightarrow 1$; $4 \rightarrow 3 \rightarrow 1$; $4 \rightarrow 2 \rightarrow 1$; $4 \rightarrow 1$)
- 4.3 A. Any positive integer. (The integers 1 through 7 are the most important.)
- B. $-\frac{1}{2}$ or $+\frac{1}{2}$. (m_s does not depend on the value of any other quantum number.)
- C. Seven ($-3, -2, -1, 0, 1, 2, 3$)
- 4.4 A. (a) X (lower $n + \ell$), (b) X (equal $n + \ell$, lower n), and
(c) Y (lower $n + \ell$)
- 4.5 A. (a) O: $1s^2 2s^2 2p^4$; (b) S: $1s^2 2s^2 2p^6 3s^2 3p^4$
B. Mn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
- 4.6 A. (a) The y -axis, (b) the z -axis, and (c) the x - and y -axes
- 4.7 A. (a) Three, (b) Two
- 4.8 A. [Rn] $7s^2 6d^1 5f^{14}$

122**CHAPTER 4 ■ Electronic Configuration of the Atom****Self-Tutorial Problems**

- 4.1 If an athlete runs around a track 12 times in an hour, what is her frequency (including the unit)?
- 4.2 Multiply the wavelength and frequency values at any point in Figure 4.1. What value results? Repeat the procedure for a second point. Does the same or different value result? Explain these results.
- 4.3 What difference is there, if any, when the instructor states “The first line in the visible spectrum of hydrogen has a definite (a) wavelength.” (b) frequency.” (c) energy of its photons.”
- 4.4 For what element is the Bohr theory most useful?
- 4.5 What values are possible for the principal quantum number n for electrons in the ground state of an atom of Ac, element 89?
- 4.6 (a) What is the difference, if any, between an s subshell and an s orbital?
(b) What is the difference, if any, between a p subshell and a p orbital?
- 4.7 (a) If 10 marbles are placed in an empty ice cream cone, how many will have the lowest position?
(b) If the cone is held steady, how many will have the lowest position possible under the circumstances?
(c) Do the 10 electrons in a neon atom in its ground state all have the same energy?

- (d) Will all 10 have the lowest energy possible under the circumstances?

- 4.8 What principles or rules affect the energies of electrons in an atom?
- 4.9 (a) Can two tickets to a concert have the same section, the same row, the same seat, and the same date?
(b) How many of these must be different to avoid seating problems?
(c) Can two electrons in the same atom have the same n value, the same ℓ value, the same m_ℓ value, and the same m_s value?
(d) How many of these must be different to have a permissible situation?
- 4.10 For the electrons of Table 4.2, is the sign of the m_s value arbitrary for (a) the first electron, (b) the second electron, (c) the fifth electron, (d) the tenth electron?
- 4.11 Explain why helium, with two outermost electrons, has the same inertness characteristic of neon and argon, each with eight outermost electrons.
- 4.12 Add the energies for the change of the electron in the hydrogen atom from the third orbit to the second plus that from the second orbit to the first (see Example 4.3 and Practice Problem 4.3 for data). Compare your answer to the energy for the change from the third orbit to the first, and explain your result.

Problems**4.1 A Brief Exploration of Light**

- 4.13 Calculate the frequency of a photon of light of wavelength 6.563×10^{-7} m, corresponding to a line in the visible spectrum of hydrogen.
- 4.14 Use the equation $E = hc/\lambda$ with E in joules, c in meters per second, and λ in meters to determine the units of h .
- 4.15 Calculate the wavelength of a photon of light of energy 4.09×10^{-19} J, corresponding to a line in the visible spectrum of hydrogen.
- 4.16 Label Figure 4.1 with an axis having units of energy.
- 4.17 Calculate the frequency and wavelength of a 4.85×10^{-19} J photon, corresponding to a line in the visible spectrum of hydrogen.
- 4.18 Calculate the energy of a photon of light of wavelength 4.340×10^{-7} m, corresponding to a line in the visible spectrum of hydrogen.
- 4.19 The frequency of a certain beam of light is 7.00×10^{11} /s. Calculate the wavelength and the energy of its photons. Determine in what portion of the electromagnetic spectrum the beam lies.

4.2 Bohr Theory

- 4.20 Describe qualitatively the relationship between energy and the electron transitions occurring in the neon gas in a neon sign.
- 4.21 List the possible series of electron transitions for an electron descending from the sixth shell to the third in a hydrogen atom.
- 4.22 How many different wavelengths of light would be emitted if many identical atoms underwent the changes described in the prior problem?

4.3 Quantum Numbers

- 4.23 What values of ℓ are permitted for an electron with $n = 4$?
- 4.24 What values of m_ℓ are permitted for an electron with $\ell = 3$?
- 4.25 What values of m_s are permitted for an electron with $n = 5$, $\ell = 3$, and $m_\ell = +2$?

■ Problems

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- 4.26** Which of the following sets of quantum numbers is (are) not permitted?
- $n = 3, \ell = 0, m_\ell = +1, m_s = -\frac{1}{2}$
 - $n = 3, \ell = 2, m_\ell = -1, m_s = -1$
 - $n = 3, \ell = -2, m_\ell = 0, m_s = -\frac{1}{2}$
 - $n = 3, \ell = 3, m_\ell = -2, m_s = +\frac{1}{2}$
- 4.27** Make a chart showing all possible values of ℓ , m_ℓ , and m_s for an electron with $n = 2$ and another with $n = 3$.
- ### 4.4 Relative Energies of Electrons
- 4.28** (a) What values of m_ℓ are permitted for an electron with $\ell = 5$?
 (b) How many different values of m_ℓ are permitted for an electron with $\ell = 5$?
- 4.29** Arrange the following electrons, identified only by their n and ℓ quantum numbers, in order of increasing energy from lowest to highest.
- $n = 6, \ell = 3$
 - $n = 6, \ell = 2$
 - $n = 5, \ell = 3$
 - $n = 5, \ell = 2$
- 4.30** Arrange the following electrons in order of increasing energy:
- $n = 5, \ell = 1$
 - $n = 4, \ell = 2$
 - $n = 4, \ell = 3$
 - $n = 6, \ell = 0$
- 4.31** Arrange the following electrons in order of increasing energy:
- $n = 5, \ell = 1, m_\ell = -1, m_s = +\frac{1}{2}$
 - $n = 5, \ell = 1, m_\ell = 0, m_s = -\frac{1}{2}$
 - $n = 5, \ell = 1, m_\ell = 1, m_s = -\frac{1}{2}$
 - $n = 5, \ell = 1, m_\ell = 0, m_s = +\frac{1}{2}$
- 4.32** Compare the energies of the following electrons, identified by their quantum numbers only:
- $n = 3, \ell = 2, m_\ell = 1, m_s = +\frac{1}{2}$
 - $n = 3, \ell = 2, m_\ell = -1, m_s = -\frac{1}{2}$
 - $n = 3, \ell = 2, m_\ell = 0, m_s = +\frac{1}{2}$
- 4.33** Arrange the following four electrons in order of increasing energy:
- $n = 4, \ell = 0, m_\ell = 0, m_s = -\frac{1}{2}$
 - $n = 3, \ell = 1, m_\ell = -1, m_s = +\frac{1}{2}$
 - $n = 3, \ell = 2, m_\ell = 0, m_s = -\frac{1}{2}$
 - $n = 4, \ell = 1, m_\ell = +1, m_s = -\frac{1}{2}$
- ### 4.5 Shells, Subshells, and Orbitals
- 4.34** What does the number of ℓ values permitted for a given n value have to do with the number of subshells in a shell?
- 4.35** What does the number of m_ℓ values permitted for a given ℓ value have to do with the number of orbitals in a subshell?
- 4.36** Explain why the helium atom is stable with only two electrons in its outermost shell, but beryllium is not.
- 4.37** How many electrons are present in each of the following atoms? Assuming that each is a neutral atom, identify the element.
- $1s^2 2s^2 2p^6 3s^2 3p^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
- 4.38** How many electrons are permitted (a) in a d orbital and (b) in a d subshell?
- 4.39** Write detailed electronic configurations for Li, C, and Mg.
- 4.40** (a) How many orbitals are in the $2p$ subshell?
 (b) How many orbitals are in the $3p$ subshell?
 (c) How many orbitals are in the $4p$ subshell?
 (d) What is the maximum number of electrons permitted in a $5p$ subshell?
- 4.41** In a given atom, what is the maximum number of electrons that can have the following quantum numbers?
- $n = 5, \ell = 2$
 - $n = 4, \ell = 3$
 - $n = 3, \ell = 0$
 - $n = 4, \ell = 1, \text{ and } m_\ell = -1$
- 4.42** (a) What is the letter designation for $\ell = 3$?
 (b) How many different m_ℓ values are possible for an electron in a subshell for which $\ell = 3$?
 (c) How many different orbitals are in an $\ell = 3$ subshell?
 (d) What is the maximum number of electrons in an $\ell = 3$ subshell?
- 4.43** (a) How many $2p$ orbitals are present in any atom?
 (b) What is the maximum number of electrons in the $2p$ subshell?
 (c) How many electrons are present in the $2p$ subshell of a fluorine atom?
 (d) Explain why the subshell is not full in the fluorine atom.
- ### 4.6 Shapes of Orbitals
- 4.44** According to Figure 4.8(c), which two $3d$ orbitals cannot have an electron in the xz -plane?
- 4.45** According to Figure 4.8(b), which $2p$ orbital cannot have an electron in the xz -plane?
- 4.46** How many d orbitals are pictured in Figure 4.8?
- 4.47** (a) How many of the p orbitals pictured in Figure 4.8(b) are oriented along an axis? (b) How many of the d orbitals pictured in Figure 4.8(c) are oriented along axes?

124**4.7 Energy Level Diagrams**

- 4.48 What is the maximum number of *unpaired* electrons in (a) an *s* subshell, (b) a *p* subshell, (c) a *d* subshell, and (d) an *f* subshell?

- 4.49 How many unpaired electrons are present in the ground state of an atom if six electrons are present in each of the following subshells? There are no other unpaired electrons.

- (a) 4*p* subshell (b) 4*d* subshell
(c) 5*f* subshell

- 4.50 Draw an energy level diagram, and determine the number of unpaired electrons in an atom of each of the following:

- (a) B (b) O (c) Ne (d) Si

- 4.51 Which of the following configurations represents the outermost shell of the ground state of phosphorus?

- (a) $\begin{array}{c} \uparrow\downarrow \\ 3s \\ \hline \end{array}$ (b) $\begin{array}{c} \uparrow\downarrow \\ 3p \\ \hline \end{array}$
(c) $\begin{array}{c} \uparrow\downarrow \\ 3s \\ \hline \end{array}$ (d) $\begin{array}{c} \downarrow\downarrow \\ 3p \\ \hline \end{array}$
(e) $\begin{array}{c} \uparrow\downarrow \\ 3p \\ \hline \end{array}$ (f) $\begin{array}{c} \uparrow\downarrow \\ 3p \\ \hline \end{array}$

- 4.52 How many unpaired electrons are in an atom in the ground state, assuming that all other subshells are either completely full or empty, if its outermost *p* subshell contains (a) three electrons, (b) five electrons, (c) four electrons?

- 4.53 Draw an energy level diagram for the cobalt atom.

- 4.54 How many unpaired electrons are in an atom in the ground state, assuming that all other subshells are either completely full or empty, if its outermost *d* subshell contains (a) four electrons, (b) six electrons, (c) seven electrons?

4.8 Periodic Variation of Electronic Configuration

- 4.55 Use the periodic table to deduce how many electrons can fit into any (a) *s* subshell, (b) *p* subshell, (c) *d* subshell, and (d) *f* subshell.

General Problems

- 4.66 The Bohr theory has been essentially replaced. Explain why *any* theory is ever rejected.

- 4.67 Identify the element from each of the following *partial* configurations of neutral atoms:

- (a) ... 4*s*² 3*d*⁵ (b) ... 5*s*² 4*d*¹⁰ 5*p*⁴
(c) ... 6*p*³ (d) ... 5*s*¹
(e) ... 3*d*¹⁰ 4*p*⁵ (f) ... 7*s*² 6*d*¹ 5*f*¹⁴

CHAPTER 4 ■ Electronic Configuration of the Atom

- 4.56 (a) How many electrons are added to an atom in the build-up process before the start of the second shell? How many elements are in the periodic table before the start of the second period?

- (b) How many electrons are added to an atom in the build-up process before the start of the third shell? How many elements are in the periodic table before the start of the third period?

- (c) How many electrons are added to an atom in the build-up process before the start of the fourth shell? How many elements are in the periodic table before the start of the fourth period?

- 4.57 Locate in the periodic table (a) the element that has the first 3*d* electron and (b) the element that is the first to complete its 2*s* subshell.

- 4.58 Write detailed electronic configurations for (a) Be, (b) Mg, (c) Ca, and (d) Sr.

- 4.59 Write detailed electronic configurations for the following:

- (a) As (b) Ar (c) Al
(d) V (e) Ni

- 4.60 Write detailed electronic configurations of the following:

- (a) Ge (b) Mn (c) N (d) Br (e) Fe

- 4.61 Write detailed electronic configurations for O, S, Se, and Te, and deduce the outermost configuration for Po.

- 4.62 Use the periodic table to write the outer electronic configuration for each of the following elements:

- (a) Tl (b) La (c) Gd

- 4.63 Use the periodic table to write outer electronic configurations for the following elements:

- (a) Pb (b) Fr (c) Lu (d) Pt

- 4.64 Use the periodic table to write outer electronic configurations for the following elements:

- (a) Rf (element 104) (b) U (c) Ba

- 4.65 Write outer electronic configurations for the following:

- (a) Os (b) Hf (c) Ce

- 4.68 The energy of each of the first six shells of hydrogen is given in Figure 4.6. Calculate the energies emitted when the electrons in many hydrogen atoms descend from the fifth shell to the second. (*Hint:* See Problem 4.21.)

- 4.69 What type (*s*, *p*, *d*, *f*) electron was the last electron added in the buildup process to

- (a) A nonmetal
(b) A transition element

■ General Problems

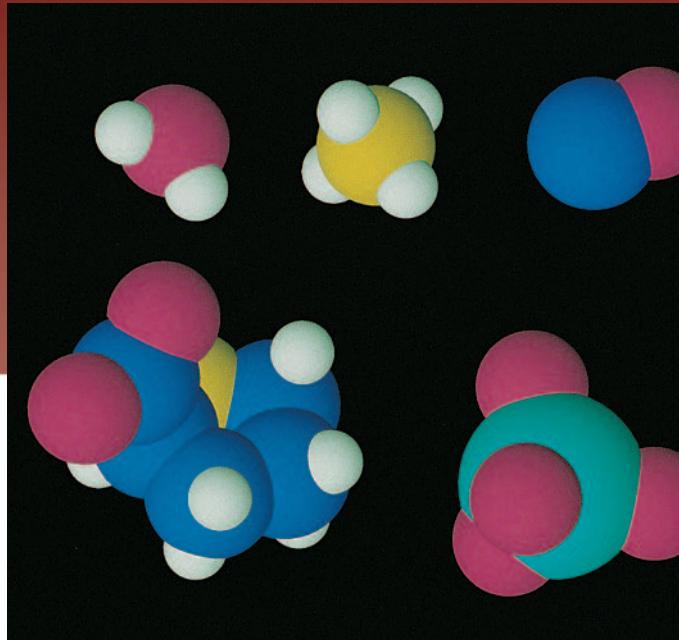
125

- (c) An inner transition element
 (d) A main group metal (two answers)
- 4.70 The orange line in the hydrogen spectrum (see Figure 4.5) is the change of the electron from the third orbit to the second; the green line is the change from the fourth orbit to the second; the two violet lines are the changes from the fifth and sixth orbits to the second, respectively. Without looking at any figures, deduce which color represents the most energy, and which represents the least. Is wavelength directly proportional to energy?
- 4.71 Can you identify the following element from its inner electronic configuration? $1s^2 2s^2 \dots$. Explain.
- 4.72 In answering the question, "What is the maximum value for ℓ for any electron in the ground state of Lr, element 103?" several students gave the following answers and reasoning. Which one is correct?
- The maximum $\ell = 6$ because the outermost shell has $n = 7$, and ℓ cannot be more than $n - 1$.
 - The maximum $\ell = 3$ because the f subshell has an ℓ value of 3, and there is no subshell with a bigger ℓ value in Lr.
 - The maximum $\ell = 1$ because the outermost shell cannot have more than 8 electrons, and $\ell = 1$ is the maximum ℓ for a filled octet.
- 4.73 Does an electron gain or lose energy in each of the following transitions?
- From a $5f$ subshell to a $4d$ subshell
 - From a $5s$ subshell to a $4p$ subshell
 - From a $6p$ subshell to a $5d$ subshell
- 4.74 What is the maximum number of *unpaired* electrons in
- the $3d$ subshell of an atom and
 - the $4f$ subshell of an atom?
- 4.75 What is wrong with each of the following ground state configurations?
- $1s^2 1p^6 2s^2 2p^3$
 - $1s^1 2s^2 2p^4$
 - $1s^2 2p^6 3d^{10} 4f^{14}$
 - $1s^2 2s^2 2p^4 3s^2 3p^6$
 - [Xe] $6s^2 5d^{10} 4f^{15}$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{14}$
 - $1s^2 2s^4 2p^6 3s^2$
 - $1s^2 2s^2 2p^6 2d^{10}$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^{10} 4p^3$
- 4.76 Which one(s) of the following configurations are *not* permitted for an atom in its ground state?
- $1s^2 2s^2 2p^2$
 - $1s^2 2s^2$
 - $1s^6 2s^6 2p^6$
 - $1s^1 2s^1$
- 4.77 How many unpaired electrons are present in the ground state of an atom if there are five electrons in each of the following subshells? There are no other unpaired electrons.
- $3p$ subshell
 - $3d$ subshell
 - $4f$ subshell
- 4.78 Is the Bohr theory or the quantum mechanical theory better to describe the electronic arrangement of
- Argon
 - Aluminum
 - Antimony
- 4.79 Deduce the expected electronic configuration of (a) Cr, (b) Cu, and (c) Ce.
- 4.80 Calculate the energy of the first line of the hydrogen spectrum. Its wavelength (λ) is 410 nm.
- 4.81 Figure 4.11 shows that the periodic table is based on the electronic structure of the atoms. Explain how Mendeleev was able to create the periodic table without knowing about the electron at all.
- 4.82 What is the maximum number of unpaired electrons in the ground state of an atom in which only the $1s$, $2s$, $2p$, $3s$, and $3p$ subshells have any electrons?
- 4.83 Which one(s) of the following sets of quantum numbers is (are) *not* permitted?
- $n = 4, \ell = 3, m_\ell = 2, m_s = -\frac{1}{2}$
 - $n = 4, \ell = 2, m_\ell = -3, m_s = +\frac{1}{2}$
 - $n = 2, \ell = 1, m_\ell = 1, m_s = -\frac{1}{2}$
 - $n = 2, \ell = 2, m_\ell = 1, m_s = +\frac{1}{2}$
 - $n = 3, \ell = 1, m_\ell = 1, m_s = -1$
- 4.84 Which metal in each of the following sets will be drawn into a magnetic field the most?
- Zn Mn V
 - Ca Cu Cd
 - Sc Cu V
 - Ti Tl Ga
- 4.85 (a) Draw an energy level diagram for iodine.
 (b) Can you use this diagram for the electronic structure of sodium?
 (c) Explain why one large energy level diagram is sufficient for all the elements.
- 4.86 Would the actual configuration of the chromium atom (see p. 119) or the configuration expected by the $n + \ell$ rule be drawn more into a magnetic field.

5

Chemical Bonding

- 5.1 Chemical Formulas
- 5.2 Ionic Bonding
- 5.3 Lewis Electron Dot Diagrams
- 5.4 Formulas for Ionic Compounds
- 5.5 Covalent Bonding



Models of simple molecules

Review Clues

- Chapter 5** Chapter 4, if studied. (Otherwise, omit the green-shaded portions of this chapter.)
- Section 5.1** Sections 1.4, 3.5
- Section 5.2** Sections 1.5, 3.3
- Section 5.3** Section 3.3
- Section 5.4** Appendix 1

Objectives

- 5.1** To interpret and write chemical formulas
- 5.2** To write octet rule electronic structures for the formation of ionic compounds and to deduce the formulas of compounds of main group metals with nonmetals
- 5.3** To write electron dot diagrams for keeping track of the valence electrons in compounds, especially those of main group elements
- 5.4** To learn how to deduce the formulas of compounds of main group metals with nonmetals, and the formulas of compounds of any combination of metal ion and nonmetal ion if we know the charges on the ions
- 5.5** To write electron dot diagrams for the compounds of two or more nonmetals bonded with shared electron pairs, and also for polyatomic ions

5.1 ■ Chemical Formulas**127**

Writing a chemical formula implies bonding of some type.

Ionic bonding involves transfer of electrons. Covalent bonding involves electron sharing. In many ternary compounds, both ionic and covalent bonding occur.

The electronic structure of an uncombined atom, first discussed in Chapter 4, determines the ability of that atom to combine with other atoms to produce molecules or ionic compounds. In this chapter, the fundamentals of chemical bonding are covered. To discuss compounds, chemical formulas are required. Moreover, when symbols for atoms are combined in a chemical formula, some type of bonding is implied. Therefore, chemical formulas are introduced first, in Section 5.1. (More information about chemical formulas will be presented in Chapter 7.) Ionic bonding, which occurs when electrons are transferred from one atom to another, is treated in Section 5.2. A convenient way to picture atoms with their outermost electrons—the electron dot diagram—is presented in Section 5.3. The number of electrons transferred from one atom to another, or the charges on the resulting ions, enable us to deduce the formulas for binary ionic compounds (Section 5.4). Atoms held together solely by covalent bonds form units called molecules (or much larger units called macromolecules). Covalent bonding, in which the sharing of electrons is the primary method of bonding, is introduced in Section 5.5, which also discusses compounds with both ionic and covalent bonding.

5.1 Chemical Formulas

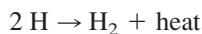
Just as a symbol identifies an element, a **formula** is a combination of symbols that identifies a compound, an ion, or a molecule of an element. However, chemical formulas do much more. A formula also indicates the relative quantities of the elements contained in the compound or ion and implies some kind of chemical bonding between the atoms.

Molecules of Elements

Formulas are used to identify molecules of free elements. A **molecule** contains two or more nonmetallic atoms bonded together. Many free (uncombined) nonmetallic elements exist as molecules, such as H₂, N₂, O₂, F₂, Cl₂, Br₂, and I₂, as well as P₄ and S₈ (Figure 5.1). The formula P₄ indicates four phosphorus atoms bonded together. This formula does not represent a compound, because only one kind of atom is present. **Elemental** phosphorus in its lowest energy form occurs in such molecules.

Seven elements occur as **diatomic molecules** (molecules with two atoms) *when they are not combined with other elements*. Fortunately, these elements are easy to remember because, except for hydrogen, they form a shape like a seven in the periodic table, starting at the element with atomic number 7 (Figure 5.2).

Hydrogen molecules (H₂) are so much more stable than separated hydrogen atoms that the reaction of the atoms to form molecules produces a lot of heat:



Seven elements occur as diatomic molecules *when they are not combined with other elements*.

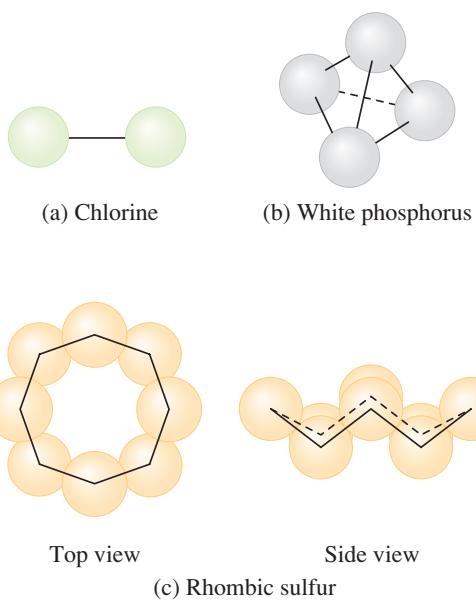
Production of a given number of H₂ molecules from hydrogen atoms produces more heat than the production of the same number of CO₂ molecules from burning carbon (charcoal) in oxygen. Construction workers take advantage of the reaction of atomic hydrogen to weld steel pieces together in the absence of oxygen. That condition is desirable because oxygen might make the steel rust.

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CHAPTER 5 ■ Chemical Bonding

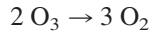
Figure 5.1 Some Elements That Occur as Molecules

- (a) Cl_2 , chlorine
- (b) P_4 , white phosphorus (the most stable form of elemental phosphorus)
- (c) S_8 , rhombic sulfur (the most stable form of elemental sulfur)



Where do the hydrogen atoms come from? They are produced by electrical discharge in a welding torch, such as is diagrammed in Figure 5.3.

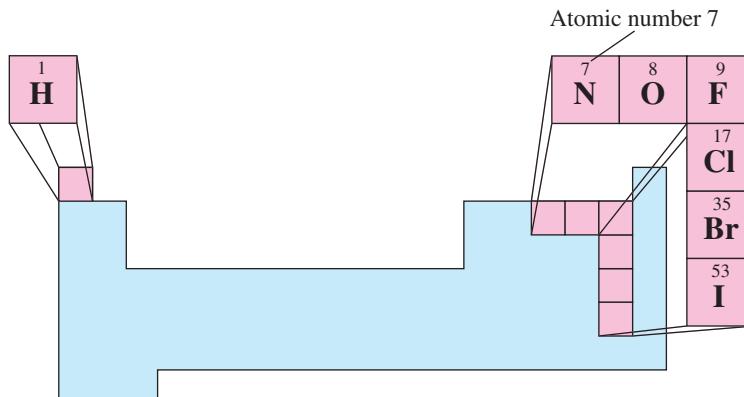
In addition to its stable elementary form, O_2 , oxygen can also exist as O_3 molecules, a form called **ozone**. Ozone can be formed when an electrical discharge passes through oxygen gas, and it is also formed in the upper atmosphere—the ozone layer—when high-energy rays from outer space bombard O_2 molecules. The ozone molecules in the upper atmosphere are important because they absorb harmful ultraviolet light from the Sun. This prevents some of that light from reaching the Earth's surface, where it could injure humans and other animals. The O_3 molecule is more reactive than O_2 and decomposes spontaneously but slowly:



Ozone is a powerful oxidizing agent. In the atmosphere near the surface of the Earth, it is irritating and injurious in concentrations greater than two parts per million. It can be used as a disinfectant and a bleach.

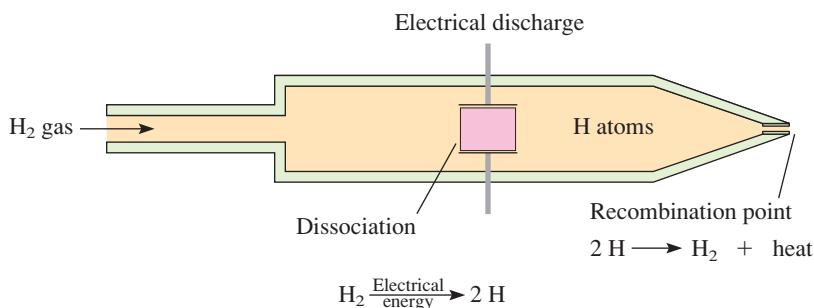
Figure 5.2 The Seven Elements That Form Diatomic Molecules

Note that the shape formed by six of these elements in the periodic table looks like the number 7, starting at atomic number 7.



5.1 ■ Chemical Formulas**129****Figure 5.3** Welding Torch

Hydrogen gas is piped into a special tube in which many of the H_2 molecules are separated into atoms by an electrical discharge. The gas flow is adjusted to the rate at which most of the H atoms recombine into molecules just as they exit from the torch. The heat produced at that point is intense enough to weld pieces of steel together.



Some other free (uncombined) elements also occur in different forms. Different forms of the same element are called **allotropes** of each other. Except for oxygen, the elements that form diatomic molecules when uncombined do not form allotropes, but many other nonmetals do. The allotropes of carbon—diamond and graphite—are perhaps best known to the general public. Sulfur and phosphorus are also notable for forming allotropes.

Binary Compounds

Atoms of two or more different nonmetals can bond together to form molecules of a compound. H_2O , CH_4 , and CH_4O are examples.

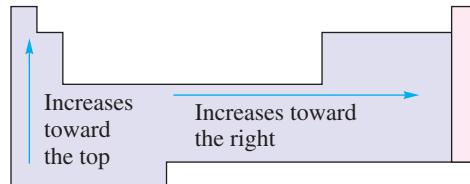
In the formula for a **binary compound** (a compound containing only two elements), the element that attracts electrons less is usually written first. The elements are assigned an **electronegativity** that reflects their affinity for electrons in chemical bonds. The elements that attract electrons most are said to have the highest electronegativities or to be the most **electronegative**. Fluorine, the most electronegative element, is assigned an electronegativity of 4.0, and the other elements have values relative to that of fluorine. The elements that attract electrons least are said to have the lowest electronegativities or to be the most **electropositive**.

Values for the electronegativities of the main group elements are presented in Figure 5.4. Except for those of the noble gases, the electronegativities of the

Figure 5.4 Electronegativities of the Main Group Elements

H 2.1							He
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9						

Figure 5.5 Periodic Variation of Electronegativity



elements increase toward the right and toward the top of the periodic table (Figure 5.5). Fluorine has the highest electronegativity of any element, and oxygen has the second highest value. The most electropositive element is francium (Fr). The metals are more electropositive than the nonmetals. Thus, in the formula of a binary compound, the metal, if one is present, is written first. If no metal is present, the nonmetal closer to the metal portion of the periodic table is written first. Some examples of binary compounds of nonmetals are CO, H₂O, SO₂, and SiO₂.

Formulas for binary compounds of hydrogen do not follow the rule just discussed. Hydrogen is written first in the formula if the compound is an acid (Chapter 8) and written later if the compound is not an acid. For example, HCl is hydrochloric acid, and NH₃ is ammonia. The position of the H in these formulas indicates that HCl is an acid and NH₃ is not. H₂O and H₂O₂ are exceptions to this rule; neither is an acid.

Formula Units

A subscript multiplies the number of atoms of the preceding element (or the number of preceding groups if the subscript follows a closing parenthesis).

The collection of atoms represented by a formula is called a **formula unit**. A chemical formula consists of symbols of element(s), often with **subscripts** that tell how many atoms of each element are present per formula unit. The subscript *follows* the symbol of the element it multiplies. If no subscript is present, one atom of the element is indicated. Parentheses may be used in a formula to group bonded atoms together, and a subscript after the closing parenthesis tells how many of that group are present per formula unit. The following formulas illustrate the meanings of subscripts in formulas:

CO	One carbon atom and one oxygen atom are bonded in one formula unit.
SO ₂	One sulfur atom and two oxygen atoms are bonded in one formula unit.
Ba ₃ (PO ₄) ₂	Three barium atoms and two PO ₄ groups, each containing one phosphorus atom and four oxygen atoms, are present in one formula unit. The atoms in the PO ₄ groups are bonded to each other in some way, as is the compound as a whole (Section 5.5).
H ₂	Two atoms of hydrogen are bonded in one formula unit.
H ₂ O	Two atoms of hydrogen and one atom of oxygen are bonded in one formula unit. This formula unit represents one molecule of water.

5.1 ■ Chemical Formulas**131**

Figure 5.6 Blue Hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (left), and White, Anhydrous CuSO_4 (right)

EXAMPLE 5.1

How many atoms of each element are present in one formula unit of each of the following compounds?

- (a) $\text{Mg}(\text{ClO}_3)_2$ (b) $(\text{NH}_4)_2\text{SO}_3$ (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) S_8

Solution

- (a) 1 Mg, 2 Cl, 6 O (b) 2 N, 8 H, 1 S, 3 O
(c) 2 C, 6 H, 1 O (d) 8 S

Practice Problem 5.1 How many atoms of each element are present in one formula unit of each of the following compounds?

- (a) Hg_2Cl_2 (b) $\text{NH}_4\text{H}_2\text{PO}_4$

A few compounds have formulas that are written with a **centered dot**, as in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. In general, the dots connect the formulas of two or more compounds that could exist independently but are bonded in some way in a single compound. The coefficient (5) after the centered dot multiplies everything after it until the end of the formula. Thus, 10 hydrogen atoms and 9 oxygen atoms are in one formula unit of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This particular formula could have been written $\text{CuSO}_4(\text{H}_2\text{O})_5$. When water is one of the compounds in a formula with a centered dot, the combination is called a **hydrate**. The compound *without* the attached water is said to be **anhydrous**, meaning “without water.” Anhydrous CuSO_4 and its hydrate are pictured in Figure 5.6.

EXAMPLE 5.2

What is the difference between the formulas $(\text{NH}_4)_3\text{PO}_3$ and $\text{N}_3\text{H}_{12}\text{PO}_3$?

Solution

Although both formulas have the same ratios of atoms of each element to atoms of all the others and to formula units of the compound, the first formula states that the atoms of nitrogen and hydrogen are bonded together in some way in each of three NH_4 groups.

Practice Problem 5.2

- (a) Write a formula that implies that a CH_3 group is connected to a CO_2H group by two CH_2 groups.
(b) Write a formula showing just the numbers of atoms of each element in this compound.

In reading formulas aloud, the number is simply stated for any subscript following a symbol, as in H_2O : “H two O.” To express parentheses followed

by a subscript 2, the words “taken twice” are used; for a subscript 3, the words “taken three times” are used, and so on. The centered dot is read “dot.” Here are some examples to illustrate these conventions:

Hg ₂ Br ₂	“H g two B r two”
Ba ₃ (PO ₄) ₂	“B a three P O four taken twice”
CH ₃ (CH ₂) ₄ CH ₃	“C H three, C H two taken four times, C H three”
CuSO ₄ ·5H ₂ O	“C u S O four dot five H two O”



Snapshot Review

- The chemical formula for a substance tells us (a) the relative numbers of atoms of each element and (b) that the elements in it are all bonded in some way.
- A. How many atoms of hydrogen are present per atom of phosphorus in (NH₄)₂HPO₄?
- B. Which element in SeCl₂ is more electronegative?
- C. What is the formula for elemental oxygen?

5.2 Ionic Bonding

The electrons in atoms are arranged in groups, those in each group having nearly the same energies. These energy levels are often referred to as shells. The first shell of any atom can hold a maximum of 2 electrons; the second shell can hold a maximum of 8 electrons; and the other shells can hold a maximum of 8 electrons when they are the outermost shell, but a greater number when they are not (Table 5.1). The **outermost shell** is the last shell that contains electrons. Before the next-to-outermost shell starts to expand past 8 electrons, the (new) outermost shell must hold 2 electrons.

Electrons can be transferred from metal atoms to nonmetal atoms to achieve a more stable, lower energy state. The noble gases are composed of stable atoms; no reactions of the first three (He, Ne, Ar) have been discovered, and the others (Kr, Xe, Rn) are almost completely unreactive. The stability of the

Table 5.1 Maximum Electron Occupancy of Shells

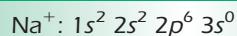
Shell Number	Maximum Occupancy as the Outermost Shell	Maximum Occupancy as an Inner Shell
1	2	2
2	8	8
3	8	18
4	8	32
5	8	50*
6	8	72*
7	8*	98*

*More than the number of electrons available in any atom

5.2 ■ Ionic Bonding**133**

Atoms tend to accept, donate, or share electrons to achieve the electronic structure of the nearest noble gas.

The valence shell is the shell of highest principal quantum number.



The number of electrons in the valence shell of an uncombined main group atom is equal to the classical periodic group number of the element.

noble gases is due to the 8 electrons in the outermost shell of each atom (2 electrons in the case of helium). In fact, 8 electrons in the outermost shell is a stable configuration for most main group atoms. Atoms other than those of the noble gases tend to form ionic or covalent bonds (or both) with other atoms to achieve this electronic configuration. The 8 electrons in the outermost shell are called an **octet**. The tendency of atoms to be stable with 8 electrons in the outermost shell is called the **octet rule**. In some compounds, one (or more) of the atoms does not obey the octet rule. Some exceptions to the octet rule will be mentioned briefly in Section 5.5.

Because the maximum number of electrons in the first shell of an atom is 2, helium is stable with 2 electrons in its only occupied shell. The other very light elements—hydrogen, lithium, and beryllium—tend to form stable states by achieving the 2-electron configuration of helium. Having 2 electrons in the first shell, *when that is the only shell and therefore the outermost shell*, is a stable state, and the 2 electrons are sometimes called a **duet**. When there is only one shell, 2 electrons in that shell act like 8 electrons in any other outermost shell. Therefore, an atom with 2 electrons in its outermost first shell is often said to obey the octet rule, although “duet rule” would be more precise.

The **valence shell** of electrons in an atom is the outermost shell of electrons of the *uncombined* atom. The electrons in that shell are called **valence electrons**. If all the electrons are removed from that shell, the next inner shell becomes the new outermost shell. For example, the sodium atom has 2 electrons in its first shell, 8 electrons in its second shell (the maximum), and its last electron in its third shell. The valence shell is the third shell. If the 1 electron is removed from the third shell, the second shell becomes the outermost shell, containing 8 electrons. The valence shell is still the (now empty) third shell. The number of electrons in the valence shell of an uncombined main group atom is equal to the classical periodic group number of the element (Figure 5.7). The exceptions to this rule are that helium has 2 valence electrons and the other noble gases have 8 valence electrons.

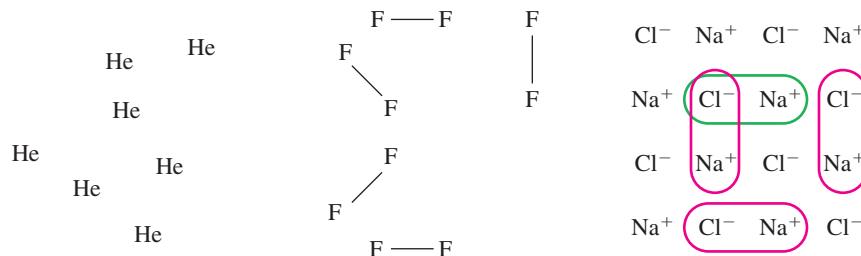
All metals react with nonmetals to form ionic compounds. Main group metals tend to transfer their valence electrons to nonmetals, and nonmetals tend to accept enough electrons from these metals to achieve their octets. For example, a sodium atom has 1 electron in its valence shell, and a chlorine atom has 7 electrons in its valence shell. When they react, the sodium atom transfers that 1 electron to the chlorine atom, forming two charged species called **ions**. Both of these ions have 8 electrons in their outermost shells. (The sodium ion has 8 electrons in its second shell, now its outermost shell.) *The electronic configurations of both ions are those of noble gas atoms* (the sodium ion has that of a neon atom, and the chlorine ion that of argon). The atoms have not been changed into noble gas atoms, however, because their nuclei have not changed.

Figure 5.7 Numbers of Valence Electrons for Atoms of Main Group Elements

Classical group number:	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0
Modern group number:	1	2	13	14	15	16	17	18
Period 1	1							2
All other periods	1	2	3	4	5	6	7	8

Figure 5.8 Formula Units of Atoms, Molecules, and Ionic Compounds

The formula units He and F₂ represent single atoms and diatomic molecules, respectively. Unlike the F₂ molecule, in which one fluorine atom is bonded to a specific other fluorine atom, in the ionic compound NaCl, one Na⁺ ion is bonded to six Cl⁻ ions that are adjacent to it. Each of the Cl⁻ ions is bonded to six Na⁺ ions that are adjacent to it. (The fifth and sixth ions are in layers in front of and behind the layer shown here; see Figure 5.9.) The ratio of Na⁺ ions to Cl⁻ ions is therefore 1:1. Any pair of Na⁺ and Cl⁻ ions, such as those circled in red or the one circled in green, is a formula unit.



The sodium ion has a single positive charge because the neutral atom has donated one negatively charged electron. The sodium ion is written as Na⁺. The ion formed from the chlorine atom has a single negative charge, resulting from the gain of the electron by the neutral chlorine atom. This ion is written as Cl⁻. Oppositely charged bodies attract each other, so Na⁺ ions and Cl⁻ ions attract each other. This kind of attraction is called an *electrostatic attraction*. In general, the transfer of electrons from one atom to another produces oppositely charged ions, which attract each other. The formula for the compound of sodium and chlorine is NaCl, which shows that one Na⁺ ion is present for each Cl⁻ ion (Figure 5.8).

All ionic compounds have an overall net charge of zero because the electrons are transferred but do not disappear. The electrons that some atoms accept to form negative ions are donated by other atoms, which become positive ions. Positively charged ions are called **cations** (pronounced “cat’-ions”), and negatively charged ions are called **anions** (pronounced “an’-ions”). The sodium ion is positive; it is a cation. The ion produced by the chlorine atom accepting an extra electron is negative; it is an anion. If an anion is a **monatomic ion** (having only one atom), its name ends in *-ide*, so Cl⁻ is called the chloride ion.

Metallic and nonmetallic elements can react with each other to form compounds by transferring electrons from the metal atoms to the nonmetal atoms. The ions formed attract each other because of their opposite charges, and these attractions are called **ionic bonds**. However, in a solid ionic compound, a single pair of ions does not bond together; instead, an almost inconceivably huge number of both types of ions forms a lattice that extends in three dimensions. The three-dimensional nature of the **sodium chloride structure** (Figure 5.9) is typical of ionic solids.

The ionic nature of these compounds (the fact that charged particles are present) can be shown by experiments in which the ions are made to carry an electric current. Pure water does not conduct electricity well. However, if a compound that consists of ions is dissolved in water and the solution is placed between **electrodes** in an apparatus like that shown in Figure 5.10, the solution will conduct electricity when the electrodes are connected to the terminals of a battery. Each type of ion moves toward the electrode that has the *opposite* charge of that of the ion. That is, cations migrate to the negative electrode, called the **cathode**, and anions migrate to the positive electrode, called the **anode**. (The names *cation* and *anion* were derived from the words *cathode* and *anode*.) For electricity to be conducted, the ions must be free to move. In the solid state, an ionic compound will not conduct because the ions are trapped in the lattice. However, if the compound is heated until it melts or if it is dissolved in water, the liquid compound or solution will conduct electricity because the ions are free to move.

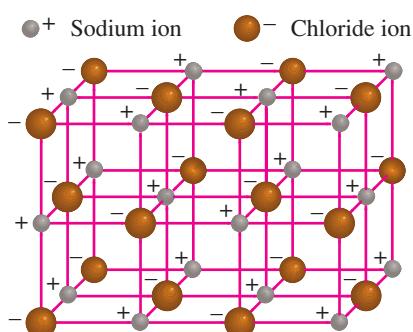


Figure 5.9 Sodium Chloride Structure

Each sodium ion is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions. The ratio of sodium ions to chloride ions is 1:1, and the formula for sodium chloride is written NaCl. This figure shows only a small portion of the structure, which extends over thousands of ions or more in each direction.

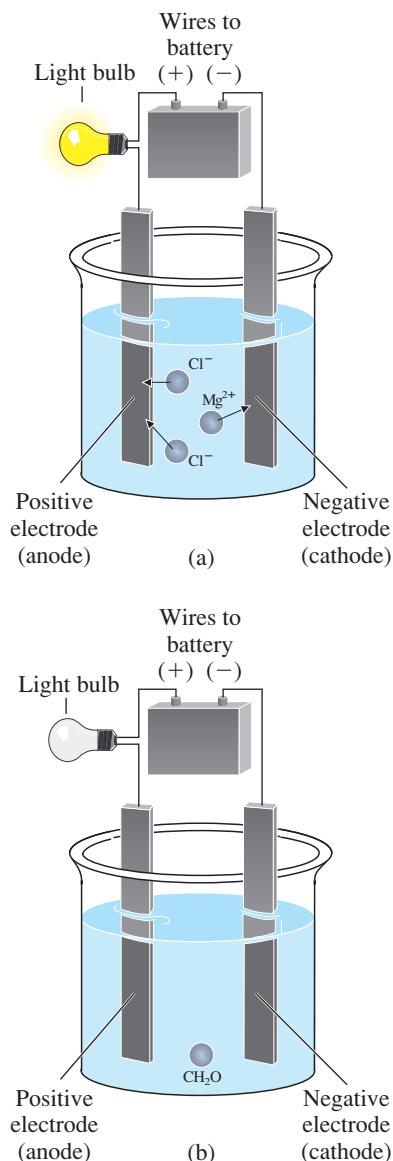
5.2 ■ Ionic Bonding**135**

Figure 5.10 Conduction of Electricity by Ions

- (a) When an ionic compound such as magnesium chloride, $MgCl_2$, is dissolved in water and a voltage is applied, the positive and negative ions carry the current (the light turns on).
- (b) When a compound such as CH_2O (formaldehyde), which is not ionic, is used, there are no charged particles to carry the current, and no flow of electricity is observed (the light is off).

Detailed Electronic Configurations of Anions (Optional)

The detailed electronic structures of monatomic ions may be deduced starting from the structures of the corresponding neutral atoms (presented in Chapter 4). Monatomic anions have simply added sufficient electrons to the outermost p subshell to complete that subshell. The $n + \ell$ rule can be used to deduce the structure of the ion as well as that of the neutral atom. For example, the electronic configuration of the nitride ion (the anion of nitrogen) is deduced, starting with the configuration of nitrogen:



The nitride ion has a triple negative charge, obtained by gaining three extra electrons. These electrons go into the $2p$ subshell:



This electronic configuration is the same as that of neon. An ion with a configuration like that of a noble gas is said to have a **noble gas configuration**.

EXAMPLE 5.3

Write the electronic configuration for the fluoride ion, F^- .

Solution



Adding an electron corresponding to the single negative charge yields the ion:



Practice Problem 5.3 Write the detailed electronic configuration of the oxide ion, O^{2-} .

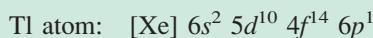
Detailed Electronic Configurations of Cations (Optional)

To form monatomic cations, metals lose electrons *from the valence shell first*. Some main group metals have more than one subshell of the valence shell occupied by electrons, in which case the electrons in the highest subshell of the valence shell are lost first. For example, the lead atom loses its $6p^2$ electrons to form Pb^{2+} . The configuration is thus

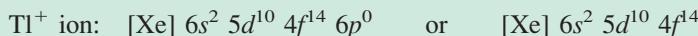


EXAMPLE 5.4

Write the outermost electronic configuration for (a) the Tl^+ ion and (b) the Tl^{3+} ion.

Solution

- (a) The outermost shell of the thallium atom has $n = 6$, and the Tl^+ ion is formed by loss of the $6p^1$ electron from that sixth shell:



- (b) The Tl^{3+} ion loses the $6p^1$ electron plus two others—the $6s^2$ electrons. Those are all the electrons in the sixth shell! Note that the $n + \ell$ rule does not apply to this case; the electrons in the outermost shell (that with the highest n value) are lost first.



Practice Problem 5.4 Write the outermost electronic configuration for (a) Bi^{3+} and (b) Pb^{4+} .

Transition metal atoms form ions by loss of their outermost electrons first (not those governed by the $n + \ell$ rule).

The electronic configurations of transition metal ions, like those of main group ions, are determined by removal of the electrons from the shell of *highest n value first*. Next, electrons may be lost from the *d* subshell next to the valence shell. The capability of removing a variable number of electrons makes it possible for most transition metals to have ions of different charges.

EXAMPLE 5.5

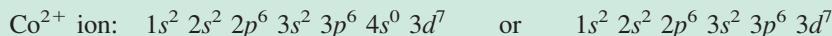
Write detailed electronic configurations for Co^{2+} and Co^{3+} .

Solution

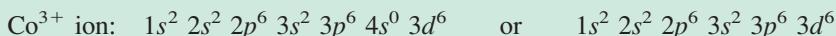
First, write the configuration for the cobalt atom:



The outermost shell electrons of the cobalt atom are lost to form the $2+$ ion:



Then a $3d$ electron is lost to form the $3+$ ion:



Practice Problem 5.5 Write the electronic configurations of Fe^{2+} and Fe^{3+} .

Inner transition metals lose electrons from their valence shells first, as do the other metals, but they also may lose electrons from the underlying *d* or *f* subshells. It should be noted that most transition and inner transition metal ions do *not* have noble gas configurations.

5.4 ■ Formulas for Ionic Compounds**137****Snapshot Review**ChemSkill Builder
3.2, 3.4

- The outermost shell of electrons in an uncombined atom of main group I–VII elements contains a number of electrons equal to the group number.
- When a metal loses electrons, its valence shell is very often left with no electrons, so the next inner shell becomes the “outermost shell” of the resulting ion.
- In Chapter 3, the number of electrons in an atom was equal to the number of protons because the atoms were uncharged. (It does not matter that they were isotopes or a mixture of isotopes of the same element.) However, in an ion, the number of electrons is not equal to the number of protons, so ions have charges.
 - A. How many electrons are in the valence shell and in the outermost shell of (a) Ca? (b) Ca^{2+} ?
 - B. Compare the number of protons and electrons in each of the following: (a) ^{79}Br , (b) Br, and (c) Br^- .

5.3 Lewis Electron Dot Diagrams

The discussion in Section 5.2 showed that the transfer of valence electrons is very important in ionic bonding. Section 5.5 will show that their sharing is very important in covalent bonding. The **Lewis electron dot diagram** is a way to picture the transfer or sharing of valence electrons that aids in understanding both processes. Keep in mind, however, that electron dot diagrams are simplified representations of atoms and not true pictures.

In an electron dot diagram, the symbol of the element represents the nucleus of the atom plus its inner shells of electrons, and dots around the symbol stand for the valence electrons. The dots are placed arbitrarily to the left or right or above or below the symbol. In unbonded atoms, two dots, at most, are located in each position. For example, atoms of the second period elements may be represented as follows:

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12.2

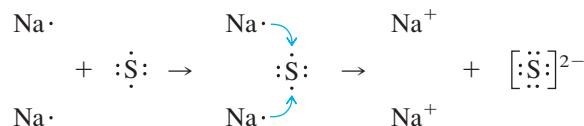
- Electron dot diagrams for uncombined atoms have the valence electrons in four possible, equivalent positions (top, bottom, both sides) with *at most* two electrons in each position.
- A. Draw an electron dot diagram for the phosphorus atom.

5.4 Formulas for Ionic Compounds

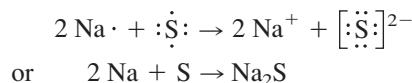
Let's consider the ionic compound formed by the reaction of sodium and sulfur. The sodium atom has 1 electron in its valence shell. (Sodium is in periodic group IA [1].) When the atom donates this electron to a nonmetal atom, the

positive ion formed has an octet like that of neon. However, the sulfur atom, with 6 valence electrons, needs 2 additional electrons. Therefore, it takes *two* sodium atoms to provide the 2 electrons for *one* sulfur atom; so the formula for sodium sulfide is Na₂S.

The reaction of sodium and sulfur to form Na₂S can be visualized easily with electron dot diagrams:



Electrons from two sodium atoms are needed to allow one sulfur atom to attain its octet. We can write the reaction more simply as follows:



Similarly, the formula of aluminium chloride is AlCl₃ because the aluminum atom has 3 valence electrons that it can donate to form the 3+ ion. Charges on the most common monatomic ions are presented in Figure 5.11.

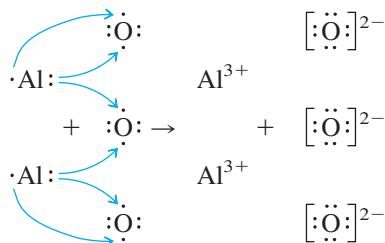
EXAMPLE 5.6

Use electron dot diagrams to picture the combination of aluminum and oxygen atoms.

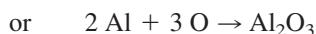
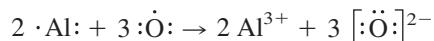
Figure 5.11 Charges on Common Monatomic Ions

I	II											III	IV	V	VI	VII	
H 1+ 1-																	
Li 1+	Be 2+																
Na 1+	Mg 2+																
K 1+	Ca 2+	Sc 3+	Ti 2+ 3+	V 2+ 3+	Cr 2+ 3+	Mn 2+ 3+	Fe 2+ 3+	Co 2+ 3+	Ni 2+ 3+ 4+	Cu 1+ 2+	Zn 2+				Se 2- 1-	Br 1-	
Rb 1+	Sr 2+								Pd 2+ 4+	Ag 1+	Cd 2+			Sn 2+ 4+		I 1-	
Cs 1+	Ba 2+								Pt 2+ 4+	Au 1+ 3+	Hg 2+ *		Pb 2+ 4+				
Fr 1+	Ra 2+																

*Mercury also forms a diatomic ion, Hg₂²⁺.

5.4 ■ Formulas for Ionic Compounds**139****Solution**

The 6 valence electrons of the two aluminum atoms are transferred to three oxygen atoms, yielding two Al^{3+} ions and three O^{2-} ions. The reaction can be written more simply as follows:



Al atom: $1s^2 2s^2 2p^6 3s^2 3p^1$
 Al $^{3+}$ ion: $1s^2 2s^2 2p^6$

Practice Problem 5.6 Use electron dot diagrams to picture the combination of magnesium and nitrogen atoms.

In compounds, the metals of periodic groups IA, IIA, and IIIB (1, 2, and 3), as well as zinc, cadmium, aluminum, and silver, always form ions with positive charges equal to the element's classical periodic group number.

The charge on every monatomic anion (except H $^-$) is equal to the classical group number of the element minus 8. The number of added electrons is the absolute value of that difference.

We can predict the charges on the ions of some elements but not others. In their compounds, the metals of periodic groups IA, IIA, and IIIB (1, 2, and 3), as well as zinc, cadmium, aluminum, and silver, always form ions with positive charges equal to the element's classical periodic group number. These elements are indicated with a blue background in Figure 5.11. The charge on every monatomic anion except H $^-$ is equal to the classical group number of the element minus 8. These elements are presented with a red background in Figure 5.11. The number of added electrons is the absolute value of that difference. (Not all nonmetals form monatomic anions, however.) Hydrogen can react with very active metals to form the hydride ion, H $^-$, which has the 2-electron configuration of helium. The maximum positive charge on a monatomic cation is 4 $+$; the maximum negative charge on a monatomic anion is 3 $-$. In addition to the generalities just presented, note that each of the elements of the first transition series except scandium forms an ion with a 2 $+$ charge, and the eight middle ones also form an ion having another charge. (The transition metals form ions having different charges by donating varying numbers—0, 1, or 2—of their inner electrons to nonmetals.)

Because the overall charge on any ionic compound is zero, we can determine the formula of an ionic compound by balancing the charges on the cations and anions. That is,

$$\text{Number of positive charges} = \text{Number of negative charges}$$

The compound of Pb $^{4+}$ and O $^{2-}$ is thus PbO₂ because there are four negative charges on two O $^{2-}$ ions to balance the four positive charges on one Pb $^{4+}$ ion.

We can even write formulas for compounds whose ions are totally unfamiliar to us, as long as we know their charges. For example, the compound of AB $^{2+}$ and XY $^{2-}$ is AB₄XY₃ and that for AB $^{2+}$ and XZ $^{3-}$ is (AB₄)₃(XZ₂)₂.

EXAMPLE 5.7

Determine the formula of the compound of calcium and oxygen.

Solution

Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
O: $1s^2 2s^2 2p^4$

Ca^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6$
 O^{2-} : $1s^2 2s^2 2p^6$

Calcium, in group IIA, has 2 valence electrons, and oxygen, in group VIA, has 6. Each oxygen atom needs 2 additional electrons to form O^{2-} , which has an octet in its valence shell, and each calcium atom can supply these 2 electrons to form Ca^{2+} . Therefore, it takes one calcium atom to supply the electrons for one oxygen atom, and the formula for calcium oxide is CaO . Alternatively, we can say that it takes one dipositive calcium ion to balance the charge on one dinegative oxide ion.

Practice Problem 5.7 Determine the formula of the compound of magnesium and nitrogen.

EXAMPLE 5.8

Determine the formula of (a) the compound containing Cr^{2+} and S^{2-} and (b) the compound containing Cr^{3+} and O^{2-} .

Solution

The relative numbers of cations and anions in a compound depend only on their charges and not on the identities of the ions.

- One Cr^{2+} ion can balance the charge on one S^{2-} ion. Therefore, the ions bond in a 1:1 ratio to form CrS .
- It takes three O^{2-} ions to balance the charge on two Cr^{3+} ions, so the formula is Cr_2O_3 .

Practice Problem 5.8 Determine the formula of (a) the compound containing Cu^{2+} and F^- and (b) the compound containing Cr^{2+} and P^{3-} .

EXAMPLE 5.9

Write the formula for each type of ion in the following compounds:

- (a) RbI (b) BaS (c) Li₂S (d) Al₂O₃

Solution

- (a) Rb^+ I^- (b) Ba^{2+} S^{2-} (c) Li^+ S^{2-} (d) Al^{3+} O^{2-}

The charges on the cations are equal to the numbers of valence electrons originally in the atoms, and the charges on the anions are equal to 8 minus the number of valence electrons. The numbers of valence electrons for these elements are easily determined from their periodic group numbers. The two lithium ions in the compound of part (c) are not bonded to each other because they are both positive and repel each other. They should not be written with a subscript (except in the formula for the compound, Li_2S , in which they are both bonded to the sulfide ion). If we want to show that two lithium ions are present, we must write 2Li^+ .

Practice Problem 5.9 Write formulas for the ions in Mg_3P_2 .

Because all compounds have overall charges of zero, we can deduce the charges on some metals' cations from the total charge on the anions bonded to them. For example, in CuCl and CuCl₂, the charges on the copper ions are 1+ and 2+, respectively. The 1+ charge on the copper ion in CuCl is required to balance the 1– charge on one Cl[–] ion. The 2+ charge on the copper in CuCl₂ is required to balance the 1– charge on each of *two* Cl[–] ions.

EXAMPLE 5.10

What is the charge on each cation in (a) Cu₂O and (b) CuO?

Solution

- (a) The charge on each cation must be 1+ because two cations are required to balance the charge on one O^{2–} ion.
- (b) The charge on the cation must be 2+, to balance the 2– charge on one O^{2–} ion.

Practice Problem 5.10 What is the charge on each cation in (a) AgCl and (b) PbO₂?



Snapshot Review



ChemSkill Builder
3.2, 3.4

- The charge on the formula of a complete compound must be zero, so the total of the positive and of the negative charges must be equal. The smallest integral numbers of cations and anions are used to achieve charge neutrality.
- Most main group cations and all monatomic anions have characteristic charges that are easy to learn, so in their compounds with other ions, the charges on the other ions are easy to deduce.

- A. Write the formula for the compound of La³⁺ and S^{2–}.
- B. Write the formulas of the ions in each of the following compounds:
(a) VCl₂ (b) PbO₂ (c) Ti₂O₃.

5.5 Covalent Bonding

Metal atoms can donate electrons to nonmetal atoms, but nonmetal atoms do not form monatomic positive ions because they would have to donate too many valence electrons to form octets. (Single nonmetal atoms do not donate electrons at all, but some groups of nonmetal atoms can. This will be discussed later in this section.)

Nonmetal atoms can accept electrons from metal atoms if such atoms are present; otherwise, they can attain an octet by **electron sharing**. A **covalent bond** consists of shared electrons. One pair of electrons shared between two atoms constitutes a *single* covalent bond, generally referred to as a **single bond**. An **unshared pair** of valence electrons is called a **lone pair**. Elements or compounds bonded only by covalent bonds form molecules.

The formula unit of a covalently bonded group of atoms is called a molecule.

Consider the hydrogen molecule, H₂. Each atom of hydrogen has one electron and would be more stable with two electrons (the helium configuration). There is no reason why one hydrogen atom would donate its electron and the other accept it. Instead, the two hydrogen atoms can *share* their electrons:

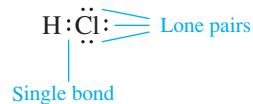


Electrons shared between hydrogen atoms are counted toward the duets of *both* atoms. In the hydrogen molecule, each hydrogen atom has a total of two electrons in its first shell and, thus, a stable configuration. Electrons shared between other nonmetal atoms are counted toward the *octets* of both.

EXAMPLE 5.11

Draw an electron dot diagram for HCl. Label the single bond and the lone pairs.

Solution



Practice Problem 5.11 Draw an electron dot diagram for Cl₂. Label the single bond and the lone pairs.

In electron dot diagrams for uncombined atoms, the four areas around the symbol can hold a maximum of two electrons each. However, be aware that up to three pairs of electrons can sometimes be placed between covalently bonded atoms.

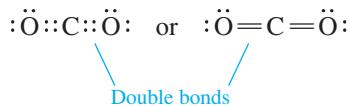
Another representation of molecules is the **structural formula**, in which each electron pair being shared by two atoms is represented by a line or dash. Electrons not being shared may be shown as dots in such a representation. Structural formulas for H₂ and HCl are



Two atoms can share more than one pair of electrons to make an octet for each atom. Consider the nitrogen molecule:



In this case, three electron pairs are shared, and each nitrogen atom has an octet of electrons. There is one lone pair of electrons on each nitrogen atom. Three pairs of electrons shared between the same two atoms constitute a **triple bond**. If two pairs of electrons are shared, a **double bond** results. Consider the carbon dioxide molecule:



The term **multiple bond** refers to either a double or triple bond.

With a few simple rules, recognizing compounds that consist of molecules is fairly easy. All compounds that are gases or liquids at room temperature are molecular. (Solid compounds may be molecular.) Most compounds that do not

5.5 ■ Covalent Bonding**143**

have a metal atom or an ammonium ion (NH_4^+) in them are molecular. When not combined with other elements, most nonmetallic elements form molecules. (The noble gases have monatomic molecules; their atoms are uncombined.)

EXAMPLE 5.12

Which of the following formula units consist of uncombined atoms, which consist of molecules, and which consist of ions?

- (a) O_2 (b) Ne (c) NO_2 (d) NH_4Cl (e) Na_2O

Solution

- (a) O_2 consists of molecules.
- (b) Ne consists of uncombined atoms.
- (c) NO_2 consists of molecules.
- (d) NH_4Cl is ionic, even though it contains no metal atoms.
- (e) Na_2O consists of ions.

Practice Problem 5.12 Which of the following formula units consist of uncombined atoms, which consist of molecules, and which consist of ions?

- (a) H_2 (b) He (c) HCl (d) HgO

Very large molecules, containing billions and billions of atoms, are called **macromolecules**. Diamond, graphite, and silica (sand) are examples (Figure 5.12). Formulas for macromolecules cannot state the number of atoms of each element

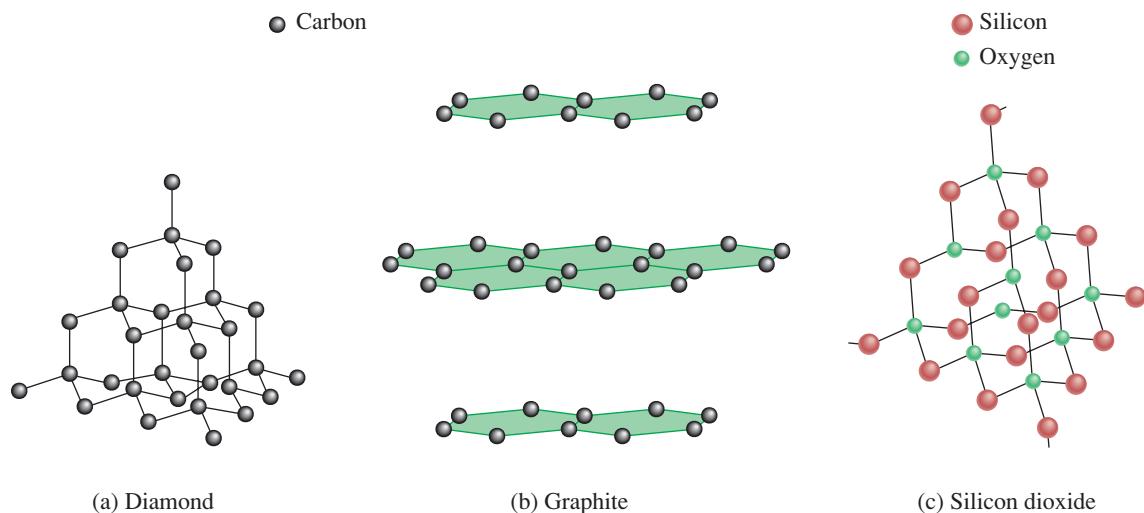


Figure 5.12 Macromolecules of diamond, graphite, and silica

All of the atoms pictured in each case, plus millions more, make up one giant molecule. (a) In diamond, carbon atoms are connected in a three-dimensional structure. (b) In graphite, carbon atoms are connected in sheets or layers. (c) Silica (silicon dioxide) has a structure somewhat like that of diamond, except that it contains silicon and oxygen atoms instead of carbon atoms, and an oxygen atom bridges each pair of silicon atoms.

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in each molecule because there are too many. Therefore, these formulas give only the simplest ratio of atoms of one element to any others present. For example, the formula for both diamond and graphite is C and that for silica is SiO₂.

Systematic Method for Drawing Electron Dot Diagrams

Drawing electron dot diagrams for some compounds or ions can get complicated. If a diagram in which each nonmetal atom except hydrogen has an octet cannot be made by using only single bonds, move pairs of unshared electrons to positions between atoms, forming double or triple bonds. However, for compounds or ions that obey the octet rule, a more systematic approach may be used. We will use PSCl₃, in which the phosphorus atom is the central atom, as an example.

Steps

Step 1: Determine the arrangement of the atoms.

Step 2: Determine the total number of valence electrons *available* from all the atoms in the formula unit.

Step 3: Determine the total number of electrons *required* to get 8 electrons around each nonmetal atom except hydrogen and 2 electrons around each hydrogen atom.

Hydrogen atoms need only 2 electrons in their outermost shells, and most main group metal ions need none.

Step 4: Subtract the number of electrons available from the number required to determine the number of shared electrons. (The shared electrons are counted for each atom; that is, they are counted twice to obtain the total number of electrons needed.)

Step 5: Distribute the shared pairs *between* adjacent atoms.

Step 6: Distribute the rest of the electrons to positions other than between atoms, making sure that the number of electrons required for each atom (step 3) is now present.

Example



$$1 \text{ P } 1 \times 5 = 5 \text{ valence electrons}$$

$$1 \text{ S } 1 \times 6 = 6 \text{ valence electrons}$$

$$3 \text{ Cl } 3 \times 7 = 21 \text{ valence electrons}$$

$$\text{total } 32 \text{ valence electrons}$$

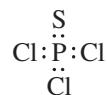
$$1 \text{ P } 8 \text{ electrons}$$

$$1 \text{ S } 8 \text{ electrons}$$

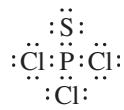
$$3 \text{ Cl } 24 \text{ electrons}$$

$$\text{total } 40 \text{ electrons}$$

$$40 - 32 = 8 \text{ electrons to be shared}$$



Each atom now has 8 electrons:



EXAMPLE 5.13

Draw an electron dot diagram for CO_2 , in which the oxygen atoms are both bonded to the carbon atom.

Solution

Atoms	Valence electrons available	Valence electrons required
C	$1 \times 4 = 4$	$1 \times 8 = 8$
2 O	$2 \times 6 = 12$	$2 \times 8 = 16$
Total	$\frac{16}{16}$	$\frac{24}{24}$

The number of electrons to be shared is $24 - 16 = 8$. Put two pairs of electrons between each pair of adjacent atoms:



Adding the other available electrons (8) yields the complete electron dot diagram:



Be sure to check that all the atoms have the proper octets (duets for hydrogen atoms) and that all valence electrons and no other electrons are shown.



Practice Problem 5.13 Draw an electron dot diagram for HN_3 , hydrazoic acid.

EXAMPLE 5.14

Draw an electron dot diagram for formaldehyde, CH_2O , in which the hydrogen and oxygen atoms are all bonded to the carbon atom.

Solution

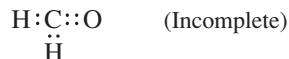
Atoms	Valence electrons available	Valence electrons required
2 H	$2 \times 1 = 2$	$2 \times 2 = 4$
C	$1 \times 4 = 4$	$1 \times 8 = 8$
O	$1 \times 6 = 6$	$1 \times 8 = 8$
Total	$\frac{12}{12}$	$\frac{20}{20}$

There are $20 - 12 = 8$ electrons shared. One double bond is needed for 8 electrons to be shared between the three pairs of atoms. The hydrogen atoms cannot be involved in a double bond because their maximum number of valence electrons is 2. Therefore, the double bond must be between the

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CHAPTER 5 ■ Chemical Bonding

carbon atom and the oxygen atom. The structure showing only the shared electrons is



Then the unshared electrons are added:



There are 8 electrons around the carbon atom and 8 electrons around the oxygen atom, as well as 2 electrons around each hydrogen atom:



Practice Problem 5.14 Draw an electron dot diagram for H_2O_2 , in which each oxygen atom is bonded to one hydrogen atom.

The first problem in drawing an electron dot diagram for a complicated structure is to determine which atoms are bonded to which other atoms. Many common molecules and ions have one atom of one element and several atoms of another. The single atom of the one element is usually the central atom, with all the other atoms bonded to it.

EXAMPLE 5.15

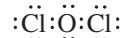
Draw an electron dot diagram for (a) Cl_2O and (b) NH_3 .

Solution

(a) The central atom is the oxygen atom:



The number of shared electrons is $24 - 20 = 4$. The complete diagram is



(b) The central atom is the nitrogen atom:



The number of shared electrons is $14 - 8 = 6$. The complete diagram is



Atoms	Valence electrons available	Valence electrons required
2 Cl	14	16
O	6	8
Total	20	24

Atoms	Valence electrons available	Valence electrons required
N	5	8
3 H	3	6
Total	8	14

Practice Problem 5.15 Draw an electron dot diagram for acetylene, C_2H_2 .

EXAMPLE 5.16

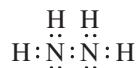
Draw an electron dot diagram for hydrazine, N_2H_4 , which has two hydrogen atoms bonded to each nitrogen.

Solution

The nitrogen atoms must be bonded to each other, because the hydrogen atoms cannot bond to two atoms. The arrangement of atoms is



The number of shared electrons is $24 - 14 = 10$. The complete diagram is



Practice Problem 5.16 Draw an electron dot diagram for NH_2OH .

Atoms	Electrons available	Electrons required
2 N	10	16
4 H	4	8
Total	14	24

Table 5.2 Some Important Polyatomic Anions

Name	Formula
Nitrate ion	NO_3^-
Sulfate ion	SO_4^{2-}
Carbonate ion	CO_3^{2-}
Phosphate ion	PO_4^{3-}
Chlorate ion	ClO_3^-
Bromate ion	BrO_3^-
Iodate ion	IO_3^-
Hydroxide ion	OH^-
Cyanide ion	CN^-
Acetate ion	$\text{C}_2\text{H}_3\text{O}_2^-$
Chromate ion	CrO_4^{2-}
Dichromate ion	$\text{Cr}_2\text{O}_7^{2-}$
Permanganate ion	MnO_4^-

Line formulas for more complicated molecules sometimes give clues as to which atoms are bonded to which others. For example, in compounds containing carbon and hydrogen atoms, perhaps along with atoms of other elements, the atoms bonded to each carbon atom are placed after that atom, as in $\text{CH}_3\text{CH}_2\text{OH}$.

Polyatomic Ions

A great many compounds contain **polyatomic ions** (“many-atom” ions). There are many polyatomic anions but relatively few polyatomic cations. The most important polyatomic cation is the ammonium ion, NH_4^+ (compare with ammonia, NH_3). Some of the most important polyatomic anions are listed in Table 5.2, the first seven of which are also presented in Figure 5.13, along with others.

The atoms *within* a polyatomic ion are bonded together with covalent bonds, but polyatomic ions as a whole are bonded to oppositely charged ions by the attraction of the opposite charges—by ionic bonding. For example, potassium chlorite, KClO_2 , contains potassium ions, K^+ , and chlorite ions, ClO_2^- . The K^+ ions are attracted to the ClO_2^- ions by their opposite charges. The chlorine and oxygen atoms within each ClO_2^- ion are covalently bonded. The electron dot diagram for potassium chlorite is simply a combination of that for the potassium ion and that for the chlorite ion. The representation can be determined by the systematic process described previously. Note that the potassium ion is bonded ionically and that it shares *no* electrons with other atoms. For that reason, no electrons are allotted for its valence shell.

The number of electrons to be shared is $24 - 20 = 4$. The structure, with only the shared electrons:



Atoms	Valence electrons available	Valence electrons required
K	1	0
Cl	7	8
2 O	12	16
Total	20	24

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CHAPTER 5 ■ Chemical Bonding

IV	V	VI	VII
CO_3^{2-}	NO_3^-		
	NO_2^-		
PO_4^{3-}	SO_4^{2-}	ClO_4^-	
PO_3^{3-}	SO_3^{2-}	ClO_3^-	
		ClO_2^-	
		ClO^-	
AsO_4^{3-}	SeO_4^{2-}	BrO_4^-	
AsO_3^{3-}	SeO_3^{2-}	BrO_3^-	
		BrO_2^-	
		BrO^-	
			IO_4^-
			IO_3^-
			IO_2^-
			IO^-

The rest of the electrons are added:



Be sure to write the charge on each ion because the charge is an integral part of the formula. For example, there is a great difference between ClO_2 and ClO_2^- .

To draw an electron dot diagram for a polyatomic ion alone, we must consider its charge when counting the number of electrons available. One extra electron is present for each negative charge, and 1 fewer electron for each positive charge.

Figure 5.13 Formulas of Some Important Polyatomic Main Group Anions

EXAMPLE 5.17

Draw an electron dot diagram for the chlorite ion, ClO_2^- .

Solution

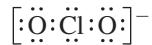
The charge on the ion signifies the presence of an extra valence electron—from some other (unspecified) atom—which must be counted as available:

Atoms	Valence electrons available	Valence electrons required
Cl	7	8
2 O	12	16
Negative charge	1	
Total	20	24

The number of electrons to be shared is $24 - 20 = 4$. The structure, with only the shared electrons:



Adding the other electrons gives



The structure of the chlorite ion is the same as when the ion was in potassium chlorite. In that case, the potassium atom donated its electron to the chlorite ion. In this case, we do not know where the extra electron came from, but it does not matter. The total number of valence electrons is still 20, and the number of electrons to be shared is still 4. The chlorite ion does not exist in isolation, even though we sometimes write it alone.

Practice Problem 5.17 Draw an electron dot diagram for the phosphate ion, PO_4^{3-} .

EXAMPLE 5.18

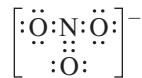
Draw an electron dot diagram for the NO_3^- ion.

Solution

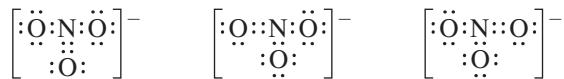
The number of shared electrons is $32 - 24 = 8$. Here is the structure with only the shared electrons shown:



Here is the structure showing all the electrons:



The double bond was arbitrarily placed between the nitrogen atom and the oxygen atom below it. However, there is no difference between that oxygen and the one to the left of the nitrogen atom or the one to its right. We could draw the double bond between nitrogen and either of those atoms instead. All the following structures are equivalent:



In fact, the extra pair of electrons spends some time in each of the three positions, and the structures are said to be **resonance structures** of each other. Note that in each one, all the *atoms* are in the *same positions*; only the electrons have changed positions.

Practice Problem 5.18 Draw all resonance structures for the NO_2^- ion.

Hydrogen atoms very often bond with oxygen atoms but seldom bond with oxygen atoms that are double-bonded to other atoms. Thus, if we have a choice between putting a hydrogen atom on an oxygen atom connected by a single bond to another atom or putting it on one connected by a double bond to another atom, we choose the former.

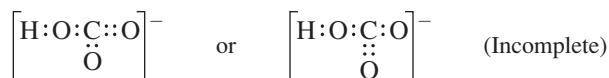
EXAMPLE 5.19

Draw all resonance structures for HCO_3^- , in which the hydrogen atom is bonded to a single-bonded oxygen atom.

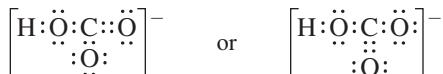
Atoms	Valence electrons available	Valence electrons required
H	1	2
C	4	8
3 O	18	24
Negative charge	1	
Total	24	34

Solution

The number of shared electrons is $34 - 24 = 10$. The structures with the shared electrons are



With all the electrons,



The hydrogen atom can bond equally well to either of the oxygen atoms that are connected to the carbon atom by a single bond, but not to the double-bonded one.

Practice Problem 5.19 Draw an electron dot diagram for HNO_2 .

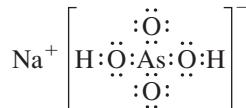
With a little experience, we will all recognize the familiar ions in formulas, which will allow us to deduce the formula of the other ion in the compound, even if it is unfamiliar to us.

EXAMPLE 5.20

Write formulas and electron dot diagrams for the ions in NaH_2AsO_4 .

Solution

We recognize that sodium always exists in its compounds as the Na^+ ion. Thus, the other ion must contain all the other atoms and must have a single negative charge. The formulas are Na^+ and H_2AsO_4^- . The electron dot diagrams are



Practice Problem 5.20 Write formulas for the ions in $\text{K}_4\text{P}_2\text{O}_7$.

Nonoctet Structures

Not all atoms in molecules or polyatomic ions obey the octet rule; those that do not are said to have **nonoctet structures**. For example, in its compounds boron, which is in the second period of the periodic table, is apt to have fewer

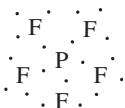
■ Prefixes/Suffixes

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than 8 electrons in the valence shell of its atoms. Thus, the boron atom in BF_3 is represented as having only 6 electrons in its valence shell:



If the central element in a molecule or polyatomic ion is in the third period or higher and does not obey the octet rule, it is apt to expand its valence shell beyond 8 electrons. The phosphorus atom in PF_5 has 10 electrons around it:



Noctet structures are discussed more extensively in more advanced texts.



Snapshot Review



ChemSkill Builder 3.2

- Polyatomic ions are discussed in the section on covalent bonding because the bonding *within* these ions is covalent.
 - Electron dot diagrams for covalently bonded atoms may have four or fewer positions for electrons around an atom, with up to 6 electrons in any one position.
 - For species that follow the octet rule, the number of electrons around nonmetal atoms other than hydrogen is 8.

A. Draw electron dot diagrams for (a) CH_3CHO and (b) C_3H_6 .
 B. Draw electron dot diagrams for (a) NCO^- and (b) CH_2O .

Key Terms

Key terms are defined in the Glossary.

- allotrope (5.1)
anhydrous (5.1)
anion (5.2)
anode (5.2)
binary compound (5.1)
cathode (5.2)
cation (5.2)
centered dot (5.1)
covalent bond (5.5)
diatomic molecule (5.1)
double bond (5.5)
duet (5.2)
electrode (5.2)
electronegative (5.1)
electronegativity (5.1)

- electron sharing (5.5)
electropositive (5.1)
elemental (5.1)
formula (5.1)
formula unit (5.1)
hydrate (5.1)
ion (5.2)
ionic bond (5.2)
Lewis electron dot diagram (5.3)
lone pair (5.5)
macromolecule (5.5)
molecule (5.1)
monatomic ion (5.2)
multiple bond (5.5)
noble gas configuration (5.2)

- nonoctet structure (5.5)
 - octet (5.2)
 - octet rule (5.2)
 - outermost shell (5.2)
 - ozone (5.1)
 - Polyatomic ion (5.5)
 - resonance structure (5.5)
 - single bond (5.5)
 - sodium chloride structure (5.2)
 - structural formula (5.5)
 - subscript (5.1)
 - triple bond (5.5)
 - unshared pair (5.5)
 - valence electron (5.2)
 - valence shell (5.2)

Prefixes/Suffixes

-ide (5.2)

Summary

Chemical formulas identify compounds, ions, or molecules. The formula implies that the atoms are held together by some kind(s) of chemical bond(s). When they are not combined with other elements, hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, and iodine exist as diatomic molecules (Figure 5.2).

In formulas for binary compounds, the more electropositive element is written first. A formula unit represents the collection of atoms in the formula. Subscripts in a formula indicate the numbers of atoms of the elements in each formula unit. For example, the formula unit H_2O has two hydrogen atoms and one oxygen atom. Formula units of uncombined elements, such as Ne, are atoms. Formula units of covalently bonded atoms are called molecules. Formula units of ionic compounds do not have any special name. In formulas, atoms bonded in special groups may be enclosed in parentheses. A subscript following the closing parenthesis multiplies everything within the parentheses. For example, a formula unit of $\text{Ba}(\text{ClO}_4)_2$ contains one barium atom, two chlorine atoms, and eight oxygen atoms. Formulas for hydrates have a centered dot preceding a number and the formula for water, such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The number multiplies everything following it to the end of the formula (Section 5.1).

Atoms of main group elements tend to accept, donate, or share electrons to achieve the electronic structure of the nearest noble gas. Metal atoms tend to donate electrons and thereby become positive ions. When combining with metals, nonmetal atoms tend to accept electrons and become negative ions. The number of electrons donated or accepted by each atom depends to a great extent on the periodic group number; each atom tends to attain a noble gas configuration. The attraction of oppositely charged ions is called an ionic bond. Transition and inner transition metal atoms donate their valence electrons first but ordinarily do not achieve noble gas configurations. Most of them can also lose electrons from an inner shell and thus can form cations with different charges (Section 5.2).

Electron dot diagrams can be drawn for atoms, ions, and molecules, using a dot to represent each valence electron. These diagrams are most useful for main group elements. The diagrams help in visualizing simple reactions and structures of polyatomic ions and molecules (Section 5.3).

Formulas for ionic compounds may be deduced from the charges on the ions, since all compounds have zero net charge. Given the constituent elements, we can predict the formula for binary compounds of most main group metals. We cannot do so for most transition metals because of their ability to form ions of different charges. (Given the specific ions, we can write a formula for any ionic compound.) Conversely, given the formula of an ionic compound, we can deduce the charges on its ions. Writing correct formulas for compounds and identifying the ions in compounds from their formulas are two absolutely essential skills (Section 5.4).

Nonmetal atoms can share electrons with other nonmetal atoms, forming covalent bonds. In electron dot diagrams, the shared electrons are counted as being in the outermost shell of *each* of the bonded atoms. A single bond consists of one shared electron pair; a double bond consists of two shared electron pairs; a triple bond consists of three shared electron pairs. Macromolecules result from covalent bonding of millions of atoms or more into giant molecules.

Drawing electron dot diagrams for structures containing only atoms that obey the octet rule can be eased by subtracting the number of valence electrons *available* from the number *required* to get an octet (or duet) around each nonmetal atom. The difference is the number of electrons to be shared in the covalent bonds. For an ion, we must subtract 1 available electron for each positive charge on the ion or add 1 available electron for each negative charge. Main group metal ions in general require no outermost electrons; but each hydrogen atom requires 2; and each other nonmetal atom requires 8. Atoms in some compounds do not follow the octet rule (Section 5.5).

Items for Special Attention

- Because formulas are used to represent unbonded atoms, covalently bonded molecules (Section 5.5), and ionically bonded compounds (Section 5.2), a formula unit can represent an atom, a molecule, or the simplest unit of an ionic compound (Figure 5.8). For example, He represents an uncombined atom; F_2 represents a molecule of an element; CO_2 represents a molecule of a compound;

and NaCl represents one pair of ions in an ionic compound.

- The seven elements that occur in the form of diatomic molecules (Figure 5.2) form such molecules *only when these elements are uncombined with other elements*. When combined in compounds, they may have one, two, three,

■ Self-Tutorial Problems**153**

- four, or more atoms per formula unit, depending on the compound.
- Learning and using a generalization is easier than memorizing individual facts. For example, once we learn that *in their compounds*, the metals of periodic groups IA, IIA, and IIIB (1, 2, and 3) form ions with charges equal to their group numbers ($1+$, $2+$, and $3+$, respectively), we do not have to learn the charges on 16 separate metal ions.
 - An ion is a charged species. A single ion is just *part* of a compound. The charges on ions are integral parts of the formulas of the ions. We must always include the charges when we write formulas for ions alone. For example, it makes quite a difference whether we are referring to SO_3 (sulfur trioxide) or SO_3^{2-} (sulfite ion). Writing the symbol or formula for a single ion does not imply that it can exist alone, but only that the ion of opposite charge is not of immediate interest. We may write the charges on both ions in an ionic compound while we are determining the compound's formula, but we never write the charge on one ion without writing the charge on the other. To finish the formula, we rewrite it without the charges. For example, we write NaCl for Na^+Cl^- .
 - All compounds, whether ionic or covalent, are electrically neutral. The total positive charge on the cations of an ionic compound must therefore be balanced by the total negative charge on the anions.
 - Except for H^- , monatomic anions have charges equal to their classical group number minus 8. (Not all nonmetals form monatomic ions.) Polyatomic anions containing oxygen and one other element are not quite that easy to predict charges for, but generally, the charge is *odd* if the periodic group of the central element is odd and *even* if the periodic group of the central element is even.
 - All the ionic compounds considered in this book are composed of only one type of cation and one type of anion.
 - Electron dot diagrams are most useful for main group elements, and the systematic procedure for drawing electron dot diagrams works only for species in which all atoms obey the octet rule.
 - Nonmetal atoms accept electrons from metal atoms if the metal atoms are available, or else they share electrons; they never donate electrons to form monatomic cations. The largest charge on any monatomic cation is $4+$, and on any monatomic anion, it is $3-$.
 - The terms *single bond*, *double bond*, and *triple bond* refer to covalent bonds only.
 - Polyatomic ions are held together by covalent bonds and are attracted to oppositely charged ions by ionic bonds.
 - After a little experience, we will recognize the monatomic and polyatomic ions introduced in this chapter. For example, every time the symbol for an alkali metal or an alkaline earth metal appears *in a compound*, it represents the ion with a charge equal to $1+$ or $2+$, respectively.
 - Both *chloride ion* and *chloride* can be used to refer to the Cl^- ion. To refer to Na^+ , however, we must always include the word *ion* because *sodium* can refer to the element, the atom, or the ion.
 - The alkali metals, the alkaline earth metals, the group IIIB metals, aluminum, zinc, cadmium, and silver have ions with charges equal to their classical group numbers, but *only in their compounds!* When the elements are uncombined, they do not form ions, and the charge on each atom is zero.

Answers to Snapshot Reviews

- 5.1 A. Nine hydrogen atoms per phosphorus atom
 B. Chlorine is more electronegative; that is why it is written after selenium.
 C. O_2
- 5.2 A. (a) Two valence and two outermost electrons (the same electrons) and (b) zero valence electrons (fourth shell) and eight outermost electrons (third shell)
 B. (a) Equal, (b) equal, (c) one more electron than proton
- 5.3 A. $:\ddot{\text{P}}:$

- 5.4 A. La_2S_3
 B. (a) V^{2+} and Cl^-
 (b) Pb^{4+} and O^{2-}
 (c) Ti^{3+} and O^{2-}
- 5.5 A. (a) $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C} & \text{C}-\text{O} \\ | & | \\ \text{H} & \text{H} \end{array}$
 (b) $\begin{array}{c} \text{H} & \text{H} & \text{H} \\ | & | & | \\ \text{H}-\text{C} & \text{C}-\text{C} & \text{C} \\ | & | & | \\ \text{H} & \text{H} & \text{H} \end{array}$
- B. (a) $[\text{N}(\text{H})_3]^+$
 (b) $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C} & \text{O} \\ | & || \\ \text{H} & \text{O} \end{array}$

Self-Tutorial Problems

- 5.1 (a) Distinguish between *valence shell* and *outermost shell*.
 (b) Distinguish between *diatomic* and *binary*.
- 5.2 Rules for writing diatomic molecules and for deducing the charges on alkali metal ions were introduced in this chapter. Which of these refers only to uncombined elements and which refers only to elements in compounds?
- 5.3 Explain why hydrogen cannot form
 (a) an H^{2+} ion
 (b) an H^{2-} ion
- 5.4 Which of the following have ionic bonds, and which have covalent bonds?
 (a) Cl_2 (b) MgCl_2 (c) SCl_2

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- 5.5 (a) What is the difference between group IA *metals* and group IA *elements*?
(b) Which of the following statements is correct?
Group IA metals form ions with a 1+ charge only.
Group IA elements form ions with a 1+ charge only.
(c) Does the same problem exist for group IIA?
- 5.6 What is the difference in bonding between CoCl_2 and COCl_2 ?
- 5.7 (a) Write the formula of the compound of Zn^{2+} and Br^- .
(b) Identify the ions present in ZnF_2 .
(c) Write the formula of the compound of Sn^{2+} and O^{2-} .
(d) Identify the ions in FeO .
- 5.8 How many electrons are “available” to draw the electron dot diagram of N^{3-} ? Where do they come from?
- 5.9 What is the charge on zinc in each of the following?
(a) ZnO (b) $\text{Zn}_3(\text{PO}_4)_2$ (c) Zn
(d) ZnCl_2 (e) ZnCr_2O_7
- 5.10 (a) What is the charge on a calcium atom?
(b) What is the charge on a calcium ion?
(c) What is the charge on a calcium nucleus?
- 5.11 (a) Which metals form ions of only one charge?
(b) Which metals form ions of 1+ charge?
- 5.12 Write the formulas for ammonia and for the ammonium ion.
- 5.13 Write the formula of the compound of
(a) UO_2^{2+} and AsO_4^{3-}
(b) $(\text{MO}_y)^{2+}$ and $(\text{XO}_z)^{3-}$, where M and X are some metal and nonmetal and y and z are variables
(c) $(\text{AX}_y)^{2+}$ and $(\text{BZ}_z)^{3-}$
(d) Does it matter to the subscripts after the parentheses what symbols are in the parentheses?

CHAPTER 5 ■ Chemical Bonding

- 5.14 (a) Is the electron dot diagram of H^- like that of any noble gas?
(b) Is that of H^+ ?
- 5.15 What is the difference between ClO_2 and ClO_2^- ?
- 5.16 Determine the formula of each of the following compounds:
(a) The compound of cadmium and sulfur
(b) The compound of Cd^{2+} and S^{2-}
(c) The product of the reaction of cadmium and sulfur
(d) Cadmium sulfide
- 5.17 In which classical periodic groups are the atoms’ valence electrons equal in number to the group number?
- 5.18 Draw electron dot diagrams for (a) LiH and (b) CaH_2 .
- 5.19 (a) Write the formula of the compound of Ag^+ and O^{2-} .
(b) Identify the ions present in Ag_2S .
- 5.20 (a) How many valence electrons, if any, are in a magnesium ion?
(b) How many electrons, if any, should a magnesium atom share in its compounds?
- 5.21 Why was the formula in Practice Problem 5.1(b) not written NH_6PO_4 ?
- 5.22 Draw an electron dot diagram for each of the following. Because the species all have the same number of electrons, explain why the diagrams are not all the same.
(a) H^- (b) He (c) Li^+ (d) Be^{2+}
- 5.23 What is the charge on (a) the sodium ion, (b) the zinc ion, (c) the oxide ion, and (d) the bromide ion?
- 5.24 What is a valid generalization about the charges on monatomic anions? What is a valid generalization about the charges on polyatomic anions containing oxygen and another element?
- 5.25 Draw an electron dot diagram for each of the following:
(a) K (b) K^+ (c) N (d) N^{3-}
- 5.26 Identify the type of bonding in each of the following:
(a) BrCl (b) Br_2 (c) NaBr

Problems**5.1 Chemical Formulas**

- 5.27 What is the difference between (a) 2 N and N_2 ? (b) N_2O_4 and 2 NO_2 ?
5.28 What is implied about bonding in the mercury(I) ion, Hg_2^{2+} ?
5.29 How many atoms of each element are present in one formula unit of each of the following?
(a) $(\text{NH}_4)_3\text{PO}_4$ (b) Li_3N (c) $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$

- 5.30 How many atoms of each element are present in one formula unit of each of the following?
(a) $\text{UO}_2(\text{ClO}_4)_2$ (b) CaCr_2O_7 (c) $(\text{NH}_4)_2\text{CrO}_4$
(d) $\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$
- 5.31 What information (from Section 5.1) is conveyed by the formula $\text{Zn}_3(\text{PO}_4)_2$?

■ Problems

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5.2 Ionic Bonding

5.32 Identify the ions in each of the following compounds:

- (a) SnO_2 (b) CrPO_4 (c) CrSO_4
 (d) NaHCO_3 (e) CaHPO_4

5.33 What difference, if any, is there between $\text{Zn}^{2+}\text{O}^{2-}$ and ZnO ?

5.34 Identify the ions in each of the following compounds:

- (a) UO_2Cl_2 (b) K_3AsO_4 (c) NH_4HCO_3
 (d) $\text{Co}(\text{NO}_3)_2$

5.35 (a) Which metals form ions with $1+$ charge? (b) Which metals form ions with $1+$ charge only?

5.36 Complete the following table:

Symbol	Atomic Number	No. of Protons	No. of Electrons	Net Charge
(a) Cl^-	—	—	—	—
(b) —	16	—	18	—
(c) —	—	19	18	—
(d) —	26	—	—	3^+
(e) —	—	78	—	2^+

5.37 Complete the following table:

Symbol	Atomic Number	No. of Protons	No. of Electrons	Net Charge
(a) Zn^{2+}	—	—	—	—
(b) —	13	—	—	3^+
(c) —	—	—	10	2^-
(d) —	—	34	—	2^-
(e) —	—	39	36	—

5.38 (optional) Write a detailed electronic configuration for each of the following ions:

- (a) Na^+ (b) Al^{3+} (c) Zn^{2+}

5.39 (optional) Write a detailed electronic configuration for each of the following ions:

- (a) N^{3-} (b) S^{2-} (c) Cl^-

5.40 (optional) Write a detailed electronic configuration for each of the following ions:

- (a) Co^{2+} (b) Cr^{3+} (c) Cu^{2+}

5.3 Lewis Electron Dot Diagrams

5.41 Draw an electron dot diagram for each of the following ions:

- (a) O^{2-} (b) Cl^- (c) N^{3-}

5.42 Draw an electron dot diagram for each of the following ions:

- (a) Na^+ (b) Ca^{2+} (c) Al^{3+} (d) Sn^{2+}

5.43 Draw electron dot diagrams for atoms of the following elements and the ions they produce when they combine:

- (a) Al and S (b) Ca and Br (c) Mg and N

5.44 Draw electron dot diagrams for atoms of the following elements and the ions they produce when they combine:

- (a) Li and F (b) Be and H (c) Al and H

5.4 Formulas for Ionic Compounds

5.45 Write the formula for the ion formed by each of the following metals in all of its compounds:

- (a) Lithium (b) Calcium (c) Zinc
 (d) Aluminum (e) Scandium

5.46 Chromium forms ions of 2^+ and 3^+ charges. Write formulas for (a) two chlorides of chromium and (b) two oxides of chromium.

5.47 Write the formula for the compound formed between each of the following pairs of ions:

- (a) Al^{3+} and S^{2-}
 (b) Ag^+ and O^{2-}
 (c) N^{3-} and Mg^{2+}

5.48 Complete the following table by writing the formula of the compound formed by the cation on the left and the anion at the top:

	O^{2-}	Br^-	N^{3-}
K^+	—	—	—
Ca^{2+}	—	—	—
Al^{3+}	—	—	—

5.49 Complete the following table by writing the formula of the compound formed by the cation at the top and the anion on the left.

	Zn^{2+}	Cr^{3+}	NH_4^+
ClO_3^-	—	—	—
SO_4^{2-}	—	—	—
PO_4^{3-}	—	—	—
$\text{Cr}_2\text{O}_7^{2-}$	—	—	—

5.50 Write the formula for the compound formed between each of the following pairs:

- (a) Na and H (b) Mg and H

5.51 For each of the following compounds, identify the individual ions, and indicate how many of each are present per formula unit:

- (a) $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ (b) $\text{Al}_2(\text{CO}_3)_3$
 (c) K_2SO_4 (d) NH_4HCO_3

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5.52 Identify the individual ions in each of the following compounds:

- (a) CaBr_2 (b) MgSO_4 (c) $\text{Mg}_3(\text{PO}_4)_2$
 (d) $\text{Al}_2(\text{SO}_4)_3$ (e) K_2O_2 (f) $\text{Sr}(\text{CN})_2$
 (g) $\text{Pb}(\text{ClO}_3)_2$

5.53 Write the formula for the compound formed by each of the following pairs of elements:

- (a) Mg and N (b) Mg and P (c) Ca and S
 (d) Al and N (e) Na and I (f) Al and P
 (g) Li and S (h) Mg and Br (i) Zn and Cl

5.54 Write the formula for the compound formed by each of the following pairs of elements:

- (a) Zinc and sulfur (b) Lithium and nitrogen
 (c) Barium and chlorine (d) Silver and iodine
 (e) Oxygen and scandium (f) Fluorine and calcium

5.55 Complete the following table by writing the formula of the compound formed by the metal at the left and the nonmetal at the top:

	Nitrogen	Sulfur	Bromine
Aluminum	_____	_____	_____
Cadmium	_____	_____	_____
Silver	_____	_____	_____

5.56 Identify the individual ions in each of the following compounds:

- (a) LiH (b) $\text{Zn}(\text{ClO}_3)_2$ (c) Rb_2O_2
 (d) NaClO_3 (e) BaCl_2 (f) $\text{Hg}_2(\text{NO}_3)_2$
 (g) $(\text{NH}_4)_2\text{HPO}_4$

5.57 How many valence electrons does a Pb^{2+} ion have?

5.58 What individual ions are present in (a) Cu_2O and (b) CuO ?

5.59 Identify the anion and *both* cations in each of the following pairs of compounds:

- (a) PtO and PtO_2
 (b) Fe_2O_3 and FeO
 (c) CrSO_4 and $\text{Cr}_2(\text{SO}_4)_3$

5.60 Complete the following table by writing the formula of the compound formed by each cation on the left with each anion at the top:

	NO_3^-	SO_4^{2-}	$\text{Cr}_2\text{O}_7^{2-}$	PO_4^{3-}
Na^+	_____	_____	_____	_____
Mg^{2+}	_____	_____	_____	_____
Zn^{2+}	_____	_____	_____	_____
Fe^{3+}	_____	_____	_____	_____

CHAPTER 5 ■ Chemical Bonding

5.61 Complete the following table by writing the formula of the compound formed by each cation on the left with each anion at the top:

	ClO_2^-	SO_4^{2-}	PO_4^{3-}	$\text{P}_2\text{O}_7^{4-}$
NH_4^+	_____	_____	_____	_____
Fe^{2+}	_____	_____	_____	_____
Al^{3+}	_____	_____	_____	_____

5.62 Identify the cation and the anion in each of the following compounds:

- (a) $\text{Lu}(\text{CN})_3$ (b) $\text{K}_2\text{Cr}_2\text{O}_7$ (c) $(\text{NH}_4)_2\text{SO}_4$
 (d) VO_2NO_3 (e) VOSO_4 (f) $\text{Ba}(\text{MnO}_4)_2$
 (g) KBrO_2 (h) NH_4HSO_3 (i) $\text{K}_2\text{S}_2\text{O}_8$

5.63 Write the formula for the compound of each of the following pairs of ions:

- (a) PO_4^{3-} and Fe^{3+}
 (b) SO_3^{2-} and NH_4^+
 (c) CO_3^{2-} and Ag^+

5.64 Write the formula of each ion in each of the following compounds:

- (a) $(\text{CH}_3\text{NH}_3)_2\text{SO}_4$ (b) VO_2ClO_4
 (c) $\text{K}_4\text{P}_2\text{O}_7$ (d) $\text{UO}_2(\text{ClO}_3)_2$
 (e) $\text{Ce}(\text{SO}_4)_2$ (f) MgCrO_4
 (g) $\text{Ba}(\text{OCN})_2$ (h) $\text{Na}_2\text{S}_2\text{O}_3$

5.65 For each of the following compounds, identify the individual ions, and indicate how many of each are present per formula unit:

- (a) AlCl_3 (b) Al_2O_3 (c) $\text{Mg}(\text{HCO}_3)_2$
 (d) $\text{Sr}_3(\text{PO}_4)_2$ (e) $(\text{NH}_4)_2\text{SeO}_4$ (f) $(\text{NH}_4)_2\text{SO}_4$
 (g) PbO_2

5.66 Identify the formulas of the ions in each of the following:

- (a) $\text{Sn}_3(\text{PO}_4)_4$ (b) UO_2SO_4

5.67 Write formulas for the ions in each of the following compounds:

- (a) KSCN (b) $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ (c) ZnSO_4
 (d) $(\text{NH}_4)_2\text{CrO}_4$ (e) NH_4NCS (f) KMnO_4
 (g) $\text{Co}(\text{OH})_2$ (h) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

5.5 Covalent Bonding

5.68 Explain why a hydrogen atom cannot be bonded with a double bond or two single bonds.

5.69 Which of the following involve ionic bonding only, which involve covalent bonding only, and which involve both?

- (a) P_2O_5 (b) BaO (c) N_2H_4
 (d) CdCO_3 (e) H_2O (f) NH_4NO_3

■ General Problems

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- 5.70 What similarities and differences are there between a molecule and a polyatomic ion?
- 5.71 Draw an electron dot diagram for each of the following:
 (a) SO_3^{2-} (b) N_3^- (c) CaO
- 5.72 Draw an electron dot diagram for each of the following:
 (a) NH_4^+ (b) OCN^- (c) SO_4^{2-}
 (d) N_2 (e) ONCl (nitrogen is the central atom)
 (f) CO
- 5.73 Write an electron dot diagram for each of the following ions:
 (a) HCO_3^- (b) HPO_4^{2-} (c) IO^-
- 5.74 What familiar ion is in each of the following compounds? Write the formula for the other ion present also.
 (a) $\text{Ba}(\text{BrO}_3)_2$ (b) $(\text{NH}_4)_2\text{SO}_4$ (c) $\text{K}_2\text{C}_2\text{O}_4$
- 5.75 What is the difference between SO_3 and SO_3^{2-} ? Draw an electron dot diagram for each.
- 5.76 Draw an electron dot diagram for each of the following:
 (a) Ethylene, C_2H_4
 (b) Hydrogen peroxide, H_2O_2
 (c) Methyl alcohol, CH_3OH
- 5.77 Draw an electron dot diagram for each of the following compounds. Indicate any double or triple bonds.
- 5.78 Draw structural formulas for the compounds in the prior problem.
- 5.79 Draw resonance structures for each of the following:
 (a) SO_3 (b) CO_3^{2-} (c) O_3
- 5.80 Draw an electron dot diagram for each of the following compounds:
 (a) CH_2Br_2 (b) CH_5N
 (c) CH_4O (d) HCN
- 5.81 Draw structural formulas for the compounds in the prior problem.
- 5.82 Draw a structural formula for each of the following:
 (a) CH_2O (b) CCl_4
 (c) NO_2Cl (nitrogen is the central atom)
- 5.83 Draw an electron dot diagram for each of the following compounds. In each of the last four compounds, the hydrogen atom is bonded to an oxygen atom.
 (a) HCl (b) HClO (c) HClO_2
 (d) HClO_3 (e) HClO_4

General Problems

- 5.84 Briefly define each of the following terms:
 (a) Ion (b) Anion (c) Octet
 (d) Lone pair (e) Ozone
 (f) Monatomic ion (g) Noble gas configuration
 (h) Polyatomic ion (i) Triple bond
- 5.85 Draw an electron dot diagram for SCN^- , in which the carbon atom is the central atom.
- 5.86 (a) How many total valence electrons are in an ammonium ion?
 (b) How many electrons, if any, should that ion share with other ions in its compounds?
- 5.87 Draw electron dot diagrams for (a) CoCl_2 and (b) COCl_2 .
- 5.88 Draw an electron dot diagram for the ammonium ion, NH_4^+ . Try to draw an electron dot diagram for the “ammonium molecule,” NH_4 , which does not exist. What do you find?
- 5.89 Draw an electron dot diagram for (a) O_2^{2-} , the peroxide ion, and (b) N_3^- , the azide ion.
- 5.90 Draw an electron dot diagram for each of the following:
 (a) NaSCN (b) CH_3OH (c) $\text{CH}_3\text{CH}_2\text{NH}_2$
- 5.91 Write the formula for the compound composed of each of the following pairs of ions:
 (a) Ca^{2+} and HCO_3^-
 (b) Mn^{2+} and ClO_3^-
 (c) NH_4^+ and AsO_4^{3-}
 (d) Ag^+ and SO_3^{2-}
- 5.92 (optional) State the octet rule in terms of detailed electronic configurations.
- 5.93 Carbon does not have lone pairs of electrons in the great majority of its compounds. (Exceptions are C_2^{2-} , CN^- , and CO .) Draw electron dot diagrams for each of two different compounds, having the non-hydrogen atoms connected in different ways, each having the formula (a) $\text{C}_2\text{H}_6\text{O}$, (b) $\text{C}_2\text{H}_7\text{N}$.
- 5.94 Draw electron dot diagrams for C_2^{2-} , CN^- , and CO . Comment on their similarity.
- 5.95 (optional) Write detailed electronic configurations for (a) N^{3-} , (b) Mg^{2+} , and (c) O^{2-} .
- 5.96 (optional) Write detailed electronic configurations for (a) Cr^{2+} , (b) Fe^{3+} , and (c) Ni^{2+} .

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- 5.97** Draw an electron dot diagram for each of the following pairs of elements and their compounds:

- (a) Calcium and bromine
(b) Magnesium and nitrogen

Contrast this problem with Problem 5.43, parts (b) and (c).

- 5.98** A certain ionic compound contains eight oxygen atoms, one nickel atom, and two chlorine atoms per formula unit. Identify the ions that make up the compound.

- 5.99** Draw a structural formula for each of the following:

- (a) H_2SO_3 (b) Na_2SO_3
(c) SO_3^{2-} (d) SO_3

- 5.100** Which of the following have any ionic bonds?

C_2H_6 $\text{Mg}(\text{ClO})_2$ $(\text{NH}_4)_3\text{PO}_4$ Pure HCl NH_3

- 5.101** Complete the following table:

Symbol	Atomic Number	No. of Protons	No. of Electrons	Net Charge
K	_____	_____	_____	_____
_____	8	_____	_____	2-
_____	_____	15	18	_____
N^{3-}	_____	_____	_____	_____
_____	20	_____	18	_____
_____	_____	_____	18	1-

- 5.102** Write formulas for the two new compounds formed if each of the following pairs of compounds traded anions:

- (a) $\text{Pb}(\text{ClO}_3)_2$ and K_2S
(b) CuCl_2 and $\text{AgC}_2\text{H}_3\text{O}_2$
(c) KCl and AgNO_3
(d) $\text{Pb}(\text{ClO}_3)_2$ and $\text{Al}_2(\text{SO}_4)_3$

- 5.103** Draw a structural formula for (a) C_2F_2 and (b) CF_4 .

- 5.104** Draw a structural formula for cyclohexane, C_6H_{12} , in which the six carbon atoms are bonded in a ring and each has two hydrogen atoms bonded to it.

- 5.105** Relatively speaking, how many atoms are covalently bonded in a diamond crystal?

- 5.106** What is the charge on the only monatomic cation of bismuth?

- 5.107** Write the formulas for the ions represented in each of the following:

- (a) $(\text{VO})_3(\text{PO}_4)_2$ (b) $\text{NH}_4\text{H}_2\text{PO}_4$
(c) $\text{Na}_{12}\text{Si}_6\text{O}_{18}$

- 5.108** Identify the cation in each of the following compounds:

- (a) CuBr (b) FePO_4 (c) FeSO_4

- 5.109** Which one of the following is ionic? NiCl_2 NiCl_3

CHAPTER 5 ■ Chemical Bonding

- 5.110** Complete the following table:

Symbol	Atomic Number	No. of Protons	No. of Electrons	Net Charge
Zn^{2+}	_____	_____	_____	_____
Cl^-	_____	_____	_____	_____
_____	_____	19	18	_____
_____	_____	_____	18	2+
_____	_____	_____	36	2-
_____	_____	81	_____	3+

- 5.111** In which of the following are there any covalent bonds?

NaHCO_3 MgO PCl_5 C_2H_6

- 5.112** (optional) We deduce the electronic configuration of copper from the periodic table, the $n + \ell$ rule, or other rules or memory devices to be

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

The actual configuration is

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Starting with *each* of these configurations, deduce the electronic configuration of Cu^{2+} , and compare the results.

- 5.113** Write formulas for *both* kinds of ions in each of the following compounds:

- (a) Mg_3N_2 (b) K_3PO_4 (c) KClO_4

- 5.114** (optional) (a) Write the outer electronic configuration of lead.

(b) On the basis of its configuration, explain why lead forms both a 2+ ion and a 4+ ion.

- 5.115** (a) How many oxygen atoms are covalently bonded to each silicon atom in SiO_2 (Figure 5.12)?

(b) How many silicon atoms are bonded to each oxygen? (*Hint:* Look at the top silicon atom and the oxygen atoms attached below it.)

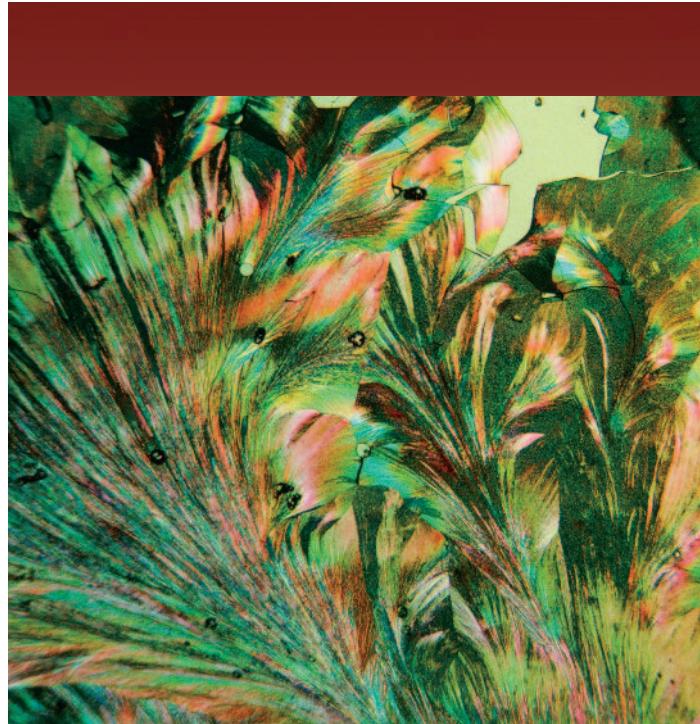
- 5.116** Consult Figure 5.12 to determine how many carbon atoms are bonded to a given carbon atom in (a) diamond and (b) graphite. (*Hint:* Look in the middle of each figure, not at the edges.)

- 5.117** The formulas that follow represent compounds with ionic bonds only, with X representing one of the main group elements. In each case, state whether X is a metal or non-metal, and determine to which main group X belongs.

- (a) Na_3X (b) XBr (c) X_2O_3
(d) XO (e) XF_4 (f) XCl_3

- 5.118** List two or more ions that have two atoms of the same element covalently bonded together.

- 5.119** How many atoms of each element are in one formula unit of (a) $\text{Ni}(\text{CO})_4$ and (b) $(\text{CH}_3\text{NH}_3)_2\text{SO}_4$?



Microscopic view of an antibiotic

6

Nomenclature

- 6.1 Binary Nonmetal-Nonmetal Compounds
- 6.2 Naming Ionic Compounds
- 6.3 Naming Acids and Acid Salts
- 6.4 Hydrates

Review Clues

- Section 6.1 Sections 1.4, 1.5, 5.1
Section 6.2 Sections 1.4, 3.3, 5.2, 5.4

Objectives

- 6.1 To name and write formulas for binary compounds of nonmetals
- 6.2 To name and write formulas for cations, anions, and ionic compounds
- 6.3 To name and write formulas for acids and acid salts
- 6.4 To name hydrates

So far in this book, we have used names for some simple chemical compounds, but we have not yet considered **nomenclature**—how to name compounds systematically. The great variety of compounds requires a systematic approach to naming them. Unfortunately, three or four different naming systems are used to name different types of compounds. Memorization of a few simple rules will allow naming of a great many compounds, but in addition to learning the rules, we must be sure to learn *when to use each one*. Learning generalities will help us to handle great quantities of information and to respond to specific questions. Even having four different systems for naming compounds is much better than using the trivial names that were first used, such as washing soda for Na_2CO_3 , calomel for Hg_2Cl_2 , lime for CaO , laughing gas for N_2O , Epsom salts for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and so forth. Imagine having to learn for each compound a name that does not even give a clue as to the elements that make it up.

This chapter covers the basic rules for naming many compounds and ions and writing formulas for them. Section 6.1 considers the naming of binary nonmetal-nonmetal compounds. The naming of ionic compounds is addressed in Section 6.2. First, the naming of cations and anions is discussed, leading into the naming of complete compounds. Section 6.3 covers the naming of acids and acid salts. Hydrates are considered briefly in Section 6.4. Tables and figures in the chapter summarize how to name compounds in a systematic way.

6.1 Binary Nonmetal-Nonmetal Compounds

The element farther to the left or farther down in the periodic table is named first.

Except for compounds of hydrogen, the formulas for compounds of two nonmetals are written and named with the element farther to the left or lower in the periodic table given first. If one element is below and to the right of the other in the periodic table, the one to the left is given first, unless that element is oxygen or fluorine.

Binary compounds of hydrogen that are not acids are given special names. Two very important examples are water, H_2O , and **ammonia**, NH_3 (Figure 6.1). (Other much less important hydrogen-containing binary compounds are also known by common names. These include phosphine, PH_3 , and arsine, AsH_3 .) Hydrogen compounds that are acids in aqueous solution are named, and their formulas are written in special ways (see Section 6.3).

EXAMPLE 6.1

Which element is named first in a binary compound of each of the following pairs of elements?

- (a) S and Cl (b) O and S (c) S and I
- (d) O and Cl (e) O and Xe

Solution

The positions of the elements in the periodic table are used to determine the order of naming.

6.1 ■ Binary Nonmetal-Nonmetal Compounds**161****Figure 6.1** Household Ammonia

A solution of (gaseous) ammonia in water.

- (a) Because sulfur lies to the left of chlorine in the periodic table (in the same period), sulfur is named first.
- (b) Because sulfur lies below oxygen in the periodic table (in the same group), sulfur is named first.
- (c) Because sulfur lies to the left of iodine in the periodic table, sulfur is named first (despite being above iodine).
- (d) Even though oxygen lies to the left of chlorine in the periodic table, chlorine is named first. Oxygen is an exception to the rule that a position toward the left is more important than a position lower in the table.
- (e) Even though oxygen lies to the left of xenon in the periodic table, xenon is named first. (Oxygen is always named last except in its compounds with fluorine.)

Practice Problem 6.1 Which element has its symbol written first in a binary compound of each of the following pairs of elements?

- (a) F and Xe (b) O and F (c) O and N

To name a binary compound of two nonmetals,

- Name the first element.
- Use the root of the second element with the ending changed to -ide.
- In addition, add a **prefix** before each name to indicate the number of atoms of each element. The prefixes are given in Table 6.1. However, if there is only one atom of the *first* element, omit the prefix *mono-* for that element. Also, if hydrogen is the first element, omit the prefix for *both* elements.
- When the name of the element starts with an *o* and the prefix ends in *a* or *o*, the *a* or *o* is usually dropped.

EXAMPLE 6.2

Name the compound with formula containing (a) four atoms of chlorine and one atom of silicon, (b) one atom of sulfur and three atoms of oxygen, (c) two atoms of bromine and one atom of sulfur, (d) two atoms of phosphorus and three atoms of sulfur.

Solution

- (a) Silicon tetrachloride (Silicon is written first since it lies to the left of chlorine.)
- (b) Sulfur trioxide (Sulfur is named first since it lies below oxygen.)
- (c) Sulfur dibromide (Sulfur is written first since it lies left of bromine, even though bromine is below it.)
- (d) Diphosphorus trisulfide (The prefix *di-* is attached to the first element since there is more than one atom of that element.)

Practice Problem 6.2 Name the compound with formula containing (a) two atoms of chlorine and three atoms of oxygen, (b) four atoms of sulfur and four atoms of nitrogen, (c) two atoms of phosphorus and five atoms of sulfur, (d) two atoms of fluorine and one atom of sulfur.

Table 6.1 Prefixes Used in Naming Binary Nonmetal-Nonmetal Compounds

Number of Atoms	Prefix*
1	mon(o)-
2	di-
3	tri-
4	tetr(a)-
5	pent(a)-
6	hex(a)-
7	hept(a)-
8	oct(a)-
9	non(a)-
10	dec(a)-

*The last *o* or *a* of the prefix is usually dropped when the element name begins with *o*.

EXAMPLE 6.3

Name each of the following compounds:

- (a) IF (b) NO (c) SO₃ (d) CO₂ (e) As₂O₅
(f) Br₂O₃ (g) PBr₅ (h) P₄O₁₀ (i) H₂S (j) SiCl₄

Solution

- (a) Iodine monofluoride (Iodine is written first because it lies below fluorine in the periodic table. The ending of *fluorine* is changed to *-ide*. The prefix *mono-* is added to *fluoride* to show that only one fluorine atom is present in the molecule, but not to iodine.)
(b) Nitrogen monoxide (Nitrogen is named first because it lies to the left of oxygen. The last *o* of the prefix *mono-* is dropped because the second element's name starts with *o*.)
(c) Sulfur trioxide (d) Carbon dioxide
(e) Diarsenic pentoxide (f) Dibromine trioxide
(g) Phosphorus pentabromide (h) Tetraphosphorus decoxide
(i) Hydrogen sulfide (j) Silicon tetrachloride

Practice Problem 6.3 Name each of the following compounds:

- (a) P₄O₆ (b) B₂O₃ (c) N₂O
(d) ICl₅ (e) IF₇ (f) PCl₃

EXAMPLE 6.4

Write formulas for

- (a) Dinitrogen pentoxide (b) Diboron trioxide
(c) Chlorine dioxide (d) Tetraarsenic hexoxide

Solution

- (a) N₂O₅ (b) B₂O₃ (c) ClO₂ (d) As₄O₆

Practice Problem 6.4 Write formulas for (a) disulfur decafluoride and (b) iodine trioxide.

**Snapshot Review**

ChemSkill Builder 3.2

- Binary compounds of nonmetals are named with a set of classical prefixes, not used for most other compounds.
- If there is only one atom of the first element, no prefix is used.
- If the element is named first in a compound, its symbol is written first in the formula, and vice versa.

- A. Name (a) Cl₂O and (b) SiF₄.
B. Write formulas for (a) iodine pentafluoride and (b) diphosphorus trisulfide.

6.2 Naming Ionic Compounds

In most cases, naming ionic compounds involves simply naming both ions. A huge majority of ionic compounds are made up of one type of cation plus one type of anion. Thus, to name most ionic compounds, we name the cation first and then the anion. The more difficult part of the process is learning to name cations and anions themselves.

The charges on the ions allow us to deduce the formula from the name of a compound, even though the numbers of each type of ion are not stated in the name. Writing formulas for ionic compounds requires deducing how many of each type of ion must be present to have a neutral compound (see Section 5.2).

The number of each type of ion is
not stated explicitly in the name.

Naming Cations

We learned in Chapter 5 that some metals always form monatomic ions having one given charge in all their compounds. In this book, we will call this type of ion the constant type. Other metals form monatomic ions with different charges (see Figure 5.11). We will call this type the variable type. There are also some polyatomic cations, but only three of these are important for this course. Thus, the first step in naming a cation is to decide which of these three types it is: polyatomic, constant type, or variable type. We name them in different ways.

POLYATOMIC CATIONS

Only three polyatomic cations are important in this course. The **ammonium ion** (NH_4^+) is very important and the mercury(I) ion (Hg_2^{2+}) is fairly important. The hydronium ion (H_3O^+) is important in Chapter 19. Others may be introduced in more advanced texts.

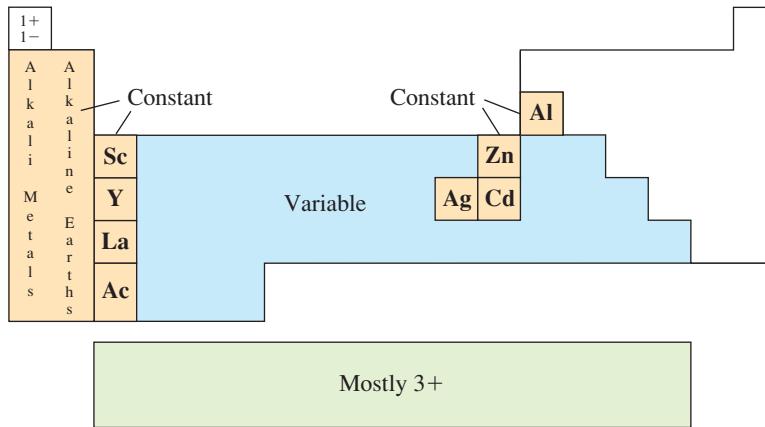
CONSTANT TYPE CATIONS

Naming the constant type of cation involves naming the element and adding the word *ion*, unless a compound is being named. For example, K^+ is the potassium ion, and Ca^{2+} is the calcium ion; KCl is potassium chloride. The alkali metals, the alkaline earth metals, zinc, cadmium, aluminum, and silver are the most important metals that form ions of the constant type (Figure 6.2). Each of these metals forms the same ion in any of its compounds, and the charge on the ion is equal to the classical periodic group number.

VARIABLE TYPE CATIONS

Naming ions of metals that form ions of more than one charge requires distinguishing between the possibilities. For example, iron forms Fe^{2+} and Fe^{3+} ions. We cannot call both of these “iron ion” because no one would know which of the two we meant. For *monatomic* cations of variable type, the *charge* in the form of a Roman numeral is attached to the element’s name to indicate which ion we are talking about. For example, Fe^{2+} is called iron(II) ion and Fe^{3+} is called iron(III) ion. This system of nomenclature is called the **Stock system**.

Figure 6.2 Cations with Constant Charges and Cations with Varying Charges



EXAMPLE 6.5

Name Co^{2+} and Co^{3+} .

Solution

Cobalt(II) ion and cobalt(III) ion, respectively.

EXAMPLE 6.6

How can we tell whether the chromium ion in the compound CrCl_2 has a 2+ or 3+ charge?

Solution

We know that the chloride ion has a 1- charge; the chromium ion must have a 2+ charge to balance the charge on two chloride ions and make the compound neutral. (See Section 5.4.)

Practice Problem 6.6 What is the charge on the anion in $(\text{NH}_4)_3\text{VO}_4$?

In writing formulas for ionic compounds from their names, we must remember the rules from Chapter 5. Be sure to balance the number of positive and negative charges! The charges on the cations are implied for some cations (the constant type) and stated explicitly in the name for the others. The charge on a monatomic anion is equal to the group number minus 8 (see Section 5.2).

EXAMPLE 6.7

Write the formula for each of the following compounds:

- (a) Magnesium sulfide (b) Sodium iodide
- (c) Lead(IV) oxide (d) Aluminum oxide

6.2 ■ Naming Ionic Compounds**165****Solution**

- (a) MgS (The magnesium, in group II, has a charge of 2+, the sulfide, in group VI, has a charge of 2–.)
 (b) NaI (c) PbO₂ (not Pb₂O₄) (d) Al₂O₃

EXAMPLE 6.8

Name (a) Cr₂O₃, (b) P₂O₃, and (c) Al₂O₃.

Solution

- (a) Chromium(III) oxide (b) Diphosphorus trioxide
 (c) Aluminum oxide

Each of these compounds, with formulas that look so similar, is named in a different way.

- (a) Chromium forms both Cr²⁺ and Cr³⁺ ions (see Figure 5.11), so the name must have a Roman numeral to distinguish which of the two is present.
 (b) Phosphorus and oxygen form a binary nonmetal-nonmetal compound, so the oxygen is named with the prefix *tri-* added to it, and its ending is changed to *-ide*. The prefix *di-* is added to the phosphorus.
 (c) Aluminum always forms a 3+ ion *in its compounds*, so no prefix or Roman numeral is necessary to tell its charge.

Note that not only is it necessary to remember the rules for the different types of compounds but, just as important, *when to use each rule!*

Practice Problem 6.8 Name (a) IBr, (b) NaBr, and (c) CuBr.

Not only is it necessary to remember the rules for the different types of compounds, but just as important, *when to use each rule!*

EXAMPLE 6.9

Name each of the following compounds:

- (a) CuS (b) Cu₂S

Solution

- (a) Copper(II) sulfide (b) Copper(I) sulfide

In Cu₂S, the two copper ions are balanced by one sulfide ion with a 2– charge; the charge on each copper ion must be 1+. In CuS, only one copper ion is present to balance the 2– charge on the sulfide ion; the charge on the copper ion is 2+. Note that the Roman numerals in the names of monatomic cations denote the *charges on the ions*. The Arabic numerals appearing as subscripts in formulas denote the *number of atoms* of that element present per formula unit. Either of these numbers can be used to deduce the other, but they are not the same!

Roman numerals in names denote charges on ions; Arabic numerals in formulas tell the number of atoms or ions present per formula unit.

Practice Problem 6.9 Write the formula for (a) platinum(II) oxide and (b) platinum(IV) oxide.

Table 6.2 Classical Names of Some Common Cations

Periodic Group	Ion of Lower Charge	Ion of Higher Charge
VIB	Cr^{2+} , chromous	Cr^{3+} , chromic
VIIIB	Mn^{2+} , manganese	Mn^{3+} , manganic
VIII	Fe^{2+} , ferrous	Fe^{3+} , ferric
VIII	Co^{2+} , cobaltous	Co^{3+} , cobaltic
VIII	Ni^{2+} , nickelous	Ni^{3+} , nickelic
IB	Cu^{+} , cuprous	Cu^{2+} , cupric
IB	Au^{+} , aurous	Au^{3+} , auric
IIB	Hg_2^{2+} , mercurous	Hg^{2+} , mercuric
IVA	Sn^{2+} , stannous	Sn^{4+} , stannic
IVA	Pb^{2+} , plumbous	Pb^{4+} , plumbic

An older nomenclature system (known as the classical system) uses suffixes to distinguish metal ions of the variable type. As Figure 5.11 shows, there are two possible monatomic cations for each variable metal listed. The ion with the higher charge is named with the ending changed to *-ic*. The ion of lower charge has its ending changed to *-ous*. For example, Cr^{2+} is called chromous ion, and Cr^{3+} is called chromic ion. For many elements, the Latin names are used instead of the English names. For example, Fe^{2+} is called ferrous ion—from *ferrum*, the Latin for iron. Table 6.2 lists classical names for some important monatomic cations. This older system is more difficult to use in two ways: (1) we must remember the other possible charge on an ion in addition to the one given, and (2) we must remember a Latin name for many of the elements.

EXAMPLE 6.10

Name V^{2+} using the Stock system. Explain why use of the classical system would be harder.

Solution

The Stock system name—vanadium(II) ion—is easy. To use the classical system, we must know the answers to at least three questions: (1) What is the charge on the other monatomic ion of vanadium? (2) Is the Latin name for vanadium used in the classical system? (3) If the Latin name is used, what is that name? The Stock system was invented to make naming easier.

Practice Problem 6.10 Name Ti^{3+} .

Naming Anions

Just as for cations, there are three types of anions for naming purposes. Monatomic anions are easy to name. A second type, **oxoanions**, are anions that contain oxygen covalently bonded to another element. Table 6.3 presents some important

6.2 ■ Naming Ionic Compounds**167****Table 6.3** Names of Some Important Oxoanions*

Hypo ____ ite (Two Fewer Oxygen Atoms)	ite (One Fewer Oxygen Atom)	ate	Per ____ ate (One More Oxygen Atom)
ClO^- hypochlorite	ClO_2^- chlorite	ClO_3^- chlorate	ClO_4^- perchlorate
BrO^- hypobromite	BrO_2^- bromite	BrO_3^- bromate	BrO_4^- perbromate
IO^- hypoiodite	IO_2^- iodite	IO_3^- iodate	IO_4^- periodate
PO_2^{3-} hypophosphite	PO_3^{3-} phosphite	PO_4^{3-} phosphate	
	NO_2^- nitrite	NO_3^- nitrate	
	SO_3^{2-} sulfite	SO_4^{2-} sulfate	
		CO_3^{2-} carbonate	

*The ions do not exist where there are spaces in the table.

Table 6.4 Names of Special Anions

Formula	Name
OH^-	Hydroxide
CN^-	Cyanide
O_2^{2-}	Peroxide
CrO_4^{2-}	Chromate
$\text{Cr}_2\text{O}_7^{2-}$	Dichromate
MnO_4^-	Permanganate
$\text{C}_2\text{H}_3\text{O}_2^-$	Acetate

The charge on each *monatomic* anion except for H^- is its classical group number minus 8.

oxoanions in a format designed to make their names easier to learn. Several other important anions, referred to as special anions in this book, are listed in Table 6.4.

MONATOMIC ANIONS

All monatomic anions are named by changing the ending of the element's name to *-ide*. For example, I^- , H^- , and O^{2-} are called iodide ion, hydride ion, and oxide ion, respectively. (The names of a few special anions also end in *-ide*; among the most important are hydroxide and cyanide ions, listed in Table 6.4.) The charge on any monatomic anion is constant and, except for that on H^- , is equal to the classical group number minus 8 (see Figure 5.11).

EXAMPLE 6.11

Why do monatomic anions (except the hydride ion) have charges equal to their group numbers minus 8?

Solution

For the nonmetals, the group number is equal to the number of valence electrons (see Chapter 5). The number of additional electrons required to form an octet is therefore 8 minus the group number. Since each electron has a single negative charge, the charge on the ions is equal to the group number minus 8. For example, sulfur in group VI has 6 valence electrons and needs $8 - 6 = 2$ more to form an octet. Since each of the 2 electrons has a negative charge, the ion has a 2^- charge (equal to $6 - 8$).

Practice Problem 6.11 Why does the hydride ion have a single negative charge?

OXOANIONS

In many important anions, oxygen atoms are covalently bonded to a central atom. These ions have extra electrons from some source, which give them their

Oxoanions of even group elements have even charges ($2-$) and those of odd group elements have odd charges ($1-$ or $3-$).

negative charges. They are called oxoanions but were formerly known as oxyanions. For the seven most important oxoanions, the name is that of the root of the central element with the ending *-ate* added. They are listed in the third column of Table 6.3. Once we have learned the names and formulas of these ions, we can deduce the formulas of the corresponding ions with fewer or more oxygen atoms. Ions ending in *-ite* have one fewer oxygen atom than the corresponding *-ate* ions. In four cases, removal of two oxygen atoms from an ion ending in *-ate* results in an ion named with the prefix *hypo-* and the ending *-ite*. For three ions that end with *-ate*, addition of one oxygen atom yields an ion named with the prefix *per-* and the ending *-ate*. Note in Table 6.3 that all the ions with a given central atom have the same charge. Note also that the charge on each third through fifth period oxoanion is equal to the classical group number minus 8, just as for the monatomic anions, but the charge on each second period oxoanion has *two fewer* negative charges (CO_3^{2-} , NO_3^- , and NO_2^-). See Figure 5.13.

EXAMPLE 6.12

Name Br^- , BrO_3^- , BrO_2^- , BrO^- , and BrO_4^- .

Solution

The names are bromide ion, bromate ion, bromite ion, hypobromite ion, and perbromate ion.

Practice Problem 6.12 Write the formula for (a) iodite ion and (b) hypoiodite ion.

EXAMPLE 6.13

What are the formulas for (a) sulfate ion and (b) carbonate ion?

Solution

The formulas are (a) SO_4^{2-} and (b) CO_3^{2-} .

Practice Problem 6.13 Write the formula for each of the following ions:

- (a) Sulfite ion (b) Chlorate ion
(c) Nitrate ion (d) Nitrite ion

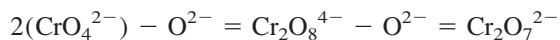
SPECIAL ANIONS

Other important anions that don't fit into the prior two categories are called special anions in this book. They are listed in Table 6.4. Names for anions that contain oxygen but are not included in Table 6.3 may sometimes be determined because of a periodic relationship between their central element and that of an ion in that table. For example, MnO_4^- is analogous to ClO_4^- because both central elements are in periodic groups numbered VII. Its name is permanganate,

6.2 ■ Naming Ionic Compounds**169**

which is analogous to perchlorate. Similarly, CrO_4^{2-} and SO_4^{2-} both have central atoms that are in periodic groups numbered VI. The name of CrO_4^{2-} is chromate, analogous to sulfate. (Not all such analogies are valid, however.)

We may wish to use the following memory device to remember the formula of the dichromate ion: Double the chromate ion and remove an oxygen atom and two charges (an “oxide ion”).

**EXAMPLE 6.14**

Name SeO_4^{2-} .

Solution

Selenium is just below sulfur in the periodic table. We can guess that the SeO_4^{2-} ion is named analogously to the SO_4^{2-} ion. The name is selenate ion.

Practice Problem 6.14 Name AsO_4^{3-} .

Naming and Writing Formulas for Ionic Compounds

Naming ionic compounds involves first naming the cation and then naming the anion. Therefore, the name of such a compound leads directly to its formula.

EXAMPLE 6.15

Name NaNO_3 .

Solution

The cation is Na^+ and the anion is NO_3^- . The name of the compound is sodium nitrate.

Practice Problem 6.15 Name BaSO_4 .

EXAMPLE 6.16

Name (a) Cu_2S and (b) $(\text{NH}_4)_2\text{SO}_4$.

Solution

(a) Each cation is Cu^+ ; the anion is S^{2-} . It is important to recognize that each cation is a monatomic ion and that the two together do not make up a different ion. The compound is copper(I) sulfide. Note that the name of the compound does not explicitly mention that there are two copper(I) ions per sulfide ion.

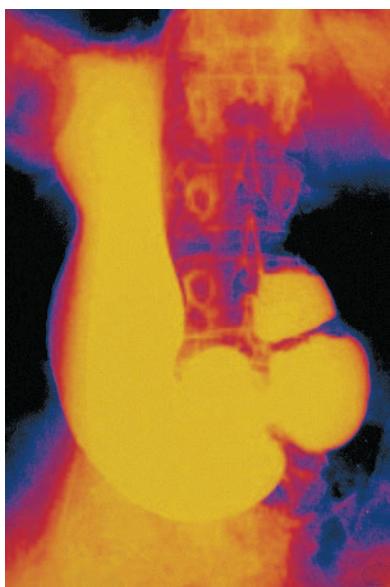


Figure 6.3 X-Ray Film of the Stomach

Barium sulfate, which is not soluble in water, is administered to humans to absorb X-rays and outline organs. Barium salts that are soluble are poisonous.

- (b) Each of the cations is NH_4^+ , the ammonium ion; the anion is the sulfate ion. The compound is ammonium sulfate.

Practice Problem 6.16 Name (a) $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ and (b) $\text{Co}(\text{ClO}_3)_3$.

EXAMPLE 6.17

Write the formula for (a) zinc nitrate and (b) cobalt(III) hypochlorite.

Solution

- (a) The zinc ion is Zn^{2+} ; the nitrate ion is NO_3^- . The formula of the compound must balance positive charges and negative charges; it is $\text{Zn}(\text{NO}_3)_2$.
- (b) The cobalt(III) ion is Co^{3+} ; the hypochlorite ion is ClO^- . The compound is $\text{Co}(\text{ClO})_3$. Parentheses are needed around the formula for the hypochlorite ion so that the subscript 3 indicates that three such ions are present. (If the parentheses were not written, the formula would appear to contain a chlorate ion, ClO_3^- .)

Practice Problem 6.17 Write the formula for (a) lead(IV) sulfate and (b) aluminum sulfide.

The differences in the names of compounds can be life-and-death details. For example, physicians sometimes prescribe a barium sulfate slurry or barium sulfate enema for patients who are about to have a stomach or intestinal X-ray film taken. The barium sulfate is opaque to X-rays and outlines the stomach or colon clearly (Figure 6.3). However, barium ion is poisonous to humans. Barium sulfate is safe only because it is too insoluble to be harmful. However, if barium *sulfite* were given instead of barium *sulfate*, the compound would dissolve in the stomach or colon, and the patient might die. The one-letter difference in the name is critical.



Snapshot Review



ChemSkill Builder 3.2, 3.3, 3.4

- Cations are named first, then anions.
- Learning the types of cations and anions enables us to choose the proper name endings for them.
- We must learn not only the rules, but when to use each one!
- The proper formulas must be written according to the rules presented in Chapter 5.

- A. Name (a) CaCl_2 , (b) NiCl_2 , and (c) $(\text{NH}_4)_2\text{SO}_3$.
- B. Write formulas for (a) lead(II) hypochlorite, (b) magnesium nitride, and (c) aluminum phosphite.

6.3 Naming Acids and Acid Salts

Acids are a special group of hydrogen-containing compounds whose properties will be covered more fully in Chapter 8. One of their most important properties is their reaction with **bases** to form **salts** (Section 8.4). Pure acids are covalent compounds, but they react to varying extents with water to form ions in solution. The hydrogen

6.3 ■ Naming Acids and Acid Salts**171**

The appearance of hydrogen first in a formula indicates that the compound is an acid.

atoms that react with water to form ions are said to be **ionizable hydrogen atoms**. The formulas of acids have the ionizable hydrogen atoms written first. In beginning courses, all compounds (except for water and hydrogen peroxide) with hydrogen written first are acids. Thus, HCl is an acid with one ionizable hydrogen atom per molecule, and H_2SO_4 is an acid with two ionizable hydrogen atoms per molecule. CH_4 and NH_3 are not acids. (In fact, NH_3 acts as a base in aqueous solution.) In other words, the appearance of hydrogen first in a formula is *not* based on hydrogen's relative position in the periodic table, as is true for other elements, but only on whether the compound is an acid.

EXAMPLE 6.18

How many hydrogen atoms per molecule of propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$, are ionizable?

Solution

One, represented by the first H, is ionizable. The other five hydrogen atoms of this compound are not ionizable, which is why they are written after the carbon atoms in the formula.

Practice Problem 6.18 How many hydrogen atoms per molecule of phthalic acid, $\text{H}_2\text{C}_8\text{H}_4\text{O}_4$, are ionizable?

Acids are related to their anions by exchanging hydrogen atoms of the acids for the same number of negative charges on the anions. For example,

Acid	Anion
HCl	Cl^-
H_2SO_4	SO_4^{2-}
H_3PO_4	PO_4^{3-}
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$

Naming Acids

Acids generally do not have the word "hydrogen" in their names. They are named by replacing the ending of the related anion by an ending including the word *acid*, as follows:

Compounds named as acids do not include the word *hydrogen* in the name. The word *acid* implies the presence of hydrogen.

Name of anion	Name of acid
Per _____ ate	Per _____ ic acid
-ate	-ic acid
-ite	-ous acid
Hypo _____ ite	Hypo _____ ous acid
-ide	Hydro _____ ic acid

Note that if the anion has a prefix *hypo-* or *per-*, so does the acid.

If the acid is a binary hydrogen compound, including HF, HCl, HBr, HI, and H_2S , the pure compound is named as if hydrogen were an alkali metal. For example, pure HCl is named hydrogen chloride, and H_2S is named hydrogen sulfide, with no prefixes for either element in either case. When the hydrogen halides are dissolved in water, they are usually named as acids. Thus HCl in

water is referred to as hydrochloric acid. H_2S is one of very few acids usually named like an alkali metal-nonmetal compound even when dissolved in water. It is called hydrogen sulfide, but the name hydrosulfuric acid (analogous to hydrochloric acid) may be used for its aqueous solution.

EXAMPLE 6.19

Name the following acids:

- (a) HNO_3 (b) H_3PO_3 (c) H_2SO_3
(d) HBrO (e) HClO_4 (f) HI

Solution

- (a) Nitric acid. The ending *-ate* of the nitrate ion is changed to *-ic acid*.
(b) Phosphorous acid. The ending *-ite* of the phosphite ion is changed to *-ous acid*. In this case, the stem is also changed to *phosphor*.
(c) Sulfurous acid. The ending *-ite* is changed to *-ous acid*, and the stem is changed from *sulf* to *sulfur*.
(d) Hypobromous acid. The ending *-ite* is changed to *-ous acid*. The prefix *hypo-* on the anion makes no difference to the suffix; the prefix is included in the acid name.
(e) Perchloric acid. The ending *-ate* of perchlorate ion is changed to *-ic acid*; the prefix *per-* is not changed.
(f) Hydroiodic acid. The prefix *hydro-* distinguishes this binary acid from HIO_3 .

Practice Problem 6.19 Name the following acids:

- (a) HIO_3 (b) H_2SO_4 (c) HClO_2

Formulas for acids can be written by replacing every negative charge on the corresponding anion with one hydrogen atom. For example, SO_4^{2-} has two negative charges; therefore, sulfuric acid has two ionizable hydrogen atoms (and no charge): H_2SO_4 . If the ion is an oxoanion, the acid is an **oxoacid**.

EXAMPLE 6.20

Write the formula for each of the following acids:

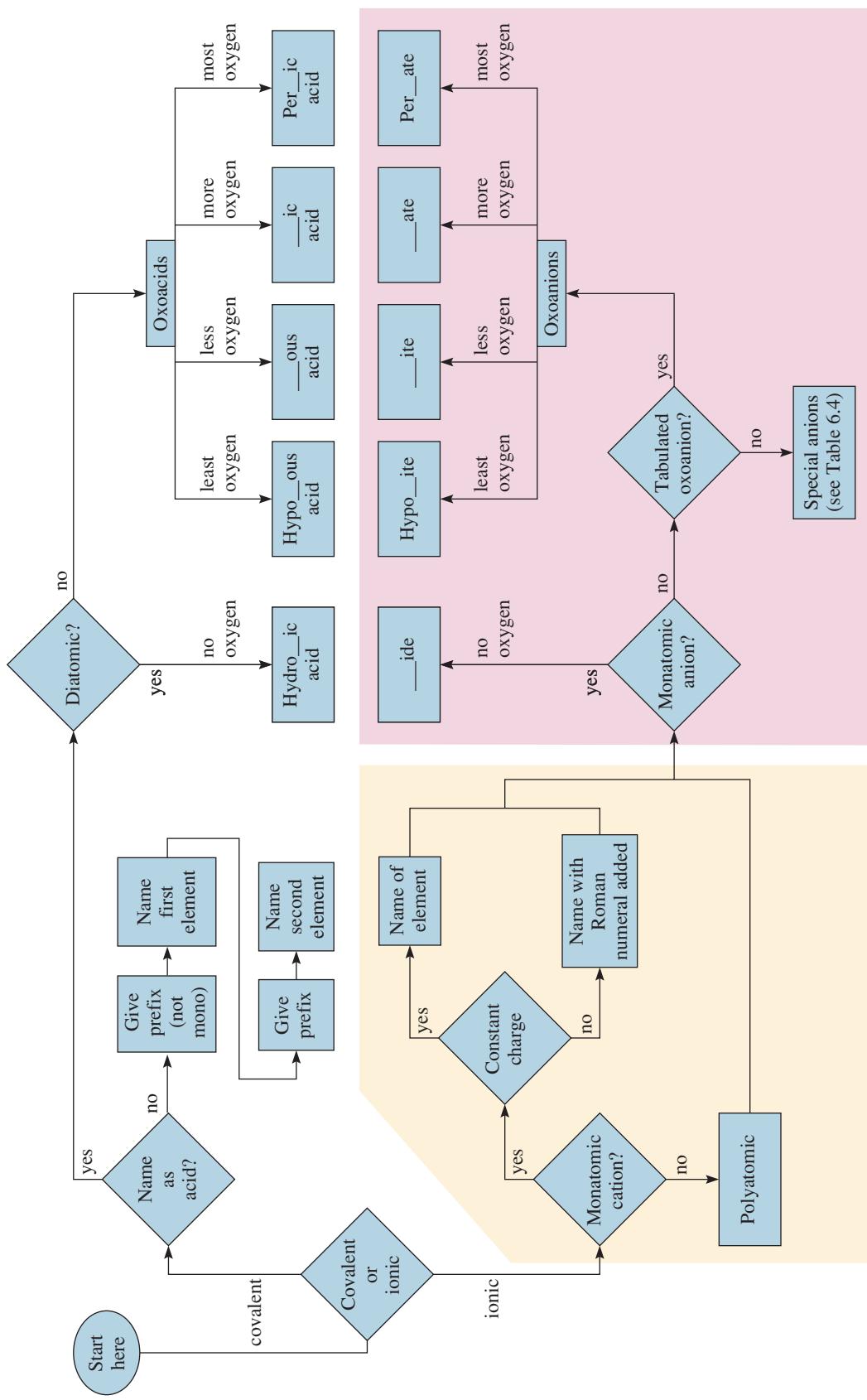
- (a) Hypophosphorous acid (b) Chloric acid (c) Perbromic acid

Solution

- (a) H_3PO_2 (b) HClO_3 (c) HBrO_4

Practice Problem 6.20 Write the formulas for (a) nitrous acid and (b) sulfuric acid.

Figure 6.4 and Table 6.5 outline a systematic procedure for naming many compounds and ions. One of these presentations may be very helpful, especially at first. (Use only one of these as needed.)

**Figure 6.4** Flow Chart Summarizing the Naming of Compounds and Ions

Use this chart or the outline of Table 6.5 if it helps you.

Table 6.5 Outline for Nomenclature*

- Is the compound (I) covalent or (II) ionic?
- I. Covalent: Is the compound (A) an acid or (B) a binary compound of two nonmetals?
- Acid: Name the compound using a suffix and possibly a prefix related to the name of the analogous anion (IIB). Add the word *acid*.
 - Binary compound: Name the first element with a prefix from Table 6.1 if there are two or more atoms. Then name the second element with a prefix from Table 6.1 (even if there is only one atom), and with the ending changed to *-ide*.
- II. Ionic: Name *both* (A) the cation and then (B) the anion.
- Cation: Is the cation (1) polyatomic, (2) a metal forming ions with more than one charge, or (3) a metal with only one ion?
 - Polyatomic: Name the ion.
 - Variable: Use the name of the metal with a Roman numeral to indicate the charge.
 - Constant: Use the name of the metal only.
 - Anion: Is the anion (1) monatomic, (2) a tabulated oxoanion, or (3) something else?
 - Monatomic: Change the ending of the element name to *-ide*.
 - Oxoanion: See Table 6.3.
 - Special: See Table 6.4.

*Use this outline or Figure 6.4; you don't need both.

Naming Acid Salts

In Section 8.4, we will see that an acid with more than one ionizable hydrogen atom can react with bases in steps, with all but the last step yielding compounds called **acid salts**. Such salts consist of a cation, such as a sodium ion, plus an anion that has one or two hydrogen atoms still attached. Just as the hydrogen atoms are covalently bonded in the pure acid, the ones that remain in the acid salt are still covalently bonded. The anion is named with the word **hydrogen** followed by the name of the parent anion. For example, NaHCO_3 has a sodium cation, Na^+ , and the hydrogen carbonate anion, HCO_3^- . The compound is sodium hydrogen carbonate. Acid salts of acids with three hydrogen atoms, such as phosphoric acid, require specification of how many hydrogen atoms remain. The prefixes *mono-* and *di-* are used for one and two hydrogen atoms, respectively. Thus, NaH_2PO_4 is sodium dihydrogen phosphate, and Na_2HPO_4 is sodium monohydrogen phosphate (or disodium hydrogen phosphate).

Acid salts, and their anions, have the word *hydrogen* in their names.

The total of the number of hydrogen atoms plus negative charges is the same for the parent acid, the anion, and any hydrogen-containing anions.

EXAMPLE 6.21

Name (a) NaHS and (b) HS^- .

Solution

(a) Sodium hydrogen sulfide (b) Hydrogen sulfide ion

6.4 ■ Hydrates**175**

Including the word *ion* in the name in part (b) is important to distinguish this ion from hydrogen sulfide, H_2S .

Practice Problem 6.21 Write the formula for (a) sodium monohydrogen phosphate and (b) magnesium dihydrogen phosphate.

An older nomenclature system, still in use to some extent, uses the word “acid” to denote an acid salt. Also, the prefix *bi-* may be used for an acid salt of an acid with two ionizable hydrogen atoms. Thus, NaHCO_3 can be called sodium bicarbonate or sodium acid carbonate instead of sodium hydrogen carbonate (Figure 6.5).

Figure 6.5 Baking Soda

Ordinary baking soda is sodium hydrogen carbonate.



ChemSkill Builder 3.5

Snapshot Review

- Acids have hydrogen written first in their formulas, but do not have the word “hydrogen” in their names.
- Acids are related to anions; for every hydrogen atom removed from the formula of an acid, one negative charge is added in the resulting anion.
- The names of acids and anions are also related:

Anion suffix	Acid suffix (and prefix)
-ate	-ic acid
-ite	-ous acid
-ide	hydro _____ ic acid

- A. Name the following acids: (a) H_3PO_3 , (b) HClO , and (c) HNO_2 .
- B. Write formulas for the following compounds: (a) sulfuric acid and (b) sodium dihydrogen phosphite

6.4 Hydrates

Hydrates are stable crystalline compounds consisting of other compounds that are stable in their own right, with certain numbers of water molecules attached (see Section 5.1). Naming and writing formulas for hydrates is easy. We simply name the compound first and then combine a Table 6.1 prefix that identifies the number of water molecules with the word “hydrate” to indicate the presence of the water molecules. For example, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is called copper(II) sulfate pentahydrate. CuSO_4 may be called *anhydrous* copper(II) sulfate, if we wish to emphasize that no water is attached.



Snapshot Review

□ Hydrates—compounds with water attached—are named with a prefix from Table 6.1 attached to the word “hydrate” to denote the number of water molecules.

- A. Name $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$.
- B. Write the formula for chromium(III) phosphate dihydrate.

Key Terms

Key terms are defined in the Glossary.

acid (6.3)
acid salt (6.3)
ammonia (6.1)
ammonium ion (6.2)
base (6.3)

hydrogen (6.3)
ionizable hydrogen atom (6.3)
nomenclature (intro)
oxoacid (6.3)
oxoanion (6.2)

prefix (6.1)
salt (6.3)
Stock system (6.2)

Prefixes/Suffixes

-ate (6.2)
bi- (6.3)
deca- (6.1)
di- (6.1)
hepta- (6.1)
hexa- (6.1)
hydro- (6.3)

hypo- (6.2)
-ic (6.2)
-ic acid (6.3)
-ide (6.1)
-ite (6.2)
mono- (6.1)
nona- (6.1)

octa- (6.1)
-ous (6.2)
-ous acid (6.3)
penta- (6.1)
per- (6.2)
tetra- (6.1)
tri- (6.1)

Summary

Metal-nonmetal compounds and ammonium compounds (containing the NH_4 group within a formula) are ionic. Other compounds are covalent, except that acids are ionized, some completely, when dissolved in water. The acids are named with a special system of their own, but pure binary acids can be named similarly to alkali metal-nonmetal compounds.

Different systems are used for naming binary covalent compounds and ionic compounds, and acids are named still other ways. For binary nonmetal-nonmetal compounds (which are covalent), name the leftmost or lower element in the periodic table first, and then name the other element. Change the ending of the second element to *-ide*, and indicate the number of atoms of that element in the molecule by a prefix (Table 6.1). If more than one

atom of the first element is present per molecule, use a prefix for that element, too. (Section 6.1)

To name an ionic compound, name the cation first and then the anion. Use just the name of the element for monatomic cations of elements that form only one cation. For monatomic cations of elements that can form more than one cation, indicated the charge on the cation by a Roman numeral in parentheses added to the name of the element. Polyatomic cations have special names, ammonium ion being the most important.

The names of monatomic anions have the ending of the element’s name changed to *-ide*. The charge on any monatomic anion (except H^-) is equal to the classical group number minus 8. The charge on each second-period oxoanion has two fewer negative charges than the

■ Answers to Snapshot Reviews

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classical group number minus 8, and the charge on each third-through fifth-period oxoanion is equal to the classical group number minus 8, just as for the monatomic anions. The names of most familiar oxoanions end in *-ate* or *-ite*, depending on the relative number of oxygen atoms per ion. Ions with more oxygen atoms than those whose names end in *-ate* have the prefix *per-* added to the name; ions with fewer oxygen atoms than those whose names end in *-ite* have the prefix *hypo-* added to the name. Names of other anions must be learned based on periodic table relationships or individually.

A Roman numeral in parentheses in the *name* of the compound designates the charge on a cation and an Arabic numeral as a subscript in the *formula* designates the number of atoms or ions. The charges enable us to deduce the numbers of ions, and vice versa, but the Roman numerals and the Arabic numerals do not represent the same quantities. (Section 6.2)

Acids can be recognized by the fact that the ionizable hydrogen atoms are written first in their formulas. The word “hydrogen” does not appear in their names; the word “acid” implies the presence of the hydrogen. Name oxoacids like the corresponding oxoanions, with the ending *-ate* changed to *-ic acid* or the ending *-ite* changed to *-ous acid*. Names of binary acids have the ending *-ide* of the corresponding anion changed to *-ic acid* and the prefix *hydro-* added. For example, Cl^- is chloride; HCl is hydrochloric acid.

Name acid salts as ionic compounds, but put the word “hydrogen” in the name of the anion (perhaps with a prefix) to indicate that at least one ionizable hydrogen atom is still present. For example, NaHCO_3 is sodium hydrogen carbonate. (Section 6.3)

Name hydrates with a prefix from Table 6.1 before the word “hydrate,” to indicate the number of water molecules. For example, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is named copper(II) sulfate pentahydrate. (Section 6.4)

Items for Special Attention

- The following list summarizes the types of compounds and ions we have learned to name in this chapter:
 - Binary nonmetal-nonmetal compounds
 - Ionic compounds
 - Cations
 - Monatomic cations
 - Variable charge
 - Constant charge
 - Polyatomic cations
 - Anions
 - Monatomic anions
 - Oxoanions
 - Special anions
 - Acids
 - Acid salts
 - Hydrates
- The prefixes in Table 6.1 are used only for naming binary nonmetal-nonmetal compounds, acid salts, and hydrates.
- It is critical to specify the charges in formulas for ions and to include the word “ion” if the name without that word means something else, such as sodium ion or hydrogen sulfide ion.
- Roman numerals in names stand for charges, and subscripts in formulas represent numbers of atoms.

- All monatomic anions have names ending in *-ide*, but not all anions with names ending in *-ide* are monatomic. Hydroxide ion, OH^- , and cyanide ion, CN^- , are important examples of diatomic ions with names ending in *-ide*.
- Parentheses are used when two or more polyatomic ions are present in a given formula, as in $\text{Mg}(\text{ClO})_2$. The subscript after the parentheses indicates the number of these ions present. In certain cases, the parentheses also distinguish between familiar ions, such as the ClO^- ions in $\text{Mg}(\text{ClO})_2$ and the ClO_2^- ion in KClO_2 .
- That hydrogen is present in an acid is implied in the name by the word “acid,” not by the word “hydrogen”. For example, HCl is hydrochloric acid. The word “hydrogen” is used in names of acid salts, such as sodium hydrogen carbonate, NaHCO_3 .
- In naming the binary compounds of hydrogen in which hydrogen is written first in the formula, *name* the compound as if hydrogen were an alkali metal (despite the fact that it is not, and that the compound is covalent). For example, HCl is named hydrogen chloride and H_2S is named hydrogen sulfide. [These compounds do form ions to a greater or lesser extent when they are dissolved in water. (Section 8.4)]

Answers to Snapshot Reviews

- 6.1 A. (a) Dichlorine monoxide (b) Silicon tetrafluoride
 B. (a) IF_5 (b) P_2S_3
- 6.2 A. (a) Calcium chloride (b) Nickel(II) chloride
 C. Ammonium sulfite
 B. (a) $\text{Pb}(\text{ClO})_2$ (b) Mg_3N_2 (c) AlPO_3

- 6.3 A. (a) Phosphorous acid (b) Hypochlorous acid
 C. Nitrous acid
 B. (a) H_2SO_4 (b) NaH_2PO_3
- 6.4 A. Barium iodide dihydrate
 B. $\text{CrPO}_4 \cdot 2\text{H}_2\text{O}$

Self-Tutorial Problems

- 6.1 Use the Table of Elements on the inside of the back cover, if necessary, to name each of the following substances:
(a) Hf (b) HF (c) NO (d) No
- 6.2 What is the difference in the meanings of the prefixes *bi-* and *di-* (as used in this chapter)?
- 6.3 Which metals form cations of the constant type? What are the charges on these cations?
- 6.4 What is the difference between ClO_2 and ClO_2^- ? Name each one.
- 6.5 What are the rules for remembering the charges on (a) monatomic anions and (b) oxoanions?
- 6.6 Classify each of the following as ionic or covalent, and name each:
(a) CaCl_2 (b) CO_2 (c) CrO (d) CCl_4
- 6.7 Name the following ions:
(a) SO_4^{2-} (b) NO_3^- (c) PO_4^{3-} (d) S^{2-}
- 6.8 Name the following ions:
(a) SO_3^{2-} (b) NO_2^- (c) PO_2^{3-} (d) Br^-
- 6.9 What can we tell from each of the following?
(a) The charges on the two ions making up a compound
(b) The fact that hydrogen is written first in a formula
(c) The fact that the name for a compound or ion ends in *-ite*
- 6.10 Classify the metal in each of the following compounds as constant type or variable type, and then name each compound:
(a) CrSO_4 (b) CoSO_4 (c) CaSO_4
(d) AlCl_3 (e) FeSO_4 (f) K_2SO_4
- 6.11 Classify each of the following compounds as ionic, covalent, or both: (a) NH_4Cl , (b) CuCl_2 , (c) KMnO_4 , (d) SCl_2 .
- 6.12 (a) What is the difference between hydrogen ion and hydride ion?
- (b) Explain why H^+ is called the hydrogen ion rather than the hydrogen(I) ion, even though hydrogen can form two different ions.
- 6.13 Write formulas for (a) chloride ion, (b) chlorate ion, and (c) chlorite ion.
- 6.14 What is the difference between NH_3 and NH_4^+ ? Name each one.
- 6.15 In which one(s) of the following nomenclature classes is the word "hydrogen" used?
(a) acids (b) acid salts
(c) binary hydrogen-nonmetal compounds
- 6.16 Pure HBr may be named as a binary nonmetal-nonmetal compound, whereas pure H_2SO_4 is always named as an acid. Explain why H_2SO_4 is not named like HBr is named.
- 6.17 What are the differences in the following, as used in naming compounds?
(a) Hypo- (b) Hydro- (c) Hydrogen
- 6.18 Name (a) Na_2SO_4 and (b) H_2SO_4 .
- 6.19 What is the difference between the two names for HCl: hydrogen chloride and hydrochloric acid?
- 6.20 Write the formula for (a) ammonium hydrogen carbonate, (b) ammonium bicarbonate, (c) ammonium acid carbonate.
- 6.21 Name each member of the following pairs, and compare the names:
(a) NaCl and HCl (pure)
(b) Na_2S and H_2S (pure)
- 6.22 Name each of the following acids:
(a) HBrO_4 (b) HBrO_3 (c) HBrO_2
(d) HBrO (e) HBr
- 6.23 What is the charge on each of the following?
(a) The hydrogen sulfite ion
(b) The dihydrogen phosphate ion
(c) The monohydrogen phosphite ion

Problems

6.1 Binary Nonmetal-Nonmetal Compounds

- 6.24 Name each of the following compounds:

- (a) N_2O_5 (b) CF_4 (c) P_2S_3
(d) SF_4 (e) BrF_3

- 6.25 Write the formula for each of the following compounds:

- (a) Carbon dioxide (b) Hydrogen bromide

- (c) Silicon tetrafluoride (d) Iodine pentafluoride

- (e) Bromine dioxide (f) Hydrogen sulfide
(g) Dinitrogen trioxide

- 6.26 Name the following substances:

- (a) HCl (pure) (b) H_2Se (c) HI (pure)

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6.27 Write the formula for each of the following compounds:

- (a) Chlorine monofluoride (b) Ammonia
 (c) Arsenic trifluoride (d) Sulfur trioxide
 (e) Phosphorus pentachloride (f) Water

6.28 Name each of the following compounds:

- (a) SO_2 (b) SiF_4 (c) AsF_3
 (d) S_2Cl_2 (e) XeF_6

6.29 Write the formula for each of the following compounds:

- (a) Sulfur hexafluoride (b) Sulfur tetrafluoride
 (c) Sulfur difluoride

6.30 Write the formula for each of the following compounds:

- (a) Iodine dioxide
 (b) Diiodine trioxide
 (c) Diiodine monoxide
 (d) Diiodine heptoxide

6.31 Name each of the following compounds:

- (a) NH_3 (b) P_4S_{10} (c) CO_2
 (d) P_2O_5 (e) CO

6.32 Write the formula for each of the following compounds:

- (a) Tetraarsenic hexoxide
 (b) Bromine monochloride
 (c) Tetrasulfur tetranitride
 (d) Diphosphorus pentasulfide

6.2 Naming Ionic Compounds

6.33 Explain why chemists often refer to S^{2-} as “sulfide” (without the word “ion”) but do not refer to K^+ as “potassium” (without the word “ion”).

6.34 Name each of the following cations:

- (a) Ca^{2+} (b) Ag^+ (c) Al^{3+}

6.35 Write the formula for each of the following ions:

- (a) Copper(I) ion (b) Nickel(II) ion
 (c) Lithium ion (d) Ammonium ion
 (e) Gold(I) ion

6.36 Name each of the following cations:

- (a) V^{2+} (b) Al^{3+} (c) Mn^{2+}

6.37 Name each of the following anions:

- (a) Cl^- (b) P^{3-} (c) O^{2-} (d) N^{3-}

6.38 Write the formula for each of the following ions:

- (a) Nitrite ion (b) Perchlorate ion
 (c) Cyanide ion (d) Phosphite ion
 (e) Dichromate ion (f) Hypoiodite ion

6.39 Name each of the following anions:

- (a) PO_4^{3-} (b) SO_4^{2-} (c) CO_3^{2-}

6.40 Name each of the following anions:

- (a) $\text{C}_2\text{H}_3\text{O}_2^-$ (b) CrO_4^{2-}
 (c) MnO_4^- (d) $\text{Cr}_2\text{O}_7^{2-}$
 (e) CN^- (f) O_2^{2-}

6.41 Name each of the following compounds:

- (a) $\text{Co}_2(\text{SO}_4)_3$ (b) $\text{Ca}_3(\text{PO}_4)_2$ (c) $(\text{NH}_4)_2\text{SO}_3$

6.42 Write the formula for each of the following compounds:

- (a) Cobalt(III) oxide (b) Nickel(II) sulfate
 (c) Lithium hydroxide (d) Copper(II) carbonate
 (e) Magnesium cyanide (f) Ammonium chlorate

6.43 Name each of the following compounds:

- (a) Cu_2O (b) CuS

6.44 Name each of the following compounds:

- (a) FePO_4 (b) MnSO_4
 (c) $(\text{NH}_4)_2\text{SO}_3$

6.45 Write the formula for each of the following compounds:

- (a) Potassium peroxide (b) Gold(III) chromate
 (c) Nickel(II) hydroxide (d) Copper(I) cyanide
 (e) Aluminum acetate (f) Ammonium dichromate

6.46 Complete the following table by writing the formula for each ionic compound whose cation is given on the left and whose anion is given at the top:

	Nitrate	Sulfate	Acetate	Phosphate
Ammonium	_____	_____	_____	_____
Calcium	_____	_____	_____	_____
Vanadium(III)	_____	_____	_____	_____
Lead(IV)	_____	_____	_____	_____

6.47 Complete the following table by writing the formula for each ionic compound whose cation is given on the left and whose anion is given at the top:

	Chloride	Hypochlorite	Phosphate
Lithium	_____	_____	_____
Mercury(II)	_____	_____	_____
Iron(II)	_____	_____	_____
Cobalt(III)	_____	_____	_____

6.48 Complete the following table by writing the formula for each ionic compound whose cation is given on the left and whose anion is given at the top:

	Hydroxide	Cyanide	Chromate	Permanganate
Sodium	_____	_____	_____	_____
Copper(II)	_____	_____	_____	_____
Iron(III)	_____	_____	_____	_____

6.49 An instructor tells the students in a class that Mg^{2+} is the only stable ion of magnesium and that Mg^+ cannot be

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prepared in a solid. What name should the instructor use for Mg^{+} ?

6.50 Name each of the following cations two ways:

- (a) Cr^{3+} (b) Co^{2+} (c) Au^{+} (d) Pt^{4+}

6.3 Naming Acids and Acid Salts

6.51 Write the formula for each of the following acids:

- (a) Phosphoric acid (b) Hydrobromic acid
(c) Chloric acid (d) Hydrosulfuric acid

6.52 Name each of the following acids:

- (a) H_2SO_4 (b) $HClO_4$ (c) H_3PO_3

6.53 What is the difference between iodous acid and hypoiodous acid?

6.54 What is the difference between hypobromous acid and hydrobromic acid?

6.55 What is the difference between hydroiodic acid and periodic acid?

6.56 Name each of the following compounds as an acid and also as a pure compound:

- (a) HBr (b) H_2S (c) HCl

General Problems

6.62 Name each of the following:

- (a) SO_3 (b) SO_3^{2-} (c) Na_2SO_3
(d) H_2SO_3 (e) K_2SO_3

6.63 Name (a) CuS and (b) Cu_2S .

6.64 Name each of the following compounds:

- (a) CoS (b) Na_2O_2
(c) HI (in water) (d) $NiSO_4$
(e) P_4O_{10} (f) Cl_2O_3
(g) Na_2SO_4 (h) K_2CrO_4

6.65 Name each of the following compounds:

- (a) XeF_6 (b) XeF_2 (c) XeF_4

6.66 Select all of the following compounds that should be named using the prefixes of Table 6.1, all that should be named with Roman numerals, and all that should have neither. Name each.

- (a) CCl_4 (b) Na_2CO_3 (c) NCl_3
(d) $Co(ClO_3)_2$ (e) Na_2SO_4 (f) SO_2

6.67 Which of the following pure compounds have covalent bonds only?

- $CaCO_3$ H_2SO_3 N_2O_3 $NH_4C_3H_5O_2$ AlF_3

CHAPTER 6 ■ Nomenclature

6.57 Classify each of the following as an acid, an acid salt, or a regular salt, and name each:

- (a) H_3PO_4 (b) KH_2PO_4
(c) Na_2HPO_4 (d) $(NH_4)_3PO_4$

6.58 Complete the following table by writing the formula for each ionic compound whose cation is given on the left and whose anion is given at the top:

	Monohydrogen Phosphate	Hydrogen Sulfate	Dihydrogen Phosphate
Magnesium	_____	_____	_____
Chromium(III)	_____	_____	_____
Ammonium	_____	_____	_____
Copper(II)	_____	_____	_____

6.59 What is the difference between the names “phosphorus,” and “phosphorous”?

6.4 Hydrates

6.60 Name (a) $Ba(ClO_2) \cdot 2H_2O$ (b) $Na_2CO_3 \cdot 7H_2O$, and (c) $FeBr_3 \cdot 6H_2O$

6.61 Write the formula for (a) iron(II) sulfate monohydrate and (b) barium bromide dihydrate.

6.68 Complete the following table by writing the formula and name of each compound formed from an anion at the top and a cation on the left:

	NO_3^-	SO_4^{2-}	PO_4^{3-}
Potassium	_____	_____	_____
Iron(II)	_____	_____	_____
Titanium(III)	_____	_____	_____

6.69 Name the following ions by the Stock system, using Table 6.2 if necessary:

- (a) Nickelous ion (b) Cuprous ion
(c) Ferric ion (d) Cupric ion
(e) Plumbous ion

6.70 Name (a) Na_2HPO_4 , (b) NaH_2PO_4 , (c) H_3PO_4 , and (d) Na_3PO_4 .

■ General Problems

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6.71 Which of the following compounds have acid properties?



6.72 Write formulas for (a) platinum(II) monohydrogen phosphate and (b) platinum(II) dihydrogen phosphate.

6.73 Write formulas for the following ions, as well as formulas and names for the corresponding acids and anions (with no hydrogen):

- (a) Hydrogen sulfate ion
- (b) Hydrogen carbonate ion
- (c) Hydrogen sulfide ion
- (d) Dihydrogen phosphate ion

6.74 Write formulas for the following substances:

- (a) Vanadium(V) oxide
- (b) Chlorous acid
- (c) Sodium dichromate
- (d) Hypoiodous acid
- (e) Platinum(II) oxide

6.75 Name each of the following compounds:

- (a) XeF_2
- (b) FeF_2
- (c) CaF_2

6.76 Which transition metal ions have a charge of 1^+ ?

6.77 Name each of the following compounds:

- (a) Al_2O_3
- (b) Cr_2O_3
- (c) N_2O_3

6.78 Name (a) HCl (as an acid), (b) HCl (pure), and (c) NaCl .

6.79 Name each of the following ions:

- (a) SO_4^{2-}
- (b) SeO_4^{2-}
- (c) PO_4^{3-}
- (d) AsO_4^{3-}

6.80 Write the formula of each of the following:

- (a) Calcium oxide
- (b) Sodium peroxide
- (c) Lead(IV) oxide
- (d) Potassium peroxide

6.81 Complete the following table by writing the formula and name of each compound formed from an anion at the top and a cation on the left:

	Carbonate	Chlorate	Arsenate
Fe^{2+}	_____	_____	_____
	_____	_____	_____
	_____	_____	_____

	Carbonate	Chlorate	Arsenate
Ca^{2+}	_____	_____	_____
	_____	_____	_____
	_____	_____	_____

	Carbonate	Chlorate	Arsenate
Cr^{3+}	_____	_____	_____
	_____	_____	_____
	_____	_____	_____

6.82 Give a more modern name for each of the following:

- (a) Nickelous bicarbonate
- (b) Chromic chloride
- (c) Ferric sulfate
- (d) Cobaltic oxide

6.83 Write the formula for sodium bisulfide.

6.84 Name each of the following substances:

- (a) Cu_2O
- (b) $\text{Mn}(\text{OH})_2$
- (c) BrF_5
- (d) HNO_3
- (e) AgBr
- (f) BF_3
- (g) H_3PO_3
- (h) Mn_2O_3
- (i) CoF_2
- (j) Ag_2O

6.85 Write the formulas for

- (a) Magnesium nitride
- (b) Aluminum sulfate
- (c) Lead(IV) oxide

6.86 Write formulas for hydrogen sulfide, hydrogen sulfide ion, and hydrosulfuric acid.

6.87 Name the cation in each of the following compounds:

- (a) $(\text{NH}_4)_2\text{SeO}_4$
- (b) K_2MoO_4
- (c) CoPO_4
- (d) CoSO_4

6.88 Name the anion in each of the following compounds:

- (a) VOSO_4
- (b) VO_2NO_3
- (c) $\text{Ba}_3(\text{PO}_4)_2$

6.89 Write formulas for (a) magnesium arsenate, (b) calcium selenate, and (c) acetic acid.

6.90 Name each of the following compounds:

- (a) H_2SO_3
- (b) N_2O
- (c) XeF_6
- (d) CrF_3
- (e) NH_3

6.91 Name (a) K_2O_2 and (b) PbO_2 . (*Hint:* Peroxide ion generally exists only in combination with metals in the form of their ion of highest charge.)

6.92 Name (a) KClO_3 and (b) $\text{Co}(\text{ClO})_3$.

6.93 Name and write formulas for both ions in (a) CaCl_2 and (b) Na_2O_2 .

6.94 Name each of the following:

- (a) Sb_2S_3
- (b) $(\text{NH}_4)_3\text{PO}_4$
- (c) IF_5
- (d) HBrO_2
- (e) TiO_2

6.95 Identify the type of substance, using the following symbols. Then name each.

IV for Ionic compounds containing metal ion of Variable type

IC for Ionic compounds containing metal ions of Constant type

A for Acids or acid salts

C for other binary Covalent compounds

E for Elements

		Type	Name
(a)	FeF ₃	_____	_____
(b)	NiO	_____	_____
(c)	ICl ₃	_____	_____
(d)	NaH	_____	_____
(e)	Au ₂ S	_____	_____
(f)	Mg(OH) ₂	_____	_____
(g)	HNO ₃	_____	_____
(h)	(NH ₄) ₂ SO ₄	_____	_____
(i)	MgSO ₃	_____	_____
(j)	H ₃ PO ₃	_____	_____
(k)	HCl	_____	_____
(l)	K ₂ CO ₃	_____	_____
(m)	(NH ₄) ₂ Cr ₂ O ₇	_____	_____

6.96 Identify the type of substance using the symbols of Problem 6.95, and write the formula for each.

- (a) Cobalt(II) carbonate
- (b) Phosphorus triiodide
- (c) Sulfurous acid
- (d) Ammonium bromate
- (e) Manganese(IV) oxide
- (f) Sulfur hexafluoride
- (g) Barium phosphate
- (h) Nitrous acid
- (i) Carbon tetrachloride
- (j) Iron(II) chloride
- (k) Diphosphorus pentasulfide

6.97 Identify the type of substance using the symbols of Problem 6.95, and write the formula for each.

- (a) Sodium permanganate
- (b) Potassium peroxide
- (c) Barium dichromate
- (d) Vanadium(III) acetate
- (e) Iron(III) hydrogen carbonate
- (f) Sulfur dioxide
- (g) Copper(II) arsenate
- (h) Tetraphosphorus hexoxide
- (i) Iodine heptafluoride
- (j) Ammonium monohydrogen phosphate
- (k) Diarsenic pentoxide
- (l) Chloric acid
- (m) Ammonium chlorate
- (n) Bromic acid

6.98 Identify the type of substance using the symbols of Problem 6.95, and name each.

- (a) KOH
- (b) (NH₄)₂SO₃
- (c) Cu₃(PO₄)₂
- (d) CO₂
- (e) Na₂CO₃
- (f) ICl₅
- (g) NH₄ClO₃
- (h) SO₂
- (i) AlPO₄

6.99 Identify the type of substance using the symbols of Problem 6.95, and name each.

- (a) PbO₂
- (b) HBrO₂
- (c) Ca(OH)₂
- (d) HC₂H₃O₂
- (e) CS₂
- (f) MnO₂
- (g) N₂O₃

6.100 Name each of the following:

- (a) CrS
- (b) Hg₂Cl₂
- (c) Mg₃N₂
- (d) Ag₂S
- (e) CaH₂
- (f) Co₃(PO₄)₂
- (g) Zn(ClO₄)₂
- (h) PCl₃
- (i) BaCl₂
- (j) CuSO₄
- (k) NH₄C₂H₃O₂

6.101 Name the following substances:

- (a) CaO
- (b) HNO₃
- (c) Ti(OH)₃
- (d) MnCrO₄
- (e) Ni(NO₃)₂
- (f) K₂Cr₂O₇
- (g) CrCl₃
- (h) NF₃
- (i) SF₄
- (j) H₂SO₃

6.102 Write formulas for the following substances:

- (a) Iron(II) bromide
- (b) Iron(III) chloride
- (c) Ammonium sulfite
- (d) Xenon tetrafluoride
- (e) Iodine trichloride
- (f) Magnesium hydride
- (g) Ammonia
- (h) Manganese(III) fluoride
- (i) Lithium nitrate
- (j) Barium peroxide

6.103 Name each of the following:

- (a) N₂O
- (b) CaS
- (c) HNO₃
- (d) Ca(NO₂)₂
- (e) Fe(NO₃)₃
- (f) Ni(CLO₃)₂
- (g) HClO₃
- (h) KNO₃
- (i) PI₃
- (j) (NH₄)₃PO₄
- (k) Li₃PO₄

6.104 Name the following substances:

- (a) Li₂SO₃
- (b) HCl
- (c) NI₃
- (d) CaCO₃
- (e) NaOH
- (f) NH₄H₂PO₄
- (g) (NH₄)₂SeO₄
- (h) Na₃AsO₄
- (i) HClO₃
- (j) KCN

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6.105 Write formulas for the following substances:

- (a) Iron(III) oxide
- (b) Cobalt(III) oxide
- (c) Bromine trifluoride
- (d) Lithium hydride
- (e) Gold(III) bromide
- (f) Magnesium perchlorate
- (g) Lithium nitride
- (h) Carbon tetrachloride
- (i) Calcium hydride

6.106 Write formulas for the following substances:

- (a) Silicon tetrafluoride
- (b) Gold(I) chloride
- (c) Phosphoric acid
- (d) Silver sulfide
- (e) Lead(IV) sulfate
- (f) Copper(II) permanganate
- (g) Tricarbon dioxide
- (h) Potassium carbonate
- (i) Chloric acid
- (j) Nickel(II) cyanide

6.107 From Figure 6.4, give the route by which you would name (a) $\text{Al}(\text{ClO}_3)_2$, (b) BrF_5 , and (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

6.108 If oxalate ion is $\text{C}_2\text{O}_4^{2-}$, what are the formula and name of its parent acid?

6.109 (a) Azide ion has the formula N_3^- . Write the formula for the corresponding acid.

(b) What is the name of that acid?

6.110 Name the following substances:

- (a) CaSO_4
- (b) $\text{HC}_2\text{H}_3\text{O}_2$
- (c) PCl_5
- (d) BrCl_3
- (e) CuO
- (f) HClO_4
- (g) KHSO_4
- (h) HBrO_2
- (i) HNO_2
- (j) $\text{Pb}(\text{HPO}_4)_2$

6.111 Write formulas for the following substances:

- (a) Ammonium hydrogen sulfide
- (b) Magnesium chlorite
- (c) Iodine heptafluoride
- (d) Oxygen difluoride
- (e) Lithium chlorite
- (f) Cobalt(II) hydroxide
- (g) Gold(III) chloride
- (h) Ammonium sulfite
- (i) Manganese(II) oxide
- (j) Lead(II) sulfide

6.112 Why do most oxoanions have the same charges as the corresponding monatomic anions?

7

Formula Calculations

- 7.1 Formula Masses
- 7.2 Percent Composition
- 7.3 The Mole
- 7.4 Empirical Formulas
- 7.5 Molecular Formulas



A liquid sample, a solid sample, and a gaseous sample

Review Clues

- | | |
|--------------------|------------------------|
| Section 7.1 | Section 5.1, Chapter 6 |
| Section 7.2 | Section A1.1 |
| Section 7.3 | Sections 2.1, 3.4 |
| Section 7.4 | Section 3.1 |
| Section 7.5 | Section 5.5 |

Objectives

- | | |
|------------|---|
| 7.1 | To calculate a formula mass |
| 7.2 | To calculate the percent composition by mass from the formula of a compound |
| 7.3 | To use the basic chemical quantity—the mole—to make calculations convenient |
| 7.4 | To determine the empirical formula from percent composition or other mass-ratio data |
| 7.5 | To determine the molecular formula from percent composition and molecular mass data or from the empirical formula and molecular mass data |

The meaning of a chemical formula was discussed in Chapter 5, and we learned how to interpret formulas in terms of the numbers of atoms of each element per formula unit. In this chapter, we will learn how to calculate the number of grams of each element in any given quantity of a compound from its formula and to do other calculations involving formulas. Formula masses are presented in Section 7.1, and percent composition is considered in Section 7.2. Section 7.3 discusses the mole—the basic chemical quantity of any substance. Moles can be used to count atoms, molecules, or ions and to calculate the mass of any known number of formula units of a substance. Section 7.4 shows how to use relative mass data to determine empirical formulas, and the method is extended to molecular formulas in Section 7.5.

7.1 Formula Masses

Because each symbol in a formula represents an atom, which has a given average atomic mass, the formula as a whole represents a collection of atoms with a given formula mass. The **formula mass** (also called **formula weight**) is the sum of the atomic masses of all atoms of every element (not merely each type of atom) in a formula unit. In general, formula masses should be calculated to as many significant digits as are given in any data presented in a problem. For problems in which no data are given, at least three significant digits should be used in values from the periodic table. For example, we can calculate the formula mass for acetic acid, the major acid in vinegar, $\text{HC}_2\text{H}_3\text{O}_2$, as follows:

Number of atoms per formula unit	Atomic mass
4 H	$4 \times 1.01 \text{ amu} = 4.04 \text{ amu}$
2 C	$2 \times 12.0 \text{ amu} = 24.0 \text{ amu}$
2 O	$2 \times 16.0 \text{ amu} = 32.0 \text{ amu}$
Formula mass = 60.0 amu	

Because calculation of formula mass is essentially adding two or more numbers, the numbers to be added may be rounded to the same number of decimal places. For example, the four H atoms in the preceding calculation might have been included as 4.0 amu. Prior multiplication might affect the number of decimal places we retain in the atomic masses (see Problem 7.14).

The three types of formula masses correspond to the three types of formula units: (1) atomic masses (also called atomic weights), (2) **molecular masses** (also called **molecular weights**), and (3) formula masses for ionic compounds (also called formula weights). The term “atomic mass” may be used whether an atom is combined or not, but it always refers to the mass of one atom of an element.

EXAMPLE 7.1

- (a) What is the atomic mass of nitrogen?
- (b) What is the molecular mass of nitrogen?

Solution

- (a) 14.00 amu.
(b) 28.00 amu because nitrogen molecules contain two atoms each.

EXAMPLE 7.2

Why is it incorrect to refer to the molecular mass of $(\text{NH}_4)_2\text{SO}_4$?

Solution

$(\text{NH}_4)_2\text{SO}_4$ is an ionic compound. It does not have molecules, and thus does not have a molecular mass.

Practice Problem 7.2 Which of the following have molecular masses?

**EXAMPLE 7.3**

Calculate the formula mass of (a) $(\text{NH}_4)_2\text{SO}_3$ and (b) $\text{Fe}(\text{NO}_3)_2$.

Solution

(a) 2 N	2×14.01 amu	=	28.02 amu
8 H	8×1.008 amu	=	8.06 amu
1 S	1×32.06 amu	=	32.06 amu
3 O	3×16.00 amu	=	48.00 amu
Formula mass			= 116.14 amu
(b) 1 Fe	1×55.85 amu	=	55.85 amu
2 N	2×14.01 amu	=	28.02 amu
6 O	6×16.00 amu	=	96.00 amu
Formula mass			= 179.87 amu

Practice Problem 7.3 Calculate the formula mass of (a) $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ and (b) $\text{Na}_2\text{Cr}_2\text{O}_7$.

**Snapshot Review**

- ☐ The formula mass—atomic mass for atoms, molecular mass for molecules, and formula mass for ionic substances—is merely the sum of the atomic masses of every *atom* in the formula unit.

- A. Calculate the formula mass for each of the following substances and state which is an atomic mass, which is a molecular mass, and which is neither: (a) Ni, (b) Ni_3 , and (c) $\text{Ni}(\text{IO}_3)_2$.

7.2 Percent Composition

If we know the total mass of each element in a formula unit and we also know the mass of the entire formula unit, we can calculate the **percent composition** of the compound. We simply divide the total mass of each element by the total mass of the formula unit and multiply each quotient by 100% to convert it to a percentage. Together, all the percentages constitute the percent composition.

EXAMPLE 7.4

Calculate the percent composition of $\text{Fe}(\text{NO}_3)_2$.

Solution

The iron in one formula unit has a mass of 55.85 amu in a total mass of 179.87 amu, as calculated in Example 7.3(b). Iron's percent by mass is 100% times the mass of an iron atom divided by the formula mass:

$$\begin{aligned}\text{Percentage of iron} &= \frac{\text{mass of iron}}{\text{mass of } \text{Fe}(\text{NO}_3)_2} \times 100.00\% \\ &= \left(\frac{55.85 \text{ amu}}{179.87 \text{ amu}} \right) \times 100.00\% = 31.05\% \text{ Fe}\end{aligned}$$

The percentages of nitrogen and oxygen are calculated in the same way:

$$\begin{aligned}\text{Percentage of nitrogen} &= \left(\frac{28.02 \text{ amu}}{179.87 \text{ amu}} \right) \times 100.00\% = 15.58\% \text{ N} \\ \text{Percentage of oxygen} &= \left(\frac{96.00 \text{ amu}}{179.87 \text{ amu}} \right) \times 100.00\% = 53.37\% \text{ O}\end{aligned}$$

Notice that the *total* mass of nitrogen or oxygen in the formula unit, not the atomic mass of nitrogen or oxygen, is used in the calculation.

The sum of all the percentages of elements in any compound should be 100%:

$$31.05\% + 15.58\% + 53.37\% = 100.00\%$$

In general, the sum may not be exactly 100% because of prior rounding to the proper number of significant digits. If we get a total of 98% or 105%, we must look for an error. (Getting 100% does not guarantee that our percentages are correct, but getting a sum that is significantly different from 100% guarantees that something is *incorrect*.)

Practice Problem 7.4 Calculate the percent composition of $(\text{NH}_4)_3\text{PO}_4$.



Snapshot Review



- The percentage of an element in a compound is 100% times the ratio of the total mass of the element divided by the formula mass. The percent composition of the compound is the percentages of all the elements.
- It does not matter if the compound is covalent or ionic.

- A. Calculate the percent composition of each of (a) methyl alcohol, CH_4O , and (b) TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$.

7.3 The Mole

The atomic mass unit (amu) is an extremely small unit, suitable for measuring masses of individual atoms and molecules. However, to measure masses on laboratory balances takes a huge number of atoms, molecules, or formula units. Chemists have to weigh a large collection of formula units, so that the total mass is measurable on a laboratory balance. (If we try to weigh one grain of rice on a scale designed to weigh people, we will get an inkling of the problem of measuring the mass of one atom or molecule. See Figure 3.7.)

The **mole** (abbreviated mol) is the standard chemical unit used to measure the quantity of a substance. A mole is defined as the number of ^{12}C atoms in *exactly* 12 g of ^{12}C . The mole is equal to 6.0221367×10^{23} particles. Thus the mole is a number, essentially like a dozen, except very much larger. This number is about the number of grains of sand that would fit into a sphere the size of the Earth. (See Problem 2.154.) This number is known as **Avogadro's number**. Remember the value of this number to at least three significant digits.

Avogadro's number was set at 6.0221367×10^{23} so that the atomic mass of each element and the number of grams per mole of that element have the same numeric value, although in different units. The atomic mass of ^{12}C is 12.00 amu, and 12.00 g is the mass of 1.000 mol of ^{12}C . The formula mass of any compound or element is also equal to its number of grams per mole. The formula mass of a substance in units of grams per mole is called the **molar mass** of the substance. (Molar mass can be abbreviated MM.)

The mole is the basic unit of quantity of chemical substance.

The molar mass of any substance is equal to the number of grams per mole of that substance.



ENRICHMENT

It is also possible to think of a mole as the number of atomic mass units in 1 gram.

EXAMPLE 7.5

Use the value of Avogadro's number, the mass of one ^{12}C atom (exactly 12 amu), and the definition of a mole to calculate the number of atomic mass units per gram.

Solution

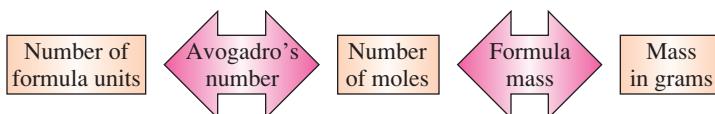
$$\frac{6.022 \times 10^{23} \text{ } ^{12}\text{C atoms}}{1 \text{ mol } ^{12}\text{C}} \left(\frac{1 \text{ mol } ^{12}\text{C}}{12.000 \text{ g}} \right) \left(\frac{12.000 \text{ amu}}{1 \text{ } ^{12}\text{C atom}} \right)$$

Avogadro's number Mass of Mass of
 1 mol 1 atom

$$= 6.022 \times 10^{23} \text{ amu/g}$$

The number of atomic mass units per gram is equal to Avogadro's number.

Practice Problem 7.5 Calculate the number of inches in 1 foot, knowing that a certain shoe box is 4.00 in. tall and that a stack of 1 dozen of these boxes is 4.00 ft tall.

7.3 ■ The Mole**189****Figure 7.1** Some Conversions Involving Moles**EXAMPLE 7.6**

Knowing that the formula mass of ethyl alcohol, $\text{C}_2\text{H}_6\text{O}$, is 46.0 amu, show that $\text{C}_2\text{H}_6\text{O}$ has a molar mass equal to 46.0 g/mol.

Solution

$$\frac{46.0 \text{ amu}}{1 \text{ formula unit}} \left(\frac{6.02 \times 10^{23} \text{ formula units}}{1 \text{ mol}} \right) \left(\frac{1.00 \text{ g}}{6.02 \times 10^{23} \text{ amu}} \right) = \frac{46.0 \text{ g}}{1 \text{ mol}}$$

Avogadro's number From Example 7.5

Practice Problem 7.6 The formula mass of H_3PO_4 is 98.0 amu. What is its molar mass (in grams per mole)?

We can use Avogadro's *number* as a conversion factor to convert moles to *numbers* of formula units, and vice versa. We can use the molar *mass* to convert moles to *masses*, and vice versa (Figure 7.1).

EXAMPLE 7.7

- (a) Calculate the number of molecules in 0.445 mol of C_4H_8 .
- (b) Calculate the mass of 0.445 mol of C_4H_8 .

Solution

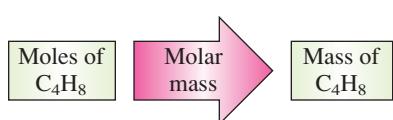
$$(a) 0.445 \text{ mol } \text{C}_4\text{H}_8 \left(\frac{6.02 \times 10^{23} \text{ molecules } \text{C}_4\text{H}_8}{1 \text{ mol } \text{C}_4\text{H}_8} \right) = 2.68 \times 10^{23} \text{ molecules } \text{C}_4\text{H}_8$$

- (b) The molar mass of C_4H_8 is $4(12.01 \text{ g}) + 8(1.008 \text{ g}) = 56.104 \text{ g}$.

$$0.445 \text{ mol } \text{C}_4\text{H}_8 \left(\frac{56.104 \text{ g } \text{C}_4\text{H}_8}{1 \text{ mol } \text{C}_4\text{H}_8} \right) = 25.0 \text{ g } \text{C}_4\text{H}_8$$

Practice Problem 7.7

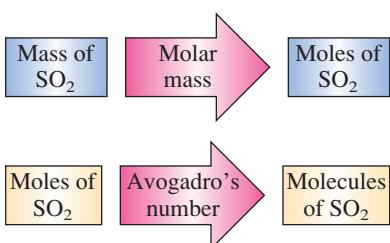
- (a) Calculate the number of moles of C_5H_{12} in 41.9 g of C_5H_{12} .
- (b) Calculate the number of moles of C_5H_{12} in a sample containing $7.15 \times 10^{23} \text{ C}_5\text{H}_{12}$ molecules.

**EXAMPLE 7.8**

Calculate the number of molecules of SO_2 in 41.31 g of SO_2 .

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CHAPTER 7 ■ Formula Calculations

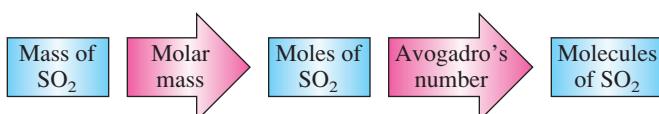
**Solution**

The molar mass of SO_2 is $32.06 \text{ g} + 2(16.00 \text{ g}) = 64.06 \text{ g}$. (The molar mass is calculated to four significant digits because the data in the problem are given to four significant digits.)

$$41.31 \text{ g } \text{SO}_2 \left(\frac{1 \text{ mol } \text{SO}_2}{64.06 \text{ g } \text{SO}_2} \right) = 0.64486 \text{ mol } \text{SO}_2$$

$$0.64486 \text{ mol } \text{SO}_2 \left(\frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol } \text{SO}_2} \right) = 3.883 \times 10^{23} \text{ molecules } \text{SO}_2$$

or

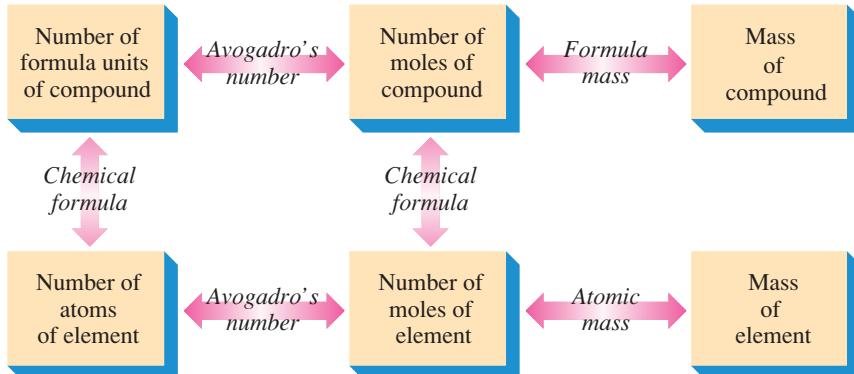


$$41.31 \text{ g } \text{SO}_2 \left(\frac{1 \text{ mol } \text{SO}_2}{64.06 \text{ g } \text{SO}_2} \right) \left(\frac{6.022 \times 10^{23} \text{ molecules } \text{SO}_2}{1 \text{ mol } \text{SO}_2} \right) = 3.883 \times 10^{23} \text{ molecules } \text{SO}_2$$

Practice Problem 7.8 Calculate the mass of 6.63×10^{24} molecules of diethyl ether, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_3$.

The chemical formula for a compound gives the ratio of atoms of each element in the compound to atoms of every other element in the compound. It also gives the ratio of dozens of atoms of each element in the compound to dozens of atoms of every other element in the compound. Moreover, it gives the ratio of *moles* of atoms of each element in the compound to *moles* of atoms of every other element in the compound. For example, a given quantity of H_2O has 2 mol of H atoms for every mole of O atoms, and a given quantity of CH_4 has 1 mol of C atoms for every 4 mol of H atoms. The mole ratio from the formula can be used as a factor to convert from moles of any element in the formula to moles of any other element or to moles of the formula unit as a whole. In Figure 7.2, these additional conversions have been added to those already presented in Figure 7.1.

Figure 7.2 Additional Conversions Involving Moles



EXAMPLE 7.9

Calculate the number of moles of hydrogen atoms in 6.170 mol of H₂O.

Solution

$$6.170 \text{ mol H}_2\text{O} \left(\frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right) = 12.34 \text{ mol H}$$

Factor from
chemical formula

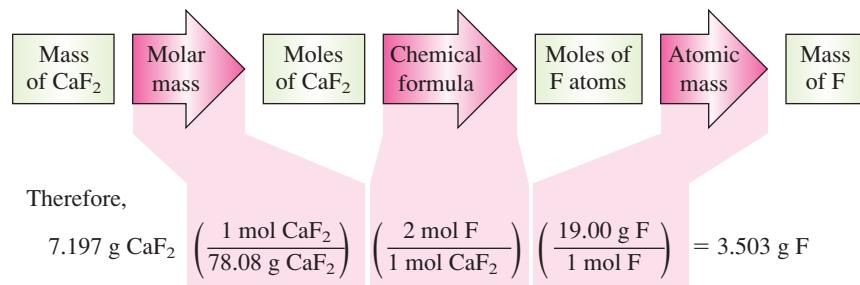
Practice Problem 7.9 Calculate the number of moles of aspirin, C₉H₈O₄, that contains 4.21×10^{23} oxygen atoms.

EXAMPLE 7.10

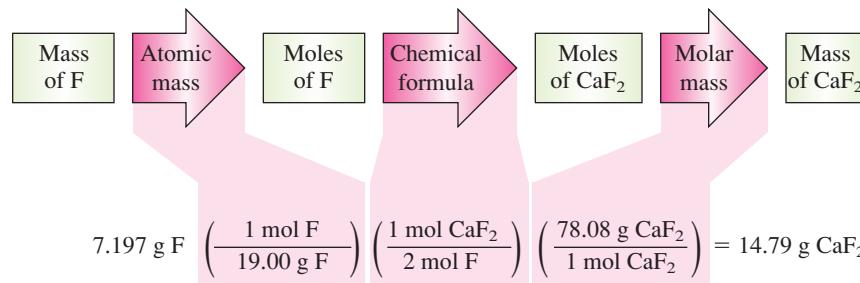
- (a) Calculate the number of grams of fluorine in 7.197 g of CaF₂.
 (b) Calculate the mass of CaF₂ that contains 7.197 g of fluorine.

Solution

- (a) The molar mass (atomic mass in grams per mole) of fluorine is 19.00 g/mol; the molar mass of CaF₂ is 78.08 g/mol.



(b)

**Practice Problem 7.10**

- (a) Calculate the mass of phosphorus in 1.50 kg of (NH₄)₃PO₄, a principal constituent of many fertilizers.
 (b) Calculate the mass of (NH₄)₃PO₄ that contains 1.50 kg of phosphorus.

The percent composition of a compound can be calculated in terms of molar masses instead of formula masses.

EXAMPLE 7.11

Calculate the percent composition of nitroglycerine, $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$, using molar masses instead of formula masses.

Solution

The mass of a mole of $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$ is

$$3(12.01 \text{ g}) + 5(1.008 \text{ g}) + 3(14.01 \text{ g}) + 9(16.00 \text{ g}) = 227.1 \text{ g}$$

The percentage of each element is given by

$$\left(\frac{3(12.01 \text{ g}) \text{ C}}{227.1 \text{ g } \text{C}_3\text{H}_5\text{N}_3\text{O}_9} \right) \times 100.0\% = 15.87\% \text{ C}$$

$$\left(\frac{5(1.008 \text{ g}) \text{ H}}{227.1 \text{ g } \text{C}_3\text{H}_5\text{N}_3\text{O}_9} \right) \times 100.0\% = 2.219\% \text{ H}$$

$$\left(\frac{3(14.01 \text{ g}) \text{ N}}{227.1 \text{ g } \text{C}_3\text{H}_5\text{N}_3\text{O}_9} \right) \times 100.0\% = 18.51\% \text{ N}$$

$$\left(\frac{9(16.00 \text{ g}) \text{ O}}{227.1 \text{ g } \text{C}_3\text{H}_5\text{N}_3\text{O}_9} \right) \times 100.0\% = 63.41\% \text{ O}$$

$$\text{Total} = 100.01\%$$

Practice Problem 7.11 Calculate the percent composition of trinitrotoluene, TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$.



Snapshot Review



ChemSkill Builder 4.1

- The mole is Avogadro's number of formula units—equal to 6.02×10^{23} units.
 - A mole of a substance has a mass (in grams) equal to its formula mass, called the *molar mass*, which can be used as a factor in solving problems.
- A. A mole of a substance with formula mass 52.4 amu has (a) how many formula units? (b) what mass?
 - B. Calculate the mass of 3.50 mol of the amino acid alanine, $\text{C}_3\text{H}_7\text{NO}_2$.
 - C. Calculate the number of molecules in 3.50 mol of alanine.

7.4 Empirical Formulas

The **empirical formula** of a compound is the formula that gives the lowest whole-number ratio of atoms of all the elements. For example, the empirical formula of fruit sugar, fructose, $\text{C}_6\text{H}_{12}\text{O}_6$, is CH_2O . The simplest ratio of carbon

7.4 ■ Empirical Formulas**193**

to hydrogen to oxygen atoms in fructose is 1 to 2 to 1. An empirical formula always has the smallest integral subscripts that give the correct ratio of atoms of the elements.

EXAMPLE 7.12

Write the empirical formulas for the compounds containing carbon and hydrogen in the following ratios:

- (a) 2 mol carbon to 3 mol hydrogen
- (b) 1.0 mol carbon to 1.5 mol hydrogen
- (c) 0.1712 mol carbon to 0.2568 mol hydrogen

Solution

- (a) The mole ratio is 2:3, so the empirical formula is C₂H₃.
- (b) The mole ratio given is not integral, but we can multiply each value by 2 to get an integral ratio of 2:3. The empirical formula is again C₂H₃.
- (c) This mole ratio is not integral, and this time it is more difficult to make it so. If we divide both values by the magnitude of the smaller one, we can get closer to an integral ratio:

$$\frac{0.1712 \text{ mol C}}{0.1712} = 1.000 \text{ mol C} \quad \frac{0.2568 \text{ mol H}}{0.1712} = 1.500 \text{ mol H}$$

Now multiply by 2, as in part (b):

$$\frac{1.000 \text{ mol C}}{1.500 \text{ mol H}} = \frac{2 \text{ mol C}}{3 \text{ mol H}}$$

This ratio is also 2:3, and again the empirical formula is C₂H₃.

Practice Problem 7.12 Write the empirical formula for a compound consisting of elements A and B, for each ratio of A to B:

- | | | | |
|------------|------------|------------|------------|
| (a) 1:1 | (b) 1:1.5 | (c) 1:1.33 | (d) 1:1.67 |
| (e) 1:1.25 | (f) 1:1.75 | (g) 1:1.20 | (h) 1:1.40 |

We can find the empirical formula from percent composition data. The empirical formula represents a ratio; therefore, it does not depend on the size of the sample under consideration. Because the empirical formula reflects a *mole* ratio, and percent composition data are given in terms of *mass*, we have to convert the masses to moles. We then convert the mole ratio, which is unlikely to be an integral ratio, to the smallest possible whole-number ratio, from which we write the empirical formula.

The steps we take to obtain an empirical formula from percent composition data are given in the left column (Steps) that follows. In the right column (Example), the empirical formula of a compound containing 39.2% phosphorus and 60.8% sulfur is calculated.

194**CHAPTER 7 ■ Formula Calculations****Steps**

Step 1: Change the percentages to numbers of grams (by assuming that 100.00 g of sample is present). (On exams, state that assumption.)

Step 2: For each element, convert the number of grams to the number of moles.

Step 3: Try to get an integral ratio by dividing *all* the numbers of moles by the magnitude of the smallest number of moles. This will make at least one number an integer.

Step 4: If necessary, multiply *all* the numbers of moles by the same small integer to clear fractions. Round off the result to an integer only when the number of moles is within 1% of the integer. Always use at least three significant digits in empirical formula calculations; otherwise, rounding errors may produce an incorrect empirical formula.

Never round off more than 1%.

Example

Because the size of the sample does not matter in determining an empirical formula, we can assume a 100.00-g sample. That way, the percentages given are automatically equal numerically to the numbers of grams of the elements. For example:

$$100.00 \text{ g compound} \left(\frac{39.2 \text{ g P}}{100.00 \text{ g compound}} \right) = 39.2 \text{ g P}$$

From the percentage

39.2 g P and 60.8 g S

$$39.2 \text{ g P} \left(\frac{1 \text{ mol P}}{30.97 \text{ g P}} \right) = 1.266 \text{ mol P}$$

$$60.8 \text{ g S} \left(\frac{1 \text{ mol S}}{32.06 \text{ g S}} \right) = 1.896 \text{ mol S}$$

$$\frac{1.266 \text{ mol P}}{1.266} = 1.00 \text{ mol P}$$

$$\frac{1.896 \text{ mol S}}{1.266} = 1.50 \text{ mol S}$$

$$1.00 \text{ mol P} \times 2 = 2.00 \text{ mol P}$$

$$1.50 \text{ mol S} \times 2 = 3.00 \text{ mol S}$$

The empirical formula is P_2S_3 .

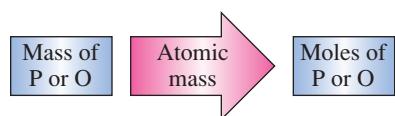
EXAMPLE 7.13

Determine the empirical formula of a compound that has a percent composition of 43.7% P and 56.3% O.

Solution

Merely change the percentage signs to grams:

$$43.7 \text{ g P} \quad \text{and} \quad 56.3 \text{ g O}$$

7.4 ■ Empirical Formulas**195**

Then convert the numbers of grams to moles:

$$43.7 \text{ g P} \left(\frac{1 \text{ mol P}}{30.97 \text{ g P}} \right) = 1.411 \text{ mol P}$$

$$56.3 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 3.519 \text{ mol O}$$

That gives the mole ratio of oxygen to phosphorus,

$$1.411 \text{ mol P} \quad \text{to} \quad 3.519 \text{ mol O}$$

but it is not an integral ratio. The best way to try to get an integral ratio is to divide *each* of the numbers of moles by the magnitude of the lower number of moles:

$$\frac{1.411 \text{ mol P}}{1.411} \quad \text{to} \quad \frac{3.519 \text{ mol O}}{1.411}$$

which simplifies to

$$1.00 \text{ mol P} \quad \text{to} \quad 2.494 \text{ mol O}$$

The numbers of moles are still not all integers, but we can see that if we multiply *each* of them by 2, we will get an integral ratio:

$$2(1.00) \text{ mol P} \quad \text{to} \quad 2(2.494) \text{ mol O}$$

which simplifies to

$$2 \text{ mol P} \quad \text{to} \quad 5 \text{ mol O}$$

The ratio is 2 mol P to 5 mol O, and the empirical formula is P_2O_5 . (Remember to write the P first, as stated in Section 5.1.)

Note that we do *not* use the molecular mass of an oxygen *molecule* (or any other diatomic molecule) in empirical formula calculations because we are interested in the mole ratio involving oxygen *atoms*. Molecular oxygen, O_2 , has nothing to do with empirical formula calculations.

Practice Problem 7.13 Determine the empirical formula of manganese(II) pyrophosphate, a compound containing 38.71% Mn, 21.82% P, and 39.46% oxygen.

We can obtain an empirical formula from mass data instead of a percent composition.

EXAMPLE 7.14

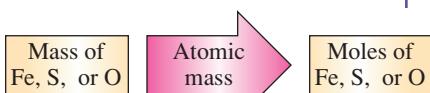
Determine the empirical formula of a compound if a sample of the compound contains 3.524 g of iron, 3.034 g of sulfur, and 4.542 g of oxygen.

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CHAPTER 7 ■ Formula Calculations

Solution

Because the data are given in grams rather than percentages, we do not have to do the first step of changing to grams. Simply change the grams to moles:



$$3.524 \text{ g Fe} \left(\frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \right) = 0.06310 \text{ mol Fe}$$

$$3.034 \text{ g S} \left(\frac{1 \text{ mol S}}{32.06 \text{ g S}} \right) = 0.09464 \text{ mol S}$$

$$4.542 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 0.2839 \text{ mol O}$$

The mole ratios are

$$0.06310 \text{ mol Fe} \quad \text{to} \quad 0.09464 \text{ mol S} \quad \text{to} \quad 0.2839 \text{ mol O}$$

Dividing by the magnitude of the smallest number of moles yields

$$1.000 \text{ mol Fe} \quad \text{to} \quad 1.500 \text{ mol S} \quad \text{to} \quad 4.499 \text{ mol O}$$

Multiplying each of these numbers by 2 yields

$$2 \text{ mol Fe} \quad \text{to} \quad 3 \text{ mol S} \quad \text{to} \quad 9 \text{ mol O}$$

and the empirical formula is $\text{Fe}_2\text{S}_3\text{O}_9$.

Practice Problem 7.14 Determine the empirical formula of “hypo,” a compound used in photographic development, if a sample contains 2.453 g of sodium, 3.422 g of sulfur, and 2.561 g of oxygen.

Most ionic compounds such as NaCl , MgBr_2 , Al_2S_3 , and NH_4NO_3 are identified by their empirical formulas, and such formulas are used for calculations involving these compounds. Compounds such as K_2O_2 , Hg_2Cl_2 , $\text{K}_2\text{C}_2\text{O}_4$, and $\text{Na}_2\text{S}_2\text{O}_8$, having certain polyatomic ions, are exceptions. For molecular substances, empirical formulas are used as a basis in determining molecular formulas, as described in the next section.

**Snapshot Review**

ChemSkill Builder 4.6

- An empirical formula—the simplest formula for a compound—is obtained from the integral mole ratio of its elements.
- To determine an empirical formula, calculate the number of moles of each element in a sample (arbitrarily choose 100 g if percentages are given), divide each of them by the smallest number of moles, and then multiply by some small integer if necessary to get integral numbers of moles.

- A. Calculate the empirical formula of a compound consisting of 87.73% C and 12.27% H.

ITEM OF INTEREST

A forensic chemist analyzes some white pills found in an aspirin bottle on an unidentified dead body. One pill is found to consist of 60.05% potassium, 18.44% carbon, and 21.51% nitrogen. A second pill contains 60.00% carbon, 4.48% hydrogen, and 35.53% oxygen and has a molar mass of 180 g/mol. Can these data help the forensic chemist deduce whether the death was accidental, murder, or suicide?

The percent composition shows that the first pill is KCN—potassium cyanide. The second pill— $C_9H_8O_4$ —could be aspirin. It looks like murder because a cyanide pill is not likely to get into an aspirin bottle accidentally, and a person committing suicide is not likely to put a cyanide pill in an aspirin bottle. As in most human affairs, however, there is no certainty to this conclusion, given only the data presented.

7.5 Molecular Formulas

The molecular formula gives the number of atoms of each element in one molecule.

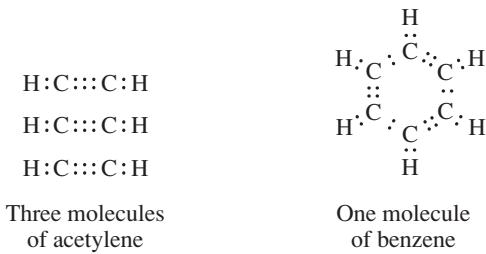
The **molecular formula** gives the number of atoms of each element in one molecule. This information includes (1) the ratio of atoms of each element to atoms of every other element in a compound, (2) the ratio of atoms of each element to molecules of the compound, and (3) the corresponding mole ratios. For example, C_2H_4 has a ratio of 2 mol of carbon atoms to 4 mol of hydrogen atoms (or more simply 1 mol of carbon atoms to 2 mol of hydrogen atoms). It also has a ratio of 2 mol of carbon atoms to 1 mol of C_2H_4 molecules and 4 mol of hydrogen atoms to 1 mol of C_2H_4 molecules. The molecular formula is always an integral multiple (1, 2, 3, . . .) of the empirical formula. Thus, the molecular formula gives all the information that the empirical formula gives plus the ratio of the number of moles of each element to moles of the compound. Molecular formulas can be written only for compounds that exist in the form of molecules.

If we calculated the percent compositions of C_2H_2 and C_6H_6 (Figure 7.3), we would find that both have the same percentages of carbon and the same percentages of hydrogen (compare Problem 7.100 at the end of the chapter). Both have the same empirical formula—CH. This result means that we cannot tell these two compounds apart from percent composition data alone. However, if we also have a molar mass, we can use that information with the percent composition data to determine not only the empirical formula but also the molecular formula.

Determining the molecular formula of a compound involves first determining the empirical formula and then determining how many empirical formula units are in a molecule of the compound.

Figure 7.3 Percent Compositions of Acetylene and Benzene

Consider a sample containing three molecules of acetylene, C_2H_2 , and another sample containing one molecule of benzene, C_6H_6 . Because both samples have the same number of carbon atoms (six) and both have the same number of hydrogen atoms (six), both obviously have the same percent composition. Because percent composition is an intensive property, the two compounds have the same percent composition, no matter how many molecules are present.

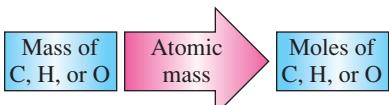


EXAMPLE 7.15

Determine the molecular formula of styrene, used to prepare the plastic wrapping material polystyrene. It is a compound of carbon and hydrogen only that contains 92.26% carbon, and has a molar mass of 104 g/mol.

Solution

Because the total of the percentages must be 100.00%, the percentage of hydrogen in the compound must be 100.00% total – 92.26% C = 7.74% H.



$$92.26 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.682 \text{ mol C}$$

$$7.74 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 7.68 \text{ mol H}$$

The ratio is 1 mol C to 1 mol H. The empirical formula is CH. Next, the molar mass (the number of grams per mole) is divided by the mass of a mole of empirical formula units to get the number of empirical formula units per molecule. The mass of 1.00 mol of CH formula units is

$$12.01 \text{ g} + 1.008 \text{ g} = 13.02 \text{ g}$$

Thus,

$$\frac{104 \text{ g/mol of molecules}}{13.02 \text{ g/mol of empirical formula units}} = \frac{8 \text{ mol of empirical formula units}}{1 \text{ mol of molecules}}$$

The empirical formula CH is multiplied by 8 to get the molecular formula, C₈H₈.

Practice Problem 7.15 Determine the molecular formula of a hydrocarbon (a compound of carbon and hydrogen only) that contains 89.94% carbon and has a molar mass of 80.2 g/mol.

One important use of molecular formulas is to identify molecular compounds. If a chemist isolates a useful substance from a plant or animal source, the chemist wants to know the formula so that the compound can be made in the laboratory. Making a compound is often more convenient and more economical than obtaining it from its natural source. Certain vitamins and penicillin are examples of such compounds.

**Snapshot Review**

ChemSkill Builder 4.6

- Molecular formulas apply to covalent substances only.
- A molecular formula may be calculated from the empirical formula and the molecular mass by dividing the molecular mass by the mass of one empirical formula unit, which gives the number of empirical formula units per molecule.

- A. Calculate the molecular formula of a compound whose empirical formula is CH₂ and whose molecular mass is 126 amu.
- B. One allotropic form of sulfur has a formula S_x, where x is a small integer. Its molecular mass is 256 amu. Calculate its molecular formula.

■ Items for Special Attention

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Key Terms

Key terms are defined in the Glossary.

Avogadro's number (7.3)
empirical formula (7.4)
formula mass (7.1)
formula weight (7.1)

molar mass (7.3)
mole (7.3)
molecular formula (7.5)

molecular mass (7.1)
molecular weight (7.1)
percent composition (7.2)

Symbols/Abbreviations

MM (molar mass) (7.3)

mol (mole) (7.3)

Summary

The formula mass (formula weight) of a substance is determined by adding the atomic masses (atomic weights) of each *atom* (not each element) in a formula unit. Molecular mass is one type of formula mass (for substances that form molecules) and is calculated in the same way as the formula mass for an ionic compound. For example, the formula mass of NH₃ is 17.0 amu, the atomic mass of three hydrogen atoms plus that of one nitrogen atom. Three or more significant digits should be used to report formula masses. (Section 7.1)

The percent composition is the percentage of each element in a compound. The percentage of an element in a compound is calculated by finding the ratio of the total mass of that element to the formula mass and multiplying that ratio by 100%. The percentages of all the elements in a compound should total 100% (within less than 1%). (Section 7.2)

The mole is defined as the number of ¹²C atoms in exactly 12 g of ¹²C, which is 6.02×10^{23} —Avogadro's number. Equal numbers of moles of two (or more) different substances have the same number of formula units but *not* the same mass. The molar mass is the mass in grams of one mole of a substance. The number of grams per mole—the molar mass—is a frequently used conversion factor, used for converting between grams and moles. (Section 7.3)

An empirical formula gives the lowest integral mole ratio of atoms of all the elements in a compound. An empirical formula may be determined from a percent composition by changing the percentages to numbers of grams (by assuming a 100-g sample) and then dividing the number of grams of each element by its atomic mass in grams. The nonintegral mole ratio that results is converted to an integral mole ratio by dividing each of the numbers of moles by the magnitude of the smallest, and then, if necessary, multiplying every one of the quotients by the same small whole number. Never round off by more than 1% during this procedure. If data are given in grams rather than as a percent composition, simply omit the first step. (Section 7.4)

Molecular formulas give all the information that empirical formulas do, plus the ratio of the number of moles of each element to the number of moles of the compound. (Molecular formulas are used only for molecular substances, not ionic substances.) A molecular formula can be determined from the empirical formula of the compound and its formula mass: First, divide the formula mass by the mass in amu of one empirical formula unit, which will result in a small integer. Then, multiply each subscript of the empirical formula by that integer. (Section 7.5)

Items for Special Attention

- A formula gives the mole ratio of one element to another and the mole ratio of each element to 1 mol of compound. With atomic masses and a chemical formula, we can calculate mass ratios—for example, percent by mass—rather easily.
- To convert to or from moles, use Avogadro's number for numbers of formula units, or the molar mass to convert to or from a mass. Use the subscripts in the formula to convert from moles of atoms of an element to or from moles of

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- atoms of another element or moles of entire formula units (see Figure 7.2). We must consider the units (for example, moles of atoms versus number of individual atoms versus mass of the atoms) as well as the species (for example, atoms of an element versus molecules of that element). These differences are apparent in the questions: “How many atoms of oxygen are in 2.00 mol of oxygen molecules?” and “What is the mass of the oxygen atoms in 1.00×10^{23} water molecules?”
- The most important skill learned in this chapter may be the ability to convert from grams to moles of a substance, and vice versa.

- Do not use the term “molecule” or “molecular mass” when discussing ionic compounds, because they do not exist as molecules.
- The unit usually used for the mass of a small number of atoms, molecules, or formula units is the amu, which is a very small fraction of a gram (about 10^{-24} g). The unit ordinarily used for the mass of molar quantities of a substance is the gram.
- The percentages of the elements making up any compound must total 100%. If the percentages of all but one element are given, the percentage of that element can easily be calculated.

Answers to Snapshot Reviews

- 7.1 A. (a) 58.71 amu, atomic mass
 (b) 394.7 amu, molecular mass
 (c) 408.5 amu, neither
 All three are formula masses.

7.2 A. (a) $\%C = \left(\frac{12.01 \text{ amu}}{32.04 \text{ amu}} \right) 100\% = 37.48\% C$
 $\%H = \left(\frac{4.032 \text{ amu}}{32.04 \text{ amu}} \right) 100\% = 12.58\% H$
 $\%O = \left(\frac{16.00 \text{ amu}}{32.04 \text{ amu}} \right) 100\% = 49.94\% O$
 (b) $\%C = \left(\frac{7[12.01 \text{ amu}]}{227.14 \text{ amu}} \right) 100\% = 37.01\% C$
 $\%H = \left(\frac{5[1.008 \text{ amu}]}{227.14 \text{ amu}} \right) 100\% = 2.219\% H$
 $\%N = \left(\frac{3[14.01 \text{ amu}]}{227.14 \text{ amu}} \right) 100\% = 18.50\% N$
 $\%O = \left(\frac{6[16.00 \text{ amu}]}{227.14 \text{ amu}} \right) 100\% = 42.26\% O$

7.3 A. (a) 6.02×10^{23} (b) 52.4 g
 B. $3.50 \text{ mol C}_3\text{H}_7\text{NO}_2 \left(\frac{89.0 \text{ g C}_3\text{H}_7\text{NO}_2}{1 \text{ mol C}_3\text{H}_7\text{NO}_2} \right)$
 $= 312 \text{ g C}_3\text{H}_7\text{NO}_2$

C.

$$3.50 \text{ mol C}_3\text{H}_7\text{NO}_2 \left(\frac{6.02 \times 10^{23} \text{ molecules C}_3\text{H}_7\text{NO}_2}{1 \text{ mol C}_3\text{H}_7\text{NO}_2} \right)$$
 $= 2.11 \times 10^{24} \text{ molecules C}_3\text{H}_7\text{NO}_2$

7.4 A. $87.73 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.305 \text{ mol C}$
 $12.27 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 12.17 \text{ mol H}$

The mole ratio of H to C is
 $12.17/7.305 = 1.666/1 = 5/3$.
 The empirical formula is C_3H_5 .

- 7.5 A. The empirical formula mass is 14.0 amu and the molecular mass is 126 amu, so there are $(126 \text{ amu})/(14.0 \text{ amu}) = 9$ empirical formula units per molecule. The molecular formula is C_9H_{18} .
 B. The empirical formula for sulfur is S, with mass 32.06 amu. There are $256 \text{ amu}/32.06 \text{ amu} = 8$ empirical formula units per molecule. S_8 is the molecular formula.

Self-Tutorial Problems

- 7.1 What small integer should we multiply each of the following ratios by to get a whole-number ratio? What ratio results in each case?

(a) $\frac{1.50}{1}$	(b) $\frac{2.25}{1}$	(c) $\frac{3.33}{1}$
(d) $\frac{3.67}{1}$	(e) $\frac{2.75}{1}$	(f) $\frac{1.20}{1}$

- 7.2 What small integer should we multiply each of the following ratios by to get a whole-number ratio? What ratio results in each case?

(a) $\frac{2.50}{1}$	(b) $\frac{1.33}{1}$	(c) $\frac{1.40}{1}$
(d) $\frac{3.25}{1}$	(e) $\frac{2.167}{1}$	(f) $\frac{1.75}{1}$

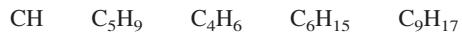
■ Self-Tutorial Problems

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- 7.3** For each of the following, select the proper units from the following list: amu, grams, grams/mole.
- Mass
 - Atomic mass
 - Molecular mass
 - Formula mass
 - Molar mass
- 7.4** For this problem, assume that all the socks are identical.
- How many pairs of socks are in 1.5 dozen pairs of socks?
 - How many socks are in 1.5 dozen socks?
 - How many pairs of socks are in 1.5 dozen socks?
 - How many socks are in 1.5 dozen pairs of socks?
 - How many dozen pairs of socks are in 1.5 dozen socks?
 - How many dozen socks are in 1.5 dozen pairs of socks?
- 7.5**
- How many chlorine molecules are in 1.50 mol of chlorine molecules?
 - How many chlorine atoms are in 1.50 mol of chlorine, atoms?
 - How many chlorine molecules are in 1.50 mol of bonded chlorine atoms?
 - How many chlorine atoms are in 1.50 mol of chlorine molecules?
 - How many moles of chlorine molecules are in 1.50 mol of bonded chlorine atoms?
 - How many moles of chlorine atoms are in 1.50 mol of chlorine molecules?
- 7.6** A 100-g sample of a certain compound contains 92.3% carbon. What percentage of carbon is contained in a 29.7-g sample of the same compound? What mass?
- 7.7**
- Compare the mass of two dozen socks rolled into pairs with the mass of the same socks unrolled.
 - Compare the mass of two dozen socks with the mass of two dozen pairs of socks.
 - Compare the mass of 2.00 mol of nitrogen atoms with that of the same atoms bonded into N_2 molecules.
 - Compare the mass of 2.00 mol of nitrogen atoms with that of 2.00 mol of nitrogen molecules.
- 7.8**
- If a certain atom has a mass of 19.0 amu, what is the mass in grams of 1.00 mol of these atoms?
 - If a certain atom has a mass of 12.0 amu, what is the mass in grams of 1.00 mol of these atoms?
 - If a certain atom has a mass of 238 amu, what is the mass in grams of 1.00 mol of these atoms?
 - Explain your results.
- 7.9** Which weighs more—a dozen grapefruit or a dozen cherries? Which contains the greater number of fruits?
- 7.10**
- If a shirt box is 1.0 in. high, how many feet high is a stack of a dozen shirt boxes?
 - If a shoe box is 4.0 in. high, how many feet high is a stack of a dozen shoe boxes?
 - If a hat box is 7.0 in. high, how many feet high is a stack of a dozen hat boxes?
 - Explain your results.
- 7.11** What information do you need to determine each of the following?
- A formula mass
 - An empirical formula
 - A molecular formula
- 7.12** What conversion factor is used to convert a number of moles of a substance to (a) the number of grams of the substance? (b) the number of formula units of the substance?
- 7.13** What conversion factor(s) is (are) used to convert a number of formula units of a substance to a mass of that substance?
- 7.14** Calculate the formula mass of each of the following to two decimal places twice, first by rounding each atomic mass to two decimal places, and second by using the entire number of significant digits in the atomic masses and rounding the formula mass:
- $C_{12}H_{26}$
 - $KClO_4$
 - PCl_3
- 7.15** Which of the following substances have molecular masses? Which have molar masses?
- BaH₂ CCl₄ C₂H₄ Ne S₈
- 7.16** Which of the following substances have molecular masses? Which have molar masses?
- NaCl P₂O₃ (NH₄)₂SO₄ Hg
- 7.17** What is a synonym for molar mass (a) for molecules? (b) for atoms? (c) for ionic compounds? What is a synonym for formula mass (d) for molecules? (e) for atoms? (f) for ionic compounds?
- 7.18** How many moles of chlorine atoms are present in 1.00 mol of $Al(ClO_3)_3$?
- 7.19** How many moles of $(NH_4)_2SO_4$ contain 1.00 mol of hydrogen atoms?
- 7.20** Is molar mass an intensive or extensive property?
- 7.21** What is the molar mass of (a) a 3.00 mol sample of NH₃? (b) a 1.50 mol sample of NH₃? (c) a 0.125 mol sample of NH₃?
- 7.22**
- What is the difference between the atomic mass of nitrogen and the molecular mass of nitrogen?
 - Why is the phrase “molar mass of nitrogen” ambiguous?
 - To what does “molar mass of nitrogen gas” refer?

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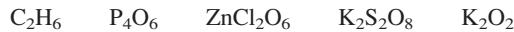
7.23 Which of the following are empirical formulas?



7.24 Which of the following are empirical formulas?



7.25 Which of the following formulas identify ionic compounds but are not empirical formulas?



7.26 What is the empirical formula of each of the following?

- (a) C₈H₁₂ (b) C₈H₁₂O₄
(c) C₃H₆O₃ (d) C₁₂H₂₂O₁₁

7.27 State whether the percent composition, the empirical formula, or the molecular formula gives the information specified in each of the following parts.

- (a) Ratio of moles of each element to moles of compound
(b) Ratio of moles of each element to each other element, and no more
(c) Ratio of masses of each element to mass of compound

7.28 What can we determine from percent composition data?

CHAPTER 7 ■ Formula Calculations

7.29 What information is given in the formula Na₂Cu(CN)₄?

7.30 Which of the following formulas identify ionic compounds but are not empirical formulas?



7.31 Calculate the molar mass of a compound if 2.50 mol has a mass of 155 g.

7.32 How many moles of atoms of each element are present in 1.00 mol of each of the following compounds?

- (a) CH₃CH₂NH₂ (b) In(C₂H₃O₂)₃
(c) Na₃CoF₆ (d) Co(NH₃)₆PO₄

7.33 How many moles of atoms of each element are present in 1.00 mol of each of the following compounds?

- (a) KHCO₃·MgCO₃·4H₂O (b) (NH₄)₂C₂O₄
(c) C₆H₁₂O₆ (d) Co₂(CO)₉

7.34 How many moles of atoms of each element are present in 1.00 mol of each of the following compounds?

- (a) Iron(III) chloride
(b) Ammonium sulfate
(c) Barium sulfide

Problems

7.1 Formula Masses

7.35 What is the smallest formula mass known for (a) any atom and (b) any molecule?

7.36 Calculate the formula mass of each of the following compounds to one decimal place:

- (a) NaHCO₃ (b) Ca(CNS)₂
(c) (NH₄)₂SO₃ (d) Na₃PO₄
(e) C₈H₁₈ (f) AsCl₃

7.37 Calculate the formula mass of each of the following substances:

- (a) Ba(CN)₂ (b) (NH₄)₂Cr₂O₇
(c) Co(ClO₃)₃ (d) UF₆
(e) BaCO₃ (f) P₄

7.38 Calculate the formula mass of (a) CuSO₄·5H₂O
(b) PbSiF₆·4H₂O.

7.39 Calculate the formula mass of each of the following compounds to one decimal place:

- (a) Ammonium sulfite
(b) Cobalt(II) sulfate
(c) Arsenic tribromide

7.2 Percent Composition

7.40 Calculate the percent composition of thiamine (a vitamin of the B complex family), C₁₂H₁₇N₄OSCl.

7.41 Calculate the percent composition of cholesterol, C₂₇H₄₅OH.

7.42 Calculate the percent composition of aspirin, C₉H₈O₄.

7.43 Calculate the percent composition of vitamin B₁₂, C₆₃H₉₀CoN₁₄P.

7.44 Calculate the percent compositions of pentene, C₅H₁₀, and cycloheptane, C₇H₁₄. Compare the values, and explain the results.

7.45 Calculate the percent compositions of cyclooctatetrene, C₈H₈, and benzene, C₆H₆. Compare the values, and explain the results.

7.46 Calculate the percent composition of ammonium monohydrogen phosphate.

7.47 Calculate the percent composition of (a) sodium dichromate and (b) potassium permanganate.

7.48 Calculate the percent composition of ethylene glycol, C₂H₆O₂, commonly used as a permanent antifreeze in cars.

■ Problems

- 7.49 Calculate the percent chlorine in DDT, $C_{14}H_9Cl_5$, an insecticide that has been discontinued because it does not biodegrade.
- 7.50 Calculate the percent composition of niacin, a B-complex vitamin, $C_6H_5NO_2$.
- 7.51 Calculate the percent composition of vitamin E, $C_{29}H_{50}O_2$.

7.3 The Mole

- 7.52 Calculate the formula mass and the molar mass of each of the following compounds to three significant figures:
 (a) $(NH_4)_2CO_3$ (b) $Ba(ClO_3)_2$ (c) CaC_2O_4
- 7.53 Calculate the number of grams of acetic acid, $HC_2H_3O_2$, in 1.76 mol of acetic acid.
- 7.54 Calculate the number of moles of butane, C_4H_{10} , in 151 g of butane.
- 7.55 Calculate the mass of 1.25 mol of (a) unbonded oxygen atoms, (b) oxygen atoms bonded into O_2 molecules, and (c) O_2 molecules.
- 7.56 Calculate the number of moles of glucose, a simple sugar, $C_6H_{12}O_6$, in 283.5 g (10.00 oz).
- 7.57 Calculate the number of grams of acetaldehyde, C_2H_4O , in 0.848 mol of acetaldehyde.
- 7.58 Calculate the number of moles of methane (natural gas), CH_4 , in 175 g of methane.
- 7.59 Calculate the number of moles in 12.9 g of a compound with a molar mass of 62.0 g/mol.
- 7.60 Calculate the number of moles in 1.93 g of a compound with a molar mass of 98.0 g/mol.
- 7.61 Calculate the mass in grams of (a) one oxygen atom. (b) one oxygen molecule.
- 7.62 Calculate the number of molecules in 12.9 g of a compound with a molar mass of 64.0 g/mol.
- 7.63 Calculate the mass of a sample of fruit sugar, fructose, $C_6H_{12}O_6$, containing 2.65×10^{20} molecules.
- 7.64 Calculate the number of grams in 2.76 mol of ethyl alcohol, C_2H_5OH .
- 7.65 Calculate the number of molecules in 6.50 mol of CH_4 .
- 7.66 (a) Calculate the number of moles that contain 9.25×10^{20} formula units of $(NH_4)_2SO_4$.
 (b) Calculate the number of molecules in 1.67 mol of trinitrotoluene, TNT, $C_7H_5N_3O_6$.
- 7.67 Calculate the mass of a sample of table sugar, sucrose, $C_{12}H_{22}O_{11}$, containing 1.91×10^{24} molecules.
- 7.68 Calculate the mass of 6.68×10^{23} molecules of PCl_3 .
- 7.69 (a) Calculate the number of moles of C_2H_4 in 44.7 g of C_2H_4 .
 (b) Calculate the number of moles of carbon atoms in 44.7 g of C_2H_4 .
 (c) Calculate the number of individual carbon atoms in 44.7 g of C_2H_4 .
- 7.70 Calculate the number of carbon atoms in 1.77 mol of butene, C_4H_8 .
- 7.71 Calculate the number of hydrogen atoms in 1.11 mol of acetaldehyde, C_2H_4O .
- 7.72 Calculate the number of grams of hydrogen in 4.11 mol of ammonia.
- 7.73 Calculate the mass of hydrogen in 6.92 g of CH_4 , methane (natural gas).
- 7.74 Calculate the number of grams of oxygen in 7.42 mol of Na_3BO_3 .
- 7.75 Calculate the number of hydrogen atoms in 41.4 g of ethyl alcohol, C_2H_6O .
- 7.76 Calculate the number of moles of H_3PO_4 that contains 6.78×10^{24} oxygen atoms.
- 7.77 Calculate the number of moles of ammonium chloride that contains 1.37×10^{24} hydrogen atoms.
- 7.78 Calculate the mass of aluminum chloride that contains 2.22×10^{23} chlorine atoms.
- 7.79 Calculate the number of grams of oxygen in 1.63 mol of $Al(ClO_4)_3$.
- 7.80 Calculate the number of hydrogen atoms in 125 g of benzene, C_6H_6 .
- 7.81 Calculate the mass of $Cr(ClO_2)_2$ that contains 5.57×10^{22} chlorine atoms.
- 7.82 Calculate the number of molecules of C_5H_{12} containing 1.44×10^{25} C atoms.
- 7.83 Calculate the mass of N in 4.75×10^{23} formula units of Mg_3N_2 .
- 7.84 Calculate the number of chlorine atoms in (a) 1.77 g of SCl_2 and (b) 1.77 g of $SOCl_2$.

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- 7.4 Empirical Formulas**
- 7.85 Decide whether each of the following is an empirical formula:
 (a) $C_2H_8N_2$ (b) $K_2S_2O_8$ (c) $Na_2Cr_2O_7$
 (d) S_4N_4 (e) $C_{12}H_{21}$
- 7.86 Decide whether each of the following is an empirical formula:
 (a) $K_4P_2O_7$ (b) C_3F_6 (c) $C_6H_{10}O_3$
 (d) Hg_2Br_2 (e) $H_2C_2O_4$

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- 7.87 Polyethylene a well-known plastic, is composed of 85.63% carbon and 14.37% hydrogen.
- How many grams of each element are in 100.0 g of polyethylene?
 - How many moles of each element are in 100.0 g of polyethylene?
 - What is the mole ratio in integers?
 - What is the empirical formula?
- 7.88 Testosterone, a hormone, is composed of 79.12% carbon, 9.79% hydrogen, and 11.10% oxygen. What is its empirical formula?
- 7.89 Polypropylene, a well-known plastic, is composed of 85.63% carbon and 14.37% hydrogen. Determine its empirical formula.
- 7.90 Styrene, used in manufacturing a well-known plastic, is composed of 92.26% carbon and 7.74% hydrogen. Determine its empirical formula.
- 7.91 Determine an empirical formula from each of the following sets of percent composition data:
- 82.66% C, 17.34% H
 - 72.03% Mn, 27.97% O
 - 43.64% P, 56.36% O
 - 37.82% C, 6.35% H, 55.83% Cl
 - 54.53% C, 9.15% H, 36.32% O
- 7.92 Determine an empirical formula from each of the following sets of percent composition data:
- 47.05% K, 14.45% C, 38.50% O
 - 77.26% Hg, 9.25% C, 1.17% H, 12.32% O
 - 66.42% C, 5.57% H, 28.01% Cl
 - 74.98% C, 5.24% H, 19.77% F
- 7.93 Determine an empirical formula from each of the following sets of percent composition data:
- 69.94% Fe, 30.06% O
 - 77.73% Fe, 22.27% O
 - 72.36% Fe, 27.64% O
- 7.94 Nitroglycerin is composed of 15.87% carbon, 2.22% hydrogen, 18.51% nitrogen, and 63.41% oxygen. Determine its empirical formula.
- 7.95 Calculate the empirical formula of each of the substances from the following analyses:
- 5.52 g C, 0.464 g H, 13.1 g F
 - 75.95 g C, 9.57 g H, 224.2 g Cl
- 7.96 Calculate the empirical formula of each of the following substances. Name each.
- 9.07 g H, 288 g O, 144 g S
 - 76.8 g Na, 80.1 g O, 53.4 g S

CHAPTER 7 ■ Formula Calculations

- 7.97 Calculate the empirical formula mass of each of the following:
- Hg_2Br_2
 - $\text{Na}_2\text{S}_2\text{O}_3$ (hypo)

7.5 Molecular Formulas

- 7.98 What is the empirical formula mass and the molecular mass of each of the following?
- C_6H_6
 - C_3H_6
 - C_2H_6
- 7.99 What is the empirical formula mass and the molecular mass of each of the following?
- C_6H_{12}
 - C_4H_6
 - C_6H_{10}
- 7.100 Calculate the percent compositions of ethyl naphthalene, $\text{C}_{12}\text{H}_{12}$, and cyclobutadiene, C_4H_4 . Compare the values, and explain the results.
- 7.101 Calculate the percent compositions of butene, C_4H_8 , and cyclooctane, C_8H_{16} . Compare the values, and explain the results.
- 7.102 Determine the molecular formula of a substance if its empirical formula is NO_2 and its molar mass is (a) 46.0 g/mol and (b) 92.0 g/mol.
- 7.103 Find the molecular formula of a substance with an empirical formula CH_2 and a molar mass (a) 56.0 g/mol, (b) 126 g/mol, (c) 210 g/mol, and (d) 78.0 g/mol.
- 7.104 Find the molecular formula of a substance if the empirical formula is CH and its molar mass is (a) 52.0 g/mol, (b) 104 g/mol, (c) 156 g/mol, and (d) 78.0 g/mol.
- 7.105 Determine the molecular formula of a sugar from its percent composition of 40.0% C, 6.67% H, 53.3% O, and its molar mass of 180 g/mol.
- 7.106 Find the molecular formula of a compound composed of 87.73% carbon and 12.27% hydrogen which has a molar mass of 82.1 g/mol.
- 7.107 Calculate the molecular formula of each of the substances from the following analyses:
- 36.93 g C, 8.27 g H, 49.20 g O, MM = 92.0 g/mol
 - 3.72 g H, 44.1 g C, 118 g O, MM = 90.0 g/mol
 - 8.65 g C, 0.484 g H, 3.36 g N, 11.5 g O, MM = 200 g/mol
 - 42.87 g C, 7.20 g H, 38.08 g O, MM = 74.1 g/mol
- 7.108 White phosphorus is one form of elemental phosphorus. Its molar mass is 124 g/mol. Calculate its molecular formula.
- 7.109 The most widely used antifreeze, ethylene glycol, is composed of 38.70% carbon, 9.74% hydrogen, and 51.56% oxygen. Its molar mass is 62.07 g/mol. Find its molecular formula.
- 7.110 Calculate the molecular formula of a substance if its percent composition is 79.91% C and 20.09% H, and its molar mass is approximately 30 g/mol.

■ General Problems

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- 7.111 Calculate the molecular formula of a substance if its percent composition is 85.63% C and 14.37% H, and its molar mass is approximately 85 g/mol.
- 7.112 Calculate the molecular formula of a compound if a sample contains 135 g of phosphorus and 175 g of oxygen and its molar mass is 284.

- 7.113 Octane and heptane are two ingredients of gasoline. Octane has 84.12% carbon and 15.88% hydrogen, and heptane has 83.90% carbon and 16.10% hydrogen. Their molecular masses are 114 amu and 100 amu, respectively. What are their molecular formulas?

General Problems

- 7.114 A 6.09-mg sample of a hydrocarbon was burned in air. The products were 17.9 mg of CO_2 and 11.0 mg of H_2O .
- What mass of oxygen was used in the combustion?
 - How many millimoles of carbon was present in the products, and in the sample?
 - How many millimoles of hydrogen was present in the products and in the sample?
 - What is the empirical formula of the sample?
- 7.115 A 17.1-mg sample of a hydrocarbon was burned in air. The products were 47.0 mg of CO_2 and 38.4 mg of water. What is the empirical formula of the hydrocarbon?
- 7.116 A certain carbohydrate (a compound containing carbon plus hydrogen and oxygen in a 2:1 atom ratio) is 40.0% carbon. Calculate its empirical formula.
- 7.117 Calculate the percent composition of soluble saccharin, $\text{C}_7\text{H}_4\text{NNaO}_3\text{S}$.
- 7.118 How many moles of carbon atoms is present in the quantity of $\text{C}_2\text{H}_6\text{O}$ that contains 4.14 g of hydrogen?
- 7.119 Calculate the percent composition of ammonium cyanide.
- 7.120 Calculate the number of hydrogen atoms in 42.7 g of a compound that contains 91.25% carbon and 8.75% hydrogen.
- 7.121 Calculate the number of molecules in 2.79 g of a compound that has a molar mass of 92.13 g/mol and contains 91.25% carbon and 8.75% hydrogen.
- 7.122 Calculate the number of hydrogen atoms in 12.8 g of a compound whose percent composition is 15.88% H and 84.12% C.
- 7.123 Calculate the number of hydrogen atoms in 41.8 g of a compound that contains 4.14% hydrogen.
- 7.124 Calculate the number of molecules in 31.7 g of a compound that has a molar mass of 82.2 g/mol.
- 7.125 Calculate the number of carbon atoms in 1.000 gallon of octane, C_8H_{18} , a major component of gasoline (1 gallon = 3.785 L; density = 0.7025 g/mL).

- 7.126 Calculate the number of molecules of vitamin A, $\text{C}_{20}\text{H}_{30}\text{O}$, in 2.34 g of vitamin A.
- 7.127 (a) Vitamin B_{12} has one cobalt atom per formula unit. The compound is 4.348% Co. Calculate its molar mass.
 (b) Vitamin D₁ has two oxygen atoms per formula unit. The compound is 4.03% O. Calculate its molar mass.
- 7.128 A sample is 39.2% KCl by mass, and the rest is water. Calculate the number of molecules of water in 14.4 g of the sample.
- 7.129 A 6.055-g sample of a hydrate of copper(II) sulfate, $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, is heated until all the water is driven off. After the anhydrous salt cools, its mass is 3.870 g. Calculate the value of x . (Hint: Treat this problem as an empirical formula problem with one of the “elements” H_2O .)
- 7.130 A scientist isolates a pure substance from a newly discovered plant in the Amazon River basin. What data does the scientist need to start to determine whether the substance is a new compound and what its formula is?
- 7.131 Calculate the percent error in rounding off the atomic mass of each of the following elements to three significant digits:
- | | |
|--------------|--------------|
| (a) Hydrogen | (b) Sulfur |
| (c) Lead | (d) Neon |
| (e) Carbon | (f) Fluorine |
- 7.132 A different method may be used to calculate the molecular formula from percent composition data plus a molar mass: First, calculate the mass of each element in 1.00 mol of compound. Next, calculate the number of moles of each of the elements in the mole of compound. Those results yield the molecular formula. Use this method to calculate the molecular formula of a hydrocarbon (a compound of carbon and hydrogen only) that contains 87.73% C and has a molar mass of 82.0 g/mol.

8

Chemical Reactions

- 8.1 The Chemical Equation
- 8.2 Balancing Equations
- 8.3 Predicting the Products of Chemical Reactions
- 8.4 Acids and Bases



A reaction liberating energy

Review Clues

- Section 8.1 Section 7.4
- Section 8.2 Section 5.1
- Section 8.3 Section 5.4
- Section 8.4 Section 6.3

Objectives

- 8.1 To interpret a balanced chemical equation in terms of mole ratios of reactants and products
- 8.2 To balance chemical equations—that is, to get the same number of atoms of each element on each side
- 8.3 To predict the products of thousands of chemical reactions by categorizing reactions
- 8.4 To predict the products of the reactions of acids with bases and metals, and to use a specialized nomenclature for acid-base reactions

8.1 ■ The Chemical Equation**207**

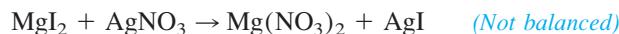
In Chapter 7, we learned how to do numerical calculations for compounds, using their formulas as a basis. This chapter lays the foundation for doing similar calculations for chemical reactions, using the balanced equation as a basis. The chemical equation is introduced in Section 8.1, and methods for balancing equations are presented in Section 8.2. To write equations, we must often be able to predict the products of a reaction from a knowledge of the properties of the reactants. Section 8.3 shows how to classify chemical reactions into types to predict the products of thousands of reactions. An important type of reaction—the acid-base reaction—is discussed in Section 8.4.

8.1 The Chemical Equation

In a chemical reaction, the substances that react are called **reactants**, or sometimes, **reagents**. The substances that are produced are called **products**. During the reaction, some or all of the atoms of the reactants change their bonding. For example, two hydrogen molecules can react with an oxygen molecule to form two water molecules (Figure 8.1). In a less familiar example—the reaction of MgI_2 with AgNO_3 —the products are $\text{Mg}(\text{NO}_3)_2$ and AgI . The metal ions have merely traded anions. All of the ions are still present after the reaction; they have just “changed partners.” We can describe the reaction, pictured in Figure 8.2, in words:

Magnesium iodide plus silver nitrate yields magnesium nitrate plus silver iodide.

We use formulas to represent the substances involved in a reaction when we write a chemical equation. In an **equation**, the formulas for reactants are placed on the left side of the arrow and those for products are placed on the right side. Either substance may be written first on each side of the equation:

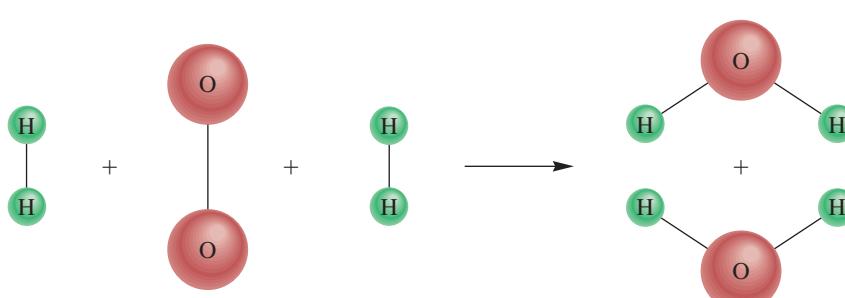


Even better, we can write a **balanced equation**, which shows the relative numbers of atoms of each of the elements involved. The unbalanced equation just presented seems to indicate that an iodide ion has disappeared during the reaction and that a nitrate ion has appeared from nowhere. As written, that equation violates the law of conservation of mass. Thus, we must always write balanced equations for reactions. The word “equation” is related to the word “equal”; an equation must have equal numbers of atoms of each element on each side. Such an equation is said to be *balanced*.

We must always write *balanced* chemical equations.

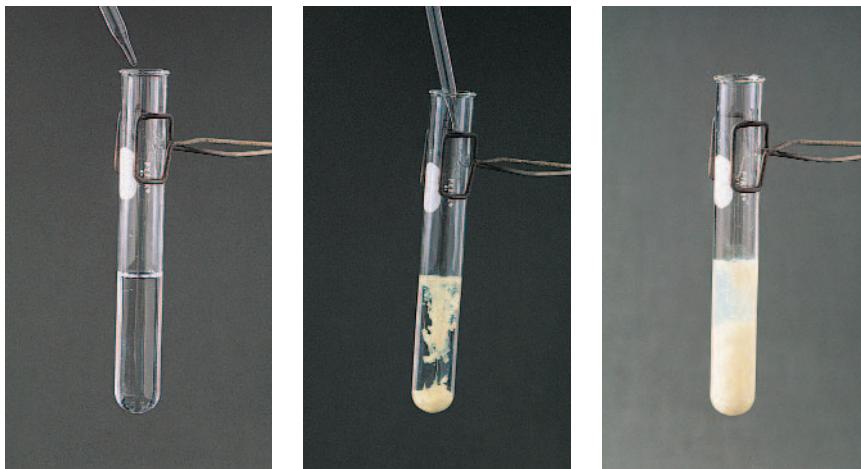
Figure 8.1 Reaction of Hydrogen and Oxygen

The bonds in the diatomic molecules H_2 and O_2 are broken, and new bonds are formed between hydrogen and oxygen atoms.

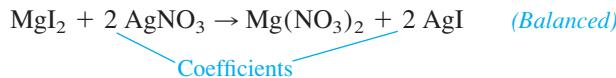


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Figure 8.2 Reaction of Aqueous Magnesium Iodide with Aqueous Silver Nitrate to Produce the Insoluble Silver Iodide and Aqueous Magnesium Nitrate



Coefficients—numbers that are written before the formulas—tell the relative numbers of formula units of reactants and products involved in a reaction and balance the number of atoms of each element involved. The coefficient does not imply any chemical bonding. *The coefficient multiplies everything in the formula:*



In a balanced chemical equation, the absence of a coefficient before a formula implies a coefficient of 1. The two formula units of AgNO_3 are composed of two Ag^+ ions and two NO_3^- ions. The two NO_3^- ions in the one formula unit of $\text{Mg}(\text{NO}_3)_2$ produced come from the two formula units of AgNO_3 .

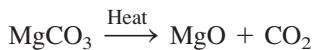
The balanced equation for the reaction of hydrogen and oxygen, illustrated in Figure 8.1, is



The coefficients in a balanced equation give the ratio of moles of each reactant and product to moles of any other reactant or product.

The coefficients in a balanced equation give the *ratio of moles* of each substance in the reaction to *moles* of any other substance. They also give the ratio of formula units of each substance to formula units of any other substance. The balanced chemical equation is the cornerstone from which we can calculate how much of one substance reacts with or is produced by a certain quantity of another substance (Chapter 10).

Reaction conditions are often written above or below the arrow, as in



Snapshot Review

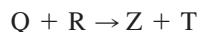
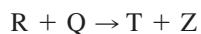


ChemSkill Builder 5.4

- ☐ A balanced equation gives the mole ratios of reactants and products as well as the ratios of formula units.

- A. For the reaction $\text{PCl}_5 + 4 \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 5 \text{HCl}$, (a) How many molecules of HCl will be produced from three molecules of PCl_5 ? (b) How many moles of HCl will be produced from 3.0 mol of PCl_5 ?

B. What difference, if any, is there between the following equations?



8.2 Balancing Equations

Our first major task of this chapter is to learn to balance equations for chemical reactions. Balancing simple equations will be covered in this chapter; equations for more complicated oxidation-reduction reactions will be considered in Chapter 16.

To complete an equation for any type of reaction, write the proper formulas for the reactants and products before starting to balance the equation.

The first step in writing a complete and balanced equation for a chemical reaction is to write correct formulas for the reactants and products. To help us as we learn, we might write the equation in words and later write the formulas. Correct formulas cannot be changed to make an equation balance! Only after the correct formulas have been written can we go on to the next step. Then, we use coefficients to change the numbers of formula units to get the same number of atoms of each element on the two sides of the equation.

For example, the unbalanced equation for the reaction of sulfur dioxide with oxygen to give sulfur trioxide is



Don't forget that elemental oxygen occurs as O_2 . With one molecule of each substance, the numbers of oxygen atoms on the two sides of the equation are not equal, so the equation is not balanced. We can balance the equation by inserting proper coefficients in front of the formulas:



The number 2 before the SO_2 indicates that there are two sulfur dioxide molecules, containing two sulfur atoms and four oxygen atoms. There are two more oxygen atoms in the O_2 molecule. Because there are two sulfur atoms and six oxygen atoms in the two SO_3 molecules, the equation is now balanced. We must always check an equation after we balance it to make sure that the numbers of atoms of each element on each side of the arrow are equal.

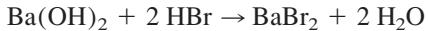
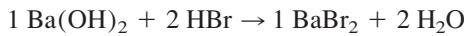
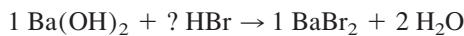
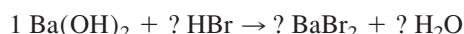
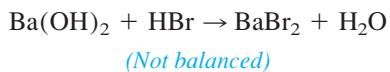
One of the problems encountered by students just learning to balance equations is that the absence of a coefficient in a balanced equation means a coefficient of 1, but the absence of a coefficient before the equation is fully balanced might mean that this substance has not yet been considered. To avoid any confusion, we can place a question mark before each formula when we start to balance an equation. (After we have had a lot of practice, we will not need to use the question marks.)

EXAMPLE 8.1

Balance the equation for the reaction of barium hydroxide and hydrobromic acid to give barium bromide and water.

Solution**Steps**

- Step 1:** Write correct formulas for the reactants and products, as discussed in Chapter 5. Do not write incorrect formulas to make balancing easier; write correct formulas!
- Step 2:** Insert question marks before each formula except the most complicated one; place a 1 there.
- Step 3:** Balance one or more of the elements in the substance with the “1” coefficient by inserting coefficients in front of the formulas for other substances. In this case, the $1\ Ba^{2+}$ in $\text{Ba}(\text{OH})_2$ yields $1\ Ba\text{Br}_2$ and the $2\ O$ in $\text{Ba}(\text{OH})_2$ yield $2\ H_2\text{O}$.
- Step 4:** Complete the equation using values already determined. In this case, the HBr is balanced by considering the $2\ Br^-$ ions in $1\ Ba\text{Br}_2$:
- Step 5:** Delete any coefficients equal to 1:
- Step 6:** Check the numbers of atoms of each element on each side:

Example

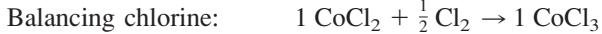
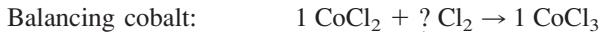
1 Ba, 2 O, 4 H, 2 Br on each side.

Practice Problem 8.1 Balance the equation for the reaction of ammonium iodide with lead(II) nitrate to yield ammonium nitrate and lead(II) iodide.

If the initial placement of the coefficient 1 yields fractional coefficients in the equation, we can get integer values by simply multiplying every coefficient (including the coefficients equal to 1) by the smallest integer that will clear the fractions.

EXAMPLE 8.2

Balance the equation for the reaction of CoCl_2 and Cl_2 , which produces CoCl_3 .

Solution

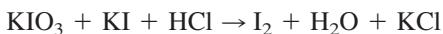
Check: 2 Co, 6 Cl on each side.

Practice Problem 8.2 Balance an equation for the reaction of octane, C_8H_{18} , with O_2 to yield CO_2 and H_2O .

When any element appears in more than one substance on the same side of the equation, we balance that element last.

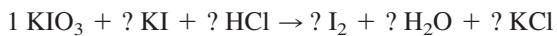
EXAMPLE 8.3

Write a balanced equation for the following reaction:

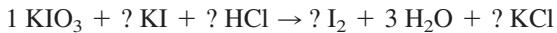


Solution

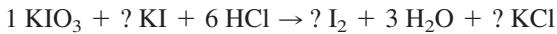
Place a 1 before KIO_3 , the most complicated-looking formula, and a question mark before each of the other formulas:



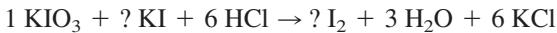
Because potassium and iodine appear in two compounds on the left side of the equation, start working with oxygen, which appears in only one compound on each side, including the compound with the “1.”



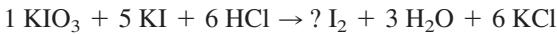
Knowing how many hydrogen atoms are on the right side of the equation, we can balance hydrogen next:



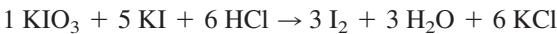
Now balance chlorine:



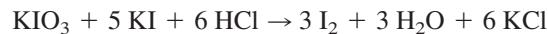
Balance the potassium, being careful to note that there is already one K^+ in the $1 KIO_3$:



Finally, balance the iodine:



The coefficient 1 may now be deleted:



Check: 6 K, 6 I, 3 O, 6 H, 6 Cl on each side.

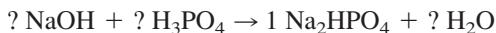
Practice Problem 8.3 Balance an equation for the reaction of H_2O with N_2O_5 to yield HNO_3 .

EXAMPLE 8.4

Write a balanced equation for the reaction of sodium hydroxide with phosphoric acid to produce sodium monohydrogen phosphate and water.

Solution

First, write the correct formulas for the reactants and products, place a 1 before the most complicated-looking formula, and place a question mark before every other formula:



Balance the sodium and phosphorus atoms first, because oxygen and hydrogen appear in two substances on each side of the equation:



Balance the hydrogen atoms:



The oxygen atoms have been balanced in the process. Finally, eliminate the coefficients equal to 1:



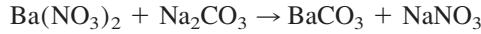
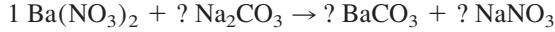
Check: 2 Na, 6 O, 5 H, 1 P on each side.

Practice Problem 8.4 Balance an equation for the reaction of ammonium sulfide with copper(II) chloride to yield copper(II) sulfide and ammonium chloride.

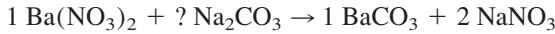
To make balancing some equations a little easier, we can balance any polyatomic ion that maintains its composition through an entire reaction as the entire ion, instead of balancing the individual atoms of the elements.

EXAMPLE 8.5

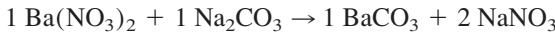
Balance the following equation using the polyatomic ions rather than the individual atoms.

**Solution**

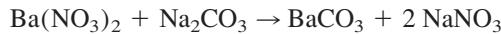
Balance the barium ion and the nitrate ions:



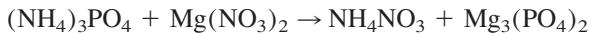
Balance the carbonate ion:



Clear the coefficients equal to 1:

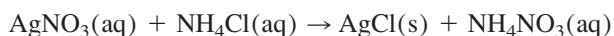


Practice Problem 8.5 Balance the following equation:



8.3 ■ Predicting the Products of Chemical Reactions**213**

Information about the **state** of a reactant or product (whether it is present as a solid, liquid, gas, or solute) may be given in a chemical equation. The following abbreviations are used: solid (s), liquid (ℓ), gas (g), and solute in aqueous solution (aq). An **aqueous solution** is a solution in water. Thus, the reaction of silver nitrate with ammonium chloride can be represented by the following equation:



The reaction of aqueous lithium carbonate with a solution of hydrochloric acid can be represented by the following equation:



Snapshot Review



ChemSkill Builder 5.4

□ Because the balanced equation is a set of reacting ratios, one coefficient is rather arbitrary. We set the coefficient of the most complex formula to 1, but we might later have to adjust all the coefficients to get integers.

- A. Balance the following equations: (a) $\text{P}_4\text{O}_6(\text{s}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{PO}_3(\ell)$,
 (b) $\text{TiCl}_4(\ell) + \text{H}_2\text{O}(\ell) \rightarrow \text{TiO}_2(\text{s}) + \text{HCl}(\text{g})$, and
 (c) $\text{CoCl}_3(\text{aq}) + \text{Co}(\text{s}) \rightarrow \text{CoCl}_2(\text{aq})$

8.3 Predicting the Products of Chemical Reactions

To the beginning student, the huge array of chemical reactions might seem bewildering. To memorize the products of each one by merely looking at the reactants would be impossible. Instead, we generalize a great number of reactions into five simple types that allows us at least to make an educated guess as to the products. To learn a few simple rules is much easier than to memorize each reaction independently. Thus we must

- Learn to classify reactions into their types by considering the reactants only.
- Learn what products might be produced by that type reaction.
- Learn how to predict if the expected reaction will actually proceed.

More complicated oxidation-reduction reactions will be presented in Chapter 16, and other complex reactions are covered in more advanced chemistry courses.

Simple chemical reactions can be divided into the following classes:

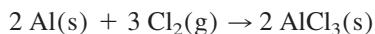
1. Combination reactions
2. Decomposition reactions
3. Single substitution (or single displacement) reactions
4. Double substitution (or double displacement) reactions

In addition, most elements and many compounds react with oxygen:

5. Combustion reactions

Combination Reactions

Combination reactions involve the reaction of two (or more) substances to form one compound. Perhaps the easiest combination reaction to recognize is one in which two free elements (at least one of which is a nonmetal) react with each other. The elements can do little except react with each other (or not react at all). For example, if we treat aluminum metal with chlorine gas, the elements can combine to form aluminum chloride:



The formula for the product of a combination reaction must be written according to the rules presented in Chapter 5. After the product has been represented by the proper formula, the equation is balanced, as shown in Section 8.2.

EXAMPLE 8.6

Complete and balance an equation for the reaction of zinc metal and oxygen gas.

Solution

Step 1: Identify the product—zinc oxide.

Step 2: Write correct formulas for reactant(s) and product(s). Remember that oxygen is one of the seven elements that occur as diatomic molecules when uncombined with other elements (Figure 5.2):



Step 3: Balance the equation:



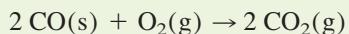
Practice Problem 8.6 Complete and balance an equation for the reaction of aluminum metal with oxygen gas.

When two nonmetallic elements combine, the product formed often depends on the relative quantities of the reactants present. For example, when carbon combines with oxygen, either of two possible compounds may be produced: carbon monoxide or carbon dioxide. When the supply of oxygen is limited, carbon monoxide is produced, but when excess oxygen is available, carbon dioxide results:



ITEM OF INTEREST

What happens in the atmosphere to the carbon monoxide generated in automobile engines? The carbon monoxide gas reacts slowly with the oxygen gas in the air to produce carbon dioxide gas:



Of course, not every pair of elements will react with each other. For example, we know that the noble gases are quite stable in their elemental forms.

8.3 ■ Predicting the Products of Chemical Reactions**215****EXAMPLE 8.7**

Predict what will happen when helium is treated with oxygen gas.

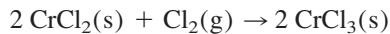
Solution

Nothing will happen; helium is too stable to react. In equation format,



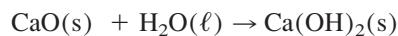
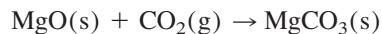
Practice Problem 8.7 Predict the products of the reaction, if any, of aluminum metal with zinc metal.

In another type of combination reaction, a compound may be able to combine with a particular free element to form another compound as the only product. This occurs most often when the free element is the same as one of the elements in the original compound. An example of such a combination reaction is



Here, the element chlorine combines with a compound of chromium and chlorine—chromium(II) chloride—to form another compound of chromium and chlorine—chromium(III) chloride—in which the chromium ion has a different positive charge.

In yet another type of combination reaction, two compounds containing the same element may be able to combine to form a single, more complex compound. The element the reactants have in common is very often oxygen:

**Decomposition Reactions**

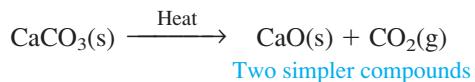
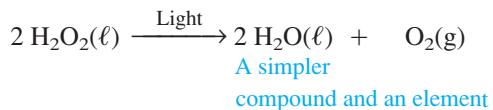
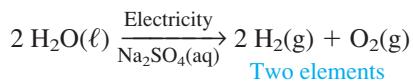
Decomposition reactions have the opposite effect from combination reactions. In a decomposition reaction, a single compound can decompose to two elements, to an element and a simpler compound, to two simpler compounds, or (rarely) to another combination of products. **Ternary compounds**, compounds containing three elements, do not decompose into three uncombined elements. Decomposition reactions are easy to identify because there is only one reactant. Table 8.1 summarizes the most common types of decomposition reactions.

Table 8.1 Common Types of Decomposition Reactions

Reactant	Products	Example
Binary compound	→ Two elements	$2 \text{H}_2\text{O} \xrightarrow{\text{Electricity}} 2 \text{H}_2 + \text{O}_2$
Binary compound	→ Compound + element	$2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$
Ternary compound	→ Compound + element	$2 \text{KClO}_3 \xrightarrow{\text{Heat}} 2 \text{KCl} + 3 \text{O}_2$
Ternary compound	→ Two compounds	$\text{CaCO}_3 \xrightarrow{\text{Heat}} \text{CaO} + \text{CO}_2$

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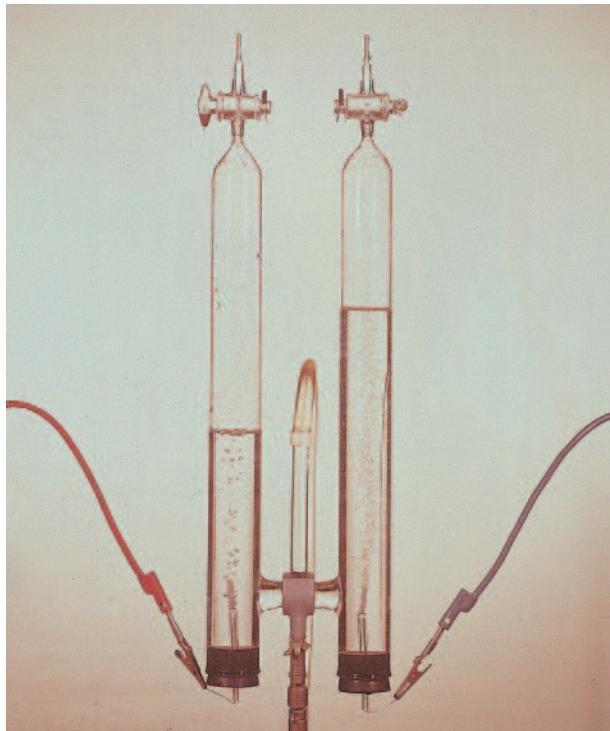
Input of energy in some form is usually required to get a compound to decompose:



To get compounds to decompose using electricity, ions must be present, and the sample must be in some liquid form. (Electricity does not pass through solid ionic compounds, even though they are composed of positive and negative ions.) The ions in a liquid are free to move and thus conduct the current. The liquid can be a **molten** (melted) ionic substance or a solution of an ionic substance in water or another liquid (Figure 8.3). If a solution is used, the compound that is more easily decomposed (the ionic compound or the water, for example) is the one that will react.

Note in the previous equations that the formulas of elemental hydrogen and oxygen are written as diatomic molecules: H₂ and O₂. Before equations are balanced, the formulas for all reactants and products must be written according to the rules given in Chapter 5.

Figure 8.3 Electrolysis Reaction



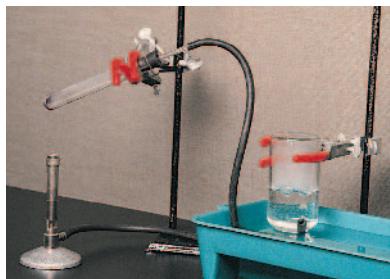
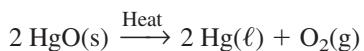
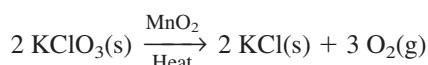
8.3 ■ Predicting the Products of Chemical Reactions**217**

Figure 8.4 Decomposition of Potassium Chlorate

Decomposition reactions are often used to prepare elements. Joseph Priestley (1733–1804), the discoverer of oxygen, used the decomposition of mercury(II) oxide, HgO, to prepare elemental oxygen (and free mercury):

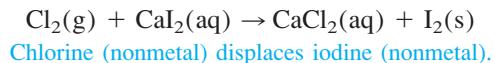


Students often decompose potassium chlorate to produce oxygen in the laboratory (Figure 8.4). This reaction is usually carried out by heating that compound in the presence of manganese(IV) oxide, MnO₂. The MnO₂ is a **catalyst**—a substance that changes the speed of a chemical reaction without undergoing a permanent change in its own composition. A catalyst is conventionally written above or below the reaction arrow:



Single Substitution Reactions

The reaction of a free element with a compound of two (or more) other elements may result in the free element displacing one of the elements originally in the compound. A free metal can generally displace a less active metal in a compound; a free nonmetal can generally displace a less active nonmetal in a compound:

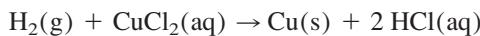
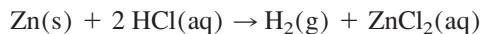


In this class of reaction, called a **single displacement reaction**, or **single substitution reaction**, elements that are inherently more reactive can displace less reactive elements from their compounds, but the opposite process does not occur:



Chemicals tend to react to go to a more stable, lower energy state. When copper reacts with silver nitrate, AgNO₃, the system goes to a lower energy state. When an aqueous solution of copper(II) nitrate, Cu(NO₃)₂, is treated with silver metal, these chemicals are already in the lower energy state, so they have no tendency to produce copper metal and silver nitrate. We say that copper is more **active**, or more **reactive**, than silver, which indicates that it has a greater tendency to leave its elemental state and form compounds. This is due to atoms of copper having a greater tendency to lose electrons than those of silver do.

To predict which single substitution reactions will occur, we need to know a little about the *relative* reactivities of some of the important metals and nonmetals. Some metals and a few nonmetals are listed in Table 8.2 in order of decreasing reactivity. A more complete list is given in Section 17.2. Hydrogen is included in the list of metals because it can be displaced from aqueous acids by reactive metals (Figure 8.5) and can displace less active metals from their compounds:



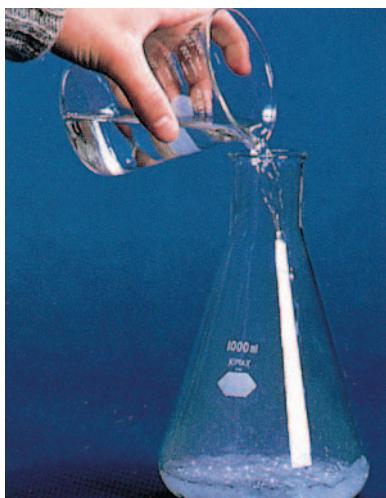


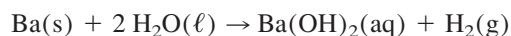
Figure 8.5 Reaction of Zinc Metal with Hydrochloric Acid

Table 8.2 Relative Reactivities of Uncombined Elements

	Metals	Nonmetals	
<i>Most active</i>	Alkali metals and alkaline earth metals	F ₂	<i>Most active</i>
	Al	O ₂	
	Mn	Cl ₂	
	Zn		
	Cr		
	Fe	Br ₂	
	Sn		
	Pb		
	H*	I ₂	<i>Less active</i>
	Cu		
	Ag		
<i>Least active</i>	Au		

*Hydrogen is included in the list of metals because it can be displaced from aqueous acids by reactive metals.

Very active metals can even displace hydrogen from water:



EXAMPLE 8.8

Using data from Table 8.2, predict which of the following pairs of substances will react. If they will react, write a balanced equation for the reaction. If they will not react, write N.R. on the right-hand side of the arrow.

- (a) Mn(s) and Zn(NO₃)₂(aq)
- (b) Ag(s) and Pb(NO₃)₂(aq)
- (c) HCl(aq) and Cr(s)
- (d) Sn(s) and CuSO₄(aq)
- (e) Ag(s) and HC₂H₃O₂(aq)

Solution

- (a) Mn(s) + Zn(NO₃)₂(aq) → Mn(NO₃)₂(aq) + Zn(s)
- (b) Ag(s) + Pb(NO₃)₂(aq) → N.R. (Ag is less active than Pb.)
- (c) 2 HCl(aq) + Cr(s) → H₂(g) + CrCl₂(aq)
- (d) Sn(s) + CuSO₄(aq) → SnSO₄(aq) + Cu(s)
- (e) Ag(s) + HC₂H₃O₂(aq) → N.R. (Ag is less active than H.)

Practice Problem 8.8 Predict whether each of the following pairs of substances will react. If they will react, write a balanced equation for the reaction. If they will not react, write N.R. on the right-hand side of the arrow.

- (a) Ba(s) and Al₂O₃(s) plus heat
- (b) NaF(aq) and Cl₂(g)

8.3 ■ Predicting the Products of Chemical Reactions**219**

Copper, silver, and gold—the coinage metals—have long been prized for their **stability**, or lack of reactivity (Figure 8.6). They can even occur uncombined in nature. Active metals do not occur naturally as free elements.

Double Substitution Reactions

In a double substitution reaction, if the ions are not converted to covalent compounds, their charges do not change when they are converted from reactants to products.

The reaction of two compounds may yield two new compounds. Many reactions that occur in aqueous solution involve two ionic compounds trading anions. This class of reactions is called **double substitution reactions**, **double displacement reactions**, or **metathesis reactions**. As usual, the correct formulas must be written for the products before the equation is balanced. In a double substitution reaction, if the ions are not converted to covalent compounds, their charges do not change as they are converted from reactants to products.

EXAMPLE 8.9

Predict the products for reactions of the following pairs of reactants, and write balanced equations:

- Aqueous barium nitrate and aqueous iron(II) sulfate
- Aqueous iron(II) chloride and aqueous silver acetate
- Solid calcium hydroxide and aqueous hydrochloric acid

Solution

First, write the names of the products:

- Barium nitrate plus iron(II) sulfate yields barium sulfate plus iron(II) nitrate. The Ba^{2+} and Fe^{2+} cations trade anions.
- Iron(II) chloride plus silver acetate yields iron(II) acetate plus silver chloride. Here, the cations also trade anions; however, the Fe^{2+} ion requires two singly charged anions to satisfy its dipositive charge. Note that the iron ion had a 2+ charge and still has that charge. Iron(III) nitrate is not expected as a product, because the Fe^{2+} ion does not change to a Fe^{3+} ion in this type of reaction.
- Calcium hydroxide plus hydrochloric acid yields calcium chloride plus water. The charge on the calcium ion remains the same throughout the reaction; the charge on the hydrogen ion changes because the water formed is covalent, not ionic.

Next, write correct formulas for all reactants and products:

- $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{FeSO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + \text{Fe}(\text{NO}_3)_2(\text{aq})$
- $\text{FeCl}_2(\text{aq}) + \text{AgC}_2\text{H}_3\text{O}_2(\text{aq}) \rightarrow \text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{aq}) + \text{AgCl}(\text{s})$
- $\text{Ca}(\text{OH})_2(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$

Finally, balance the equations:

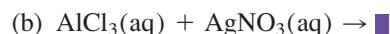
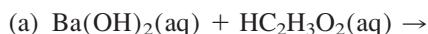
- $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{FeSO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + \text{Fe}(\text{NO}_3)_2(\text{aq})$
- $\text{FeCl}_2(\text{aq}) + 2 \text{AgC}_2\text{H}_3\text{O}_2(\text{aq}) \rightarrow \text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{aq}) + 2 \text{AgCl}(\text{s})$
- $\text{Ca}(\text{OH})_2(\text{s}) + 2 \text{HNO}_3(\text{aq}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{aq}) + 2 \text{H}_2\text{O}(\ell)$



Figure 8.6 Gold, Silver, and Copper Coins

Silver tarnishes slowly in air to form silver sulfide, Ag_2S ; it is more reactive than gold. Although copper is also used in coins, it is more reactive than the other coinage metals. Copper coins tarnish or corrode relatively quickly.

Practice Problem 8.9 Complete and balance the equation for each of the following reactions:



In aqueous solution, neither H_2CO_3 (carbonic acid) nor NH_4OH (ammonium hydroxide) is stable; they decompose to yield water and CO_2 or NH_3 respectively. If either H_2CO_3 or NH_4OH is expected to be a product of a double substitution reaction, CO_2 plus H_2O , or NH_3 plus H_2O , will be produced instead. Other unstable compounds are encountered much less frequently.

EXAMPLE 8.10

Predict the products of the following reactions:



Solution

(a) Ordinarily, we would predict that the ions will trade partners to yield LiClO_3 and H_2CO_3 . However, water and carbon dioxide are produced instead of H_2CO_3 :



(b) Ordinarily, we would predict that the ions will trade partners to yield NaCl and NH_4OH . However, instead of ammonium hydroxide, water and ammonia are produced:



Practice Problem 8.10 Complete and balance the following equations:



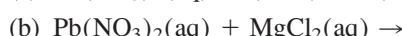
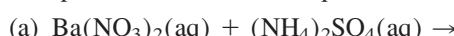
Table 8.3 Water Solubility of Some Common Ionic Compounds

Soluble in Water	Insoluble in Water
All chlorates	BaSO_4
All acetates	Most oxides
All nitrates	Most sulfides
All compounds of alkali metals	Most phosphates
All compounds containing the ammonium ion	
All chlorides except those listed in the next column	AgCl , PbCl_2 , Hg_2Cl_2 , and CuCl

The driving force behind double substitution reactions is the formation of a covalent compound (including water or a gaseous compound) or an insoluble ionic compound from ions in solution. A solid formed from ions in solution is called a **precipitate**. We can thus predict that a reaction will occur if soluble ionic compounds yield at least one insoluble ionic compound or one covalent compound. We need to be familiar with the **solubilities** of some common ionic compounds in water. Some types of ionic compounds that are soluble or insoluble in water are listed in Table 8.3. A more comprehensive tabulation of solubilities is presented in Table 8.4 for reference, not necessarily to be memorized.

EXAMPLE 8.11

Complete and balance the equation for each of the following reactions:



8.3 ■ Predicting the Products of Chemical Reactions**221****Table 8.4** Solubility Reference Table*

	ClO_3^-	Cl^-	SO_4^{2-}	CO_3^{2-}	SO_3^{2-}	PO_4^{3-}	CrO_4^{2-}	BO_3^{3-}	S^{2-}	OH^-	O^{2-}
	NO_3^-	Br^-	I^-	$\text{C}_2\text{H}_3\text{O}_2^-$							
Pb^{2+}	s	ss-i	i	i	i	i	i	i	i	i	i
$\text{Na}^+, \text{K}^+, \text{NH}_4^+$	s	s	s	s	s	s	s	s	s	d	
Hg_2^{2+}	s	i	i	i	i	i	i	i	i	i	i
Hg^{2+}	s	s-i**	s	i	i	i	i	i	i	i	i
Ag^+	s	i	ss	i	i	i	i	i	i	i	i
Mg^{2+}	s	s	s	s	s	s	s	i	i	i	i
Ca^{2+}	s	s	i	i	i	s	s	s	d		
Ba^{2+}	s	s	i	i	i	s	s	s	d		

Key: s = soluble (greater than about 1 g solute/100 g of water)

ss = slightly soluble (approximately 0.1–1 g solute/100 g of water)

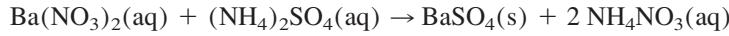
i = insoluble (less than about 0.1 g solute/100 g of water)

d = decomposes in water

*Memorize this Table only if directed to do so by your instructor.

** HgCl_2 is soluble, HgBr_2 is less soluble, and HgI_2 is insoluble**Solution**

- (a) We see from Table 8.3 that BaSO_4 is insoluble in water. Thus, the following reaction will occur:



Barium sulfate precipitates.

- (b) $\text{Pb}(\text{NO}_3)_2(\text{aq}) + \text{MgCl}_2(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) + \text{Mg}(\text{NO}_3)_2(\text{aq})$

Lead(II) chloride is insoluble in cold water (and only slightly soluble in hot water).

Practice Problem 8.11 Complete and balance the equation for each of the following reactions:



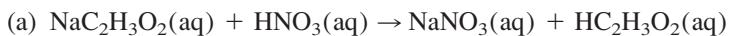
In addition to learning the solubility rules, we also must be familiar with the nature of the bonding in compounds to be able to predict if double substitution reactions will proceed as written. We learned in Chapter 5 that covalent compounds have no metallic elements, and no ammonium ion in them. It might be helpful to note that formation of a covalent compound includes

- (a) Formation of a gas (All gases at room temperature are covalent.)
- (b) Formation of water
- (c) Formation of a *weak acid* or *weak base*. (Weak acids and bases in solution are more than 95% covalent. They will be discussed in Section 8.4.) Weak acids include all acids *except* HCl , HClO_3 , HClO_4 , HBr , HI , HNO_3 , and H_2SO_4 . These acids are *strong*, that is, they are completely ionic in water solution. The weak base that we will focus on is ammonia, NH_3 .

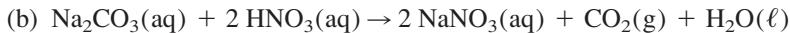
EXAMPLE 8.12

Complete and balance the following equations:

- (a) $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow$
(b) $\text{Na}_2\text{CO}_3(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow$

Solution

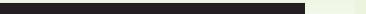
HNO_3 is strong, and thus ionic. The salts are also ionic. However, acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is weak, and the formation of this covalent compound causes this reaction to go.



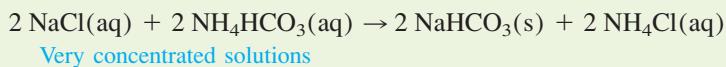
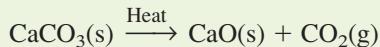
The formation of the covalent compounds $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ drives this reaction. CO_2 is readily seen to be covalent because it is a gas.

Practice Problem 8.12 Complete and balance the following equations:

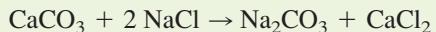
- (a) $\text{NH}_4\text{NO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
(b) $\text{NH}_4\text{I}(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow$

**ITEM OF INTEREST**

An industrial process called the *Solvay process* uses the following set of reactions to produce Na_2CO_3 (known as washing soda). The reactants are inexpensive, and Na_2CO_3 is a very important industrial compound used in the manufacture of soap, glass, paper, detergents, and other chemicals.



If we add all the reactants and all the products in these equations and then delete the compounds that appear on both sides, we get the following overall equation:

**EXAMPLE 8.13**

Can industrial chemists simply combine CaCO_3 and NaCl to get Na_2CO_3 and CaCl_2 ?

8.3 ■ Predicting the Products of Chemical Reactions**223****Solution**

The proposed reactants are more stable than the desired products because CaCO_3 is insoluble in water, and Na_2CO_3 and CaCl_2 are both soluble. Thus, this direct reaction is not feasible.

EXAMPLE 8.14

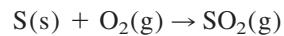
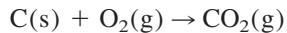
What type of reaction is each of the steps of the Solvay process?

Solution

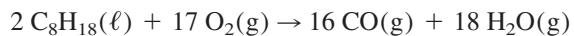
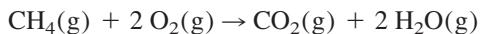
In the order shown, the six reactions are classed as (1) decomposition, (2) combination, (3) double substitution, (4) decomposition, (5) combination, and (6) double substitution followed by decomposition.

Combustion Reactions

Everyone is familiar with the process called *burning*. Burning, also called **combustion**, is the rapid reaction of a wide variety of materials with oxygen gas. Combustion reactions of elements can also be classified as combination reactions; the *type* of reaction is not as important as the *products*. For example, we can refer to the following reactions as combination reactions or combustion reactions:



The combustion reactions of **hydrocarbons**—compounds composed of carbon and hydrogen only—are especially important as sources of useful energy. We burn methane, CH_4 , called natural gas, in our homes to provide heat, and we combust octane, C_8H_{18} , in our cars to provide mechanical energy:



In such reactions, either carbon monoxide or carbon dioxide may be produced, in addition to water. If sufficient oxygen is present, carbon dioxide is produced. If the supply of oxygen is limited, as in a car engine, carbon monoxide is the product. (With very limited oxygen, soot—a form of carbon—and water are produced.) *In any case, water is a product.*

Water is one product of the combustion of hydrocarbons.

EXAMPLE 8.15

Which of the following reactions was carried out in a limited supply of oxygen?



Solution

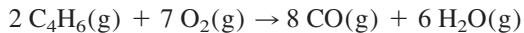
The reaction of C_6H_{10} produced CO, so that reaction was run in limited oxygen. If the combustion reaction of C_6H_{10} is carried out in excess oxygen, the equation is written as follows:



Practice Problem 8.15 What will be the effect if between 11 and 17 mol of oxygen is available for the combustion of 2 mol of C_6H_{10} ?

EXAMPLE 8.16

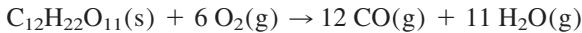
Write a balanced equation for the reaction of butyne, C_4H_6 , in a limited oxygen supply.

Solution

The combustion reactions of compounds containing carbon, hydrogen, and oxygen (which include the carbohydrates we use for food) also produce either carbon monoxide or carbon dioxide, depending on the relative quantity of oxygen available.

EXAMPLE 8.17

Write a complete and balanced equation for the reaction of sucrose, table sugar, $C_{12}H_{22}O_{11}$, in a limited supply of oxygen.

Solution

Practice Problem 8.17 Write a complete and balanced equation for the combustion reaction of sucrose with excess oxygen.

**Snapshot Review**

ChemSkill Builder
5.1, 5.2, 5.4, 5.5, 5.6

- We must classify chemical reactions into types in order to have a chance to predict the products given the reactants. Five simple types are given here, with which it should be fairly easy to make educated guesses as to the correct products. Be sure to practice these problems repeatedly.

A. Complete and balance the following equations:

- $BaO(s) + H_2O(l) \rightarrow$
- $Al(s) + H_2SO_4(aq) \rightarrow$
- $HCl(aq, \text{excess}) + Na_2CO_3(aq) \rightarrow$

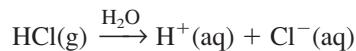
8.4 Acids and Bases

There is another common way to classify chemical reactions: acid-base reactions, oxidation-reduction reactions, and reactions of more complicated types (beyond the scope of this book). Acid-base reactions are considered to involve the reactions of hydrogen ions with hydroxide ions. The reactions of acids and bases will be taken up in this section, and a more sophisticated view of these reactions is presented in Chapter 19. Oxidation-reduction reactions involve the transfer of electrons from one substance to another. Many combination reactions, many decomposition reactions, all single substitution reactions, and all combustion reactions are of this type, but more complex examples are presented in Chapters 16 and 17.

The reactions of acids with active metals fit into the single substitution class discussed in Section 8.3. Reactions of acids with bases are double substitution reactions, also discussed in Section 8.3. However, the reactions of acids and bases are so important that they have a special terminology that we need to know.

According to the most fundamental theory concerning acids and bases—the **Arrhenius theory**—an **acid** is a compound that furnishes hydrogen ions, H⁺, to an aqueous solution, and a **base** is a compound that furnishes hydroxide ions, OH⁻, to an aqueous solution. The hydrogen ion does not exist alone, as H⁺, but is stable in aqueous solution in the form H₃O⁺, which is frequently represented as H^{+(aq)}.

In beginning courses, formulas for acids (and no other compounds except water and hydrogen peroxide) are written with the ionizable hydrogen atoms first, as in HCl.



Methane, CH₄, ammonia, NH₃, and sucrose (table sugar), C₁₂H₂₂O₁₁, are examples of compounds that are not acids because they do not provide hydrogen ions to aqueous solutions. Their hydrogen atoms are therefore not written first in their formulas. For certain acids, such as acetic acid, HC₂H₃O₂, and citric acid, H₃C₆H₅O₇, only the hydrogen atom(s) written first is (are) capable of being ionized; the other hydrogen atoms do not yield H⁺ in solution.

Properties of Acids and Bases

Caution: Do not taste chemicals unless specifically directed to do so by your instructor.

Caution: Never touch concentrated solutions of strong bases, such as liquid Drano, because they are capable of dissolving the fat in the skin.

Acids in general have a sour taste, turn indicators (Section 11.3) certain colors, and react with bases to form salts. For example, the sour taste of lemon is the taste of citric acid, and the sour taste of vinegar is due mainly to acetic acid, its principal acid component. Simple acids have one or more hydrogen atoms per molecule.

Bases feel slippery, turn indicators certain colors that differ from those acids produce, and react with acids to form salts. We may experience the slipperiness of a base by putting our fingertips in some dilute ammonia water. Simple bases contain one or more hydroxide ions or are able to react with water to some extent to form hydroxide ions. For example, ammonia is a base because of the following reaction:

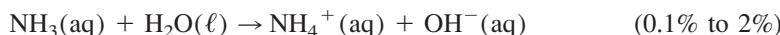
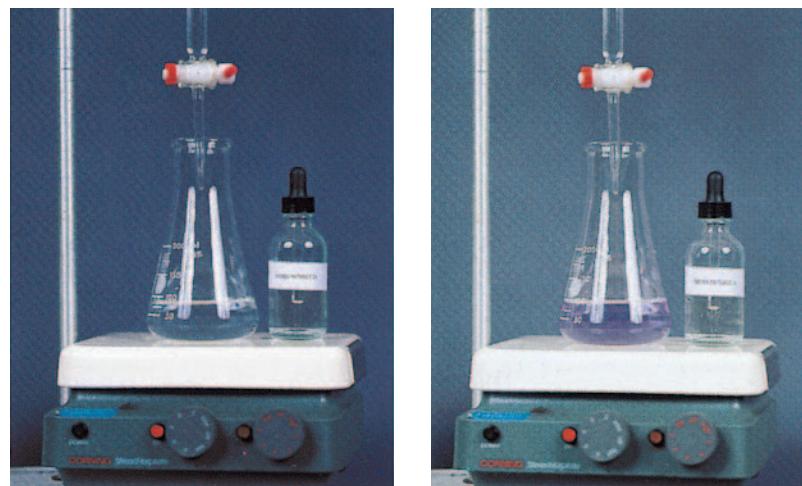
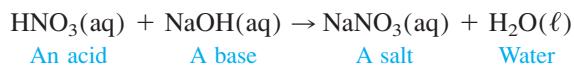


Figure 8.7 Neutralization Reaction

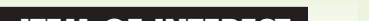


Double Substitution Reactions of Acids and Bases

The most important reactions of acids and bases are their reactions with each other to form salts and water:

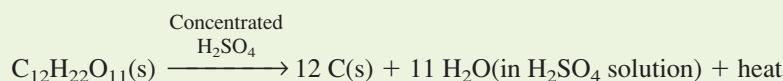


A **salt** is any compound of a cation other than H^+ with an anion other than OH^- or O^{2-} . [The word “salt” in everyday conversation means sodium chloride (table salt), which is only one example of a salt under this definition.] Such reactions, actually specific examples of double substitution reactions, are called **neutralization reactions** (Figure 8.7) because they produce products that are more neutral than acids or bases. **Neutral** means “neither acidic nor basic.”



ITEM OF INTEREST

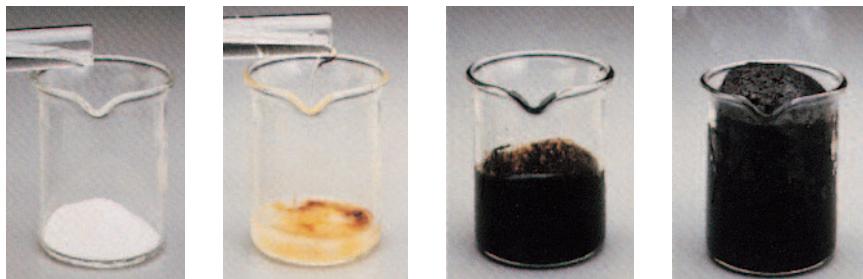
Many individual compounds that are acids have additional properties that make them dangerous. These dangerous compounds give acids a bad name to the general public. For example, LSD (lysergic acid diethylamide) is a mind-affecting hallucinogenic agent, but this property is in addition to any acid properties of the compound. Concentrated sulfuric acid, used in auto batteries, is a powerful oxidizing agent and dehydrating agent. A lump of sugar placed into concentrated sulfuric acid has the elements of water pulled from its molecules, leaving carbon (Figure 8.8):



Nitric acid, especially when concentrated but even in dilute solution, is another powerful oxidizing agent. In contrast, boric acid is such a weak acid that it is sometimes used in solution to bathe infected eyes.

8.4 ■ Acids and Bases**227**

Figure 8.8 Dehydration of Sugar by Sulfuric Acid



EXAMPLE 8.18

Which one(s) of the following is (are) acids?

- (a) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (b) $\text{H}_2\text{C}_2\text{O}_4$ (c) NH_2OH
 (d) $\text{HC}_4\text{H}_7\text{O}_2$ (e) H_2SO_3

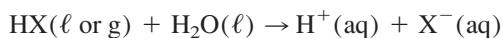
Solution

(b), (d), and (e) are acids; they are the only ones with hydrogen written first in the formula. The $\text{HC}_4\text{H}_7\text{O}_2$ has additional hydrogen atoms that do not react with bases; that is why they are not included with the H atom at the beginning of the formula.

Common Strong Acids

HCl
HBr
HI
 HClO_3
 HClO_4
 HNO_3
 H_2SO_4

All hydrogen-containing acids are covalent compounds when they are not in solution; they ionize when they react with water:



Those that react nearly 100% to form ions are called **strong acids**. Those that react only to a limited extent are called **weak acids**. The common strong acids are HCl, HBr, HI, HClO_3 , HClO_4 , HNO_3 , and H_2SO_4 . Practically all other acids are weak.

Thus double substitution reactions will go to form weak acids or bases—compounds that are mainly covalent even in water solution—but they will not go to form strong acids or bases in water solution.

EXAMPLE 8.19

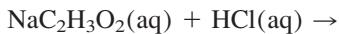
Which of the following reactions will proceed?

- (a) $\text{HF}(\text{aq}) + \text{NaBr}(\text{aq}) \rightarrow \text{HBr}(\text{aq}) + \text{NaF}(\text{aq})$
 (b) $\text{NaF}(\text{aq}) + \text{HBr}(\text{aq}) \rightarrow \text{NaBr}(\text{aq}) + \text{HF}(\text{aq})$

Solution

(b) This reaction takes place because the largely covalent HF is formed from the H^+ and F^- ions in solution. The $\text{HBr}(\text{aq})$ is fully ionized—it is a strong acid—and NaF is also ionic, containing Na^+ and F^- ions. Reaction (a) does not go because ions would be formed by reaction of a mainly covalent compound.

Practice Problem 8.19 Predict whether the following reaction will proceed:

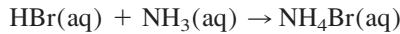
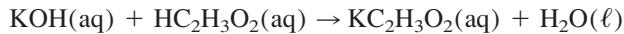


Bases provide hydroxide ions to aqueous solution. Soluble metal hydroxides, including those of the alkali metals and barium, are examples. The soluble metal hydroxides are ionic even when they are pure solids; *they remain ionic in water*. When they are dissolved in water, the hydroxide ions are totally separated from the metal ions. A soluble metal hydroxide is a **strong base**. A **weak base** is not 100% ionized. Ammonia, the most common weak base, reacts with water to a small extent to provide hydroxide ions:

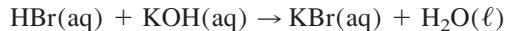


For example, if 1.00 mol of NH_3 is dissolved in a liter of water, only 0.004 mol of NH_4^+ and 0.004 mol of OH^- will be present. Almost all (0.996 mol) of the NH_3 remains in its molecular form.

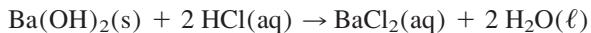
Weak acids and weak bases react with water to a small extent but they react with strong bases or acids essentially completely:



A strong acid and a strong base react with each other completely to form a salt and water:

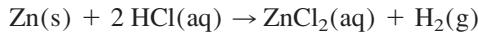


The driving force for double substitution reactions is formation of insoluble ionic compounds or covalent compounds from ions in solution. However, if an equation has an insoluble compound on one side and a covalent compound on the other, which way does the reaction go? In many cases like this, the formation of covalent compounds is more important than the formation of insoluble ionic compounds, as shown by the reaction of $\text{Ba}(\text{OH})_2$ with HCl. Acids usually react with insoluble bases to produce salts and water:

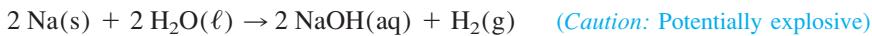


Single Substitution Reactions of Acids

Acids can react with metals more active than hydrogen (see Table 8.2) to produce a salt and hydrogen gas:



Extremely active metals, such as the alkali and alkaline earth metals, can even react with water to produce hydrogen gas plus the corresponding metal hydroxide. For example:



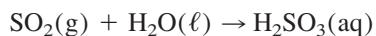
Acidic and Basic Anhydrides

Most metal oxides in which the metal ion has a 1+ or 2+ charge are **basic anhydrides**, and most nonmetal oxides are **acidic anhydrides**. In general, an

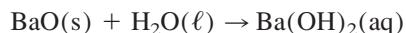
8.4 ■ Acids and Bases**229**

Anhydrides are like instant coffee; add water to get the acid or base.

anhydride is any compound that can result by loss of water from another compound. If water is added to an acidic anhydride, the anhydride becomes an acid. For example, sulfur dioxide plus water yields sulfurous acid:

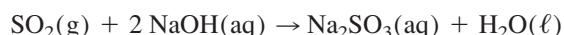


If water is added to a basic anhydride, the anhydride becomes a base. For example, barium oxide plus water yields barium hydroxide:



The first of the previous reactions is responsible for a good portion of the acid rain problem troubling the industrialized world. Sulfur, present in small quantities as an impurity in coal and oil, is converted to sulfur dioxide when the coal or oil is burned; then the sulfur dioxide reacts with the moisture in the air to produce sulfurous acid. Sulfurous acid can react with the oxygen in air to produce sulfuric acid. These acids are washed from the air by rain (or snow), and the solution can cause some corrosion of concrete and metal in buildings. Acids in the air and in the rain or snow also injure trees and other plants, as well as animals, including humans. In high concentrations, acids and acid anhydrides in the air can make breathing difficult, especially for people who are already in poor health.

Acidic anhydrides can react directly with bases, and basic anhydrides can react directly with acids. The same salt is produced as would be produced by the acid and base:



An acidic anhydride and a basic anhydride can even react with each other in a combination reaction:



EXAMPLE 8.20

Complete and balance an equation for each of the following reactions, and explain the relationships among the four.

- (a) $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow$
- (b) $\text{H}_2\text{SO}_4 + \text{CaO} \rightarrow$
- (c) $\text{SO}_3 + \text{Ca}(\text{OH})_2 \rightarrow$
- (d) $\text{SO}_3 + \text{CaO} \rightarrow$

Solution

- (a) $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4 + 2 \text{H}_2\text{O}$
- (b) $\text{H}_2\text{SO}_4 + \text{CaO} \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
- (c) $\text{SO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
- (d) $\text{SO}_3 + \text{CaO} \rightarrow \text{CaSO}_4$

The reaction of an acid and a base yields a salt and water. The reaction of the acid or base with the anhydride of the other yields the same salt but less water, and the reaction of the two anhydrides yields the same salt but no water.

Practice Problem 8.20 Classify the reactions of parts (a) and (d) of Example 8.20 according to the classes of Section 8.3.

EXAMPLE 8.21

Complete and balance an equation for each of the following reactions:

- (a) $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow$
(b) $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow$

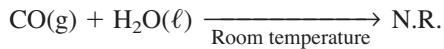
Solution

- (a) $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{ HNO}_2$
(b) $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{ NaOH}$

Practice Problem 8.21 Complete and balance an equation for each of the following reactions:

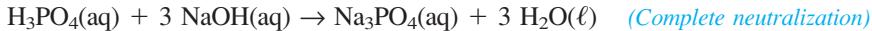
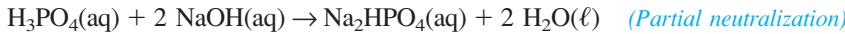
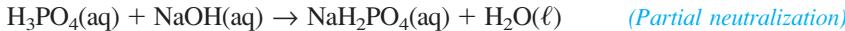
- (a) $\text{N}_2\text{O}_3 + \text{NaOH} \rightarrow$
(b) $\text{Na}_2\text{O} + \text{HNO}_3 \rightarrow$

A few nonmetal oxides, including CO and N_2O , are not acidic anhydrides; they do not react with water under ordinary conditions to form acids or with bases to form salts:

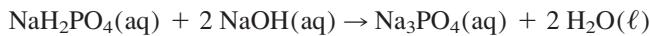
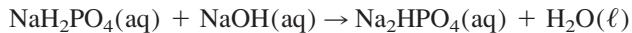


Acid Salts

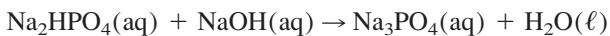
Acids containing more than one ionizable hydrogen atom, such as H_2SO_3 and H_3PO_4 , can be *partially* neutralized if less base is used than is needed for complete neutralization. The salt formed contains ionizable hydrogen atoms and therefore is still capable of reacting with bases:



A substance produced by a partial neutralization, such as NaH_2PO_4 or Na_2HPO_4 , is partially a salt and partially an acid. As the product of an acid and a base, it is a salt. However, it is capable of neutralizing more base, so it can also act as an acid:



or

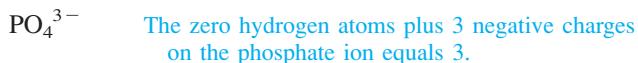


Such a substance is called an **acid salt**. The name of the compound includes the word *hydrogen* to denote the fact that one or more ionizable hydrogen atoms remain. The prefix *mono-* or *di-* may be used when it is necessary to indicate how many hydrogen atoms are present:



In an older nomenclature system, the word “acid” was used to denote an acid salt. In another old system, the prefix *bi-* was used for a half-neutralized acid that originally contained two ionizable hydrogen atoms. Thus, sodium bicarbonate and sodium acid carbonate are other names that have been used for NaHCO_3 .

In the anion of an acid salt, the number of hydrogen atoms plus the magnitude of the charge on the ion equals the magnitude of the charge on the oxoanion and also equals the number of hydrogen atoms in the acid:



EXAMPLE 8.22

What is the charge on the hydrogen sulfite ion?

Solution

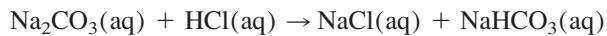
The charge is 1^- in HSO_3^- .

Practice Problem 8.22 What is the charge on the monohydrogen phosphate ion?

Carbonates and Acid Carbonates

Carbonates are compounds containing the carbonate ion. **Acid carbonates** are compounds containing the hydrogen carbonate ion. Just as acid-base reactions are an important type of double substitution reaction, the reactions of carbonates and acid carbonates with acids are an important subtype of acid-base reaction.

Carbonates undergo double substitution reactions with acids to form carbon dioxide and water or acid carbonates, depending on the relative quantity of acid added:



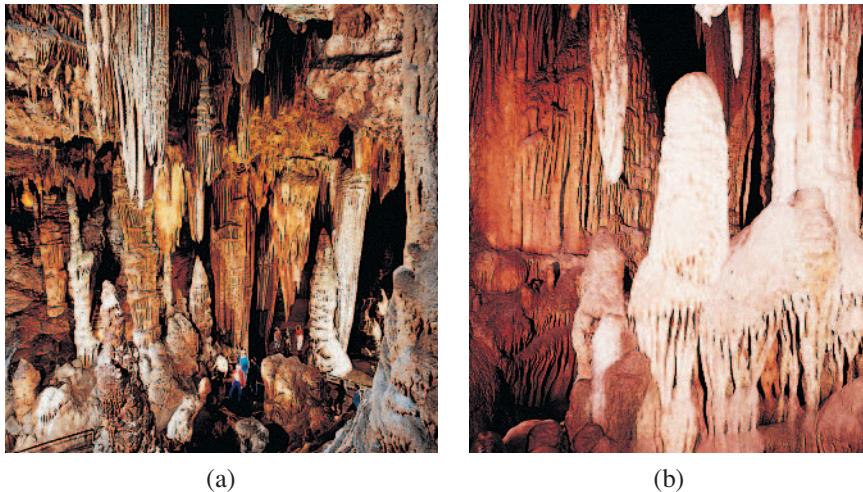
The acid either totally or partially neutralizes the carbonate.

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CHAPTER 8 ■ Chemical Reactions

Figure 8.9 Formation of Caves

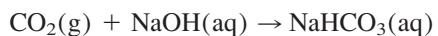
(a) Huge underground chambers, such as the Luray Caverns in the Blue Ridge Mountains of Virginia, are formed over eons by the reaction of carbon dioxide dissolved in water with solid limestone, CaCO_3 . (Note the people near the bottom center of the picture.) (b) Water containing calcium hydrogen carbonate, $\text{Ca}(\text{HCO}_3)_2$, dripped from the ceiling of the limestone cavern and deposited solid calcium carbonate, CaCO_3 , when the concentration of carbon dioxide was low. A droplet hanging from the ceiling formed a tiny portion of a stalactite; a droplet that hit the floor formed a tiny portion of a stalagmite.



(a)

(b)

Carbon dioxide, an acidic anhydride, can react with a base to form an acid carbonate or a carbonate:



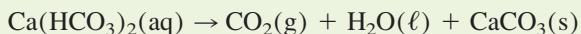
The base either partially or totally neutralizes the carbon dioxide.

ITEM OF INTEREST

Carbon dioxide present in relatively high concentration in water can dissolve insoluble carbonates to yield soluble acid carbonates:

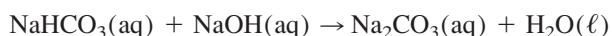


The reaction of limestone (CaCO_3) with water containing carbon dioxide in relatively high concentration can form natural caves, such as Luray Caverns in Virginia (Figure 8.9). If the carbon dioxide concentration is lowered, the reverse reaction can occur:



Thus, water dripping from the ceiling of a cavern can deposit CaCO_3 a tiny particle at a time, and over long periods can form stalactites and stalagmites.

Acid carbonates undergo double substitution reactions with either acids or bases, neutralizing them:



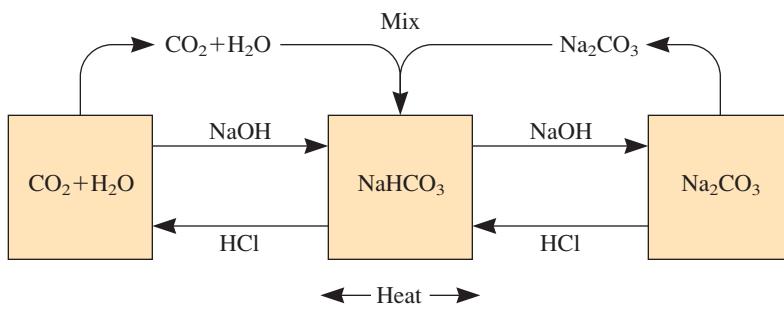
These types of reactions are summarized in Figure 8.10.

■ Symbols/Abbreviations

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Figure 8.10 Acid-Base Reactions Involving Carbonates and Acid Carbonates

Heating an acid carbonate, such as sodium hydrogen carbonate, produces the corresponding carbonate plus carbon dioxide and water. Mixing a carbonate, such as sodium carbonate, with carbon dioxide and water produces the corresponding acid carbonate, such as sodium hydrogen carbonate.



Snapshot Review

- Most reactions of acid plus metal or base can be included in the single or double substitution reactions of Section 8.3.
- Acids and bases are so important that a special nomenclature has grown up around them.
- Carbonates, acid salts, and acid and base anhydrides are similar to acids and bases in some of their chemical properties.

- A. Write a balanced chemical equation for the reaction of H_2SO_4 and $\text{Ba}(\text{OH})_2$, as well as the acid or base with the anhydride of the other, and of the two anhydrides themselves.
- B. Write a balanced chemical equation for the reaction of K_3PO_4 with
 - (a) an equal number of moles of HCl ,
 - (b) twice as many moles of HCl ,
 - (c) three times as many moles of HCl .

Key Terms

Key terms are defined in the Glossary.

acid (8.4)
acid carbonate (8.4)
acidic anhydride (8.4)
acid salt (8.4)
active (8.3)
anhydride (8.4)
aqueous solution (8.2)
Arrhenius theory (8.4)
balanced equation (8.1)
base (8.4)
basic anhydride (8.4)
carbonate (8.4)
catalyst (8.3)
coefficient (8.1)

combination reaction (8.3)
combustion (8.3)
decomposition reaction (8.3)
double displacement reaction (8.3)
double substitution reaction (8.3)
equation (8.1)
hydrocarbon (8.3)
metathesis reaction (8.3)
molten (8.3)
neutral (8.4)
neutralization reaction (8.4)
precipitate (8.3)
product (8.1)
reactant (8.1)

reactive (8.3)
reagent (8.1)
salt (8.4)
single displacement reaction (8.3)
single substitution reaction (8.3)
solubility (8.3)
stability (8.3)
state (8.2)
strong acid (8.4)
strong base (8.4)
ternary compound (8.3)
weak acid (8.4)
weak base (8.4)

Symbols/Abbreviations

(aq) (aqueous solution) (8.2)

(ℓ) (liquid) (8.2)

(s) (solid) (8.2)

(g) (gas) (8.2)

N.R. (no reaction) (8.3)

Summary

The balanced equation represents a chemical reaction. It not only identifies the reactants and the products, but also gives quantitative information on the ratios of all substances involved in the reaction (Section 8.1).

To balance an equation—that is, to make the numbers of atoms of each of the elements the same on both sides of the equation—we place coefficients in front of each formula in the equation. The state of each substance may be indicated as gas (g), liquid (l), solid (s), or solute in aqueous solution (aq) (Section 8.2).

With a little experience, we can predict the products of simple reactions from the nature of the reactants. In writing formulas for the products, always use the rules given in Chapter 5; do not write incorrect formulas to make balancing an equation easier. Simple reactions can be divided into five types: combination reactions, decomposition reactions, single substitution reactions, double substitution reactions, and combustion reactions. Identifying the type of reaction can help greatly in deducing the product(s). If two free elements are given, they can either combine or do nothing; they cannot be broken down into simpler substances. If only one compound is given, it probably will decompose, especially if energy is

provided. An element and a compound can react to give a new compound and another free element. The relative reactivity of the elements (Table 8.2) determines whether a single substitution reaction can occur. Two ionic compounds can swap ions to produce two new compounds. Solubility in water (Table 8.3) often determines whether a double substitution reaction can occur. Rapid reaction with oxygen is combustion. Carbon-containing compounds react with limited oxygen to produce carbon monoxide or react with excess oxygen to give carbon dioxide (Section 8.3).

Acids and bases react according to the rules in Section 8.3, but their reactions are so common that further details need to be learned. The double substitution reaction of an acid with a base is called a neutralization reaction. The products are water and a salt. Strong acids react with water completely to form ions, and weak acids react with water only slightly, but both kinds of acids react with bases to form salts. Substances that react with water to form acids or bases are called anhydrides. Acids containing more than one ionizable hydrogen atom can be partially neutralized, forming acid salts. Carbonates and acid carbonates react similarly to bases (Section 8.4).

Items for Special Attention

- Never treat spilled acid or base with strong base or strong acid. Excess of the reagent might do more harm than the original acid or base, and the heat of the neutralization reaction might also cause problems. Instead, flood with water, and later treat with sodium hydrogen carbonate, NaHCO_3 , which is almost neutral and produces safe reaction products. Called baking soda in everyday life, sodium hydrogen carbonate is as effective at home as it is in the laboratory.
- Note the difference between the words “acidic” and “acetic,” which sound alike.

- We can often apply a generality to answer a specific question. For example, you can tell that Na_2MoO_4 is soluble in water even if we have never seen this formula before. According to Table 8.3, all alkali metal compounds are soluble, and this compound is an alkali metal salt.
- There are no basic salts (corresponding to acid salts) resulting from partial neutralization of bases with more than one hydroxide ion per formula unit.

Answers to Snapshot Reviews

- 8.1 A. (a) 15 molecules of HCl (b) 15 mol of HCl
B. There is no difference.
- 8.2 A. (a) $\text{P}_4\text{O}_6(\text{s}) + 6 \text{H}_2\text{O}(\ell) \rightarrow 4 \text{H}_3\text{PO}_3(\ell)$
(b) $\text{TiCl}_4(\ell) + 2 \text{H}_2\text{O}(\ell) \rightarrow \text{TiO}_2(\text{s}) + 4 \text{HCl}(\text{g})$
(c) $2 \text{CoCl}_3(\text{aq}) + \text{Co}(\text{s}) \rightarrow 3 \text{CoCl}_2(\text{aq})$
- 8.3 A. (a) $\text{BaO}(\text{s}) + \text{H}_2\text{O}(\ell) \rightarrow \text{Ba}(\text{OH})_2(\text{s})$
(b) $2 \text{Al}(\text{s}) + 3 \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Al}_2(\text{SO}_4)_3(\text{aq}) + 3 \text{H}_2(\text{g})$
(c) $2 \text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow 2 \text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$

- 8.4 A. $\text{H}_2\text{SO}_4(\text{aq}) + \text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{BaSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\ell)$
 $\text{H}_2\text{SO}_4(\text{aq}) + \text{BaO}(\text{s}) \rightarrow \text{BaSO}_4(\text{s}) + \text{H}_2\text{O}(\ell)$
 $\text{SO}_3(\text{g}) + \text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{BaSO}_4(\text{s}) + \text{H}_2\text{O}(\ell)$
 $\text{SO}_3(\text{g}) + \text{BaO}(\text{s}) \rightarrow \text{BaSO}_4(\text{s})$
- B. $\text{K}_3\text{PO}_4(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{K}_2\text{HPO}_4(\text{aq})$
 $\text{K}_3\text{PO}_4(\text{aq}) + 2 \text{HCl}(\text{aq}) \rightarrow 2 \text{KCl}(\text{aq}) + \text{KH}_2\text{PO}_4(\text{aq})$
 $\text{K}_3\text{PO}_4(\text{aq}) + 3 \text{HCl}(\text{aq}) \rightarrow 3 \text{KCl}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq})$

■ Self-Tutorial Problems

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Self-Tutorial Problems

- 8.1** Assign each of the following types to one of the five classes of reactions presented in Section 8.3:

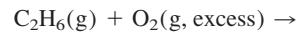
Reactants	Products
(a) 2 elements	1 compound
(b) 1 compound	2 elements
(c) 2 compounds	2 different compounds
(d) 1 element + 1 compound	1 element + 1 compound
(e) 1 compound	1 element + 1 compound
(f) 1 compound + O ₂	2 or more compounds
(g) 1 element + 1 compound	1 compound

- 8.2** Explain how to recognize that O₂ and MgO will not react with each other in a single substitution reaction.
- 8.3** Rewrite the following equations with integral coefficients:
- (a) CrF₂(s) + $\frac{1}{2}$ F₂(g) → CrF₃(s)
- (b) CoCl₃(s) + $\frac{1}{2}$ Co(s) → $\frac{3}{2}$ CoCl₂(s)
- (c) CuCl(s) + $\frac{1}{2}$ Cl₂(g) → CuCl₂(s)
- (d) $\frac{2}{3}$ H₃PO₄(aq) + CaCO₃(s) →
 $\frac{1}{3}$ Ca₃(PO₄)₂(s) + H₂O(ℓ) + CO₂(g)
- (e) NH₃(g) + $\frac{5}{4}$ O₂(g) → NO(g) + $\frac{3}{2}$ H₂O(g)
- 8.4** Write a balanced chemical equation for each of the following reactions:
- (a) SO₂(g) + PCl₅(s) → SOCl₂(ℓ) + POCl₃(ℓ)
- (b) SO₂(g) + Cl₂(g) → SO₂Cl₂(ℓ)
- 8.5** What is the difference, if any, among (a) the reaction of sodium with chlorine, (b) the combination of sodium and chlorine, and (c) the formation of sodium chloride from its elements?
- 8.6** Consider the reaction of aqueous chlorine with aqueous zinc iodide.
- (a) Identify the reaction type.
- (b) Write correct formulas for all reactants and products.
- (c) Write a balanced equation.
- 8.7** Explain how a catalyst resembles a marriage broker.
- 8.8** A certain double substitution reaction produced silver chloride and potassium acetate. What were the reactants?
- 8.9** Can a single substitution reaction occur between an element and a compound of that same element?

- 8.10** Can a double substitution reaction occur between two compounds containing one ion in common?

- 8.11** Are oxides of reactive metals or oxides of unreactive metals more likely to decompose into their two elements when heated?

- 8.12** What type of reaction is the following? What are the products?



- 8.13** In a certain double substitution reaction, CrCl₃ is a reactant. Is Cr(NO₃)₃ or Cr(NO₃)₂ more likely to be a product?

- 8.14** Do the classes of reactions described in Section 8.3 include all possible types of chemical reactions?

- 8.15** Which table in this chapter should be used when working with single substitution reactions, and which ones with double substitution reactions?

- 8.16** Which of the following compounds are acids?



- 8.17** Classify each of the following as an acidic anhydride, a basic anhydride, or neither:



- 8.18** Which, if any, of the common acids exist completely in the form of ions (a) as a pure compound and (b) in aqueous solution?

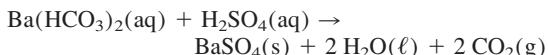
- 8.19** What products are expected in each of the following cases?

- (a) KClO₃ is heated in the presence of MnO₂ as a catalyst.
 (b) KClO₃ is heated in the presence of MnO₂.
 (c) KClO₃ and MnO₂ are heated together.
 (d) KClO₃ is heated.

- 8.20** What type of substance can act as an acid but does not have hydrogen written first in its formula?

- 8.21** What is the difference between “acidic” and “acetic”?

- 8.22** Give two reasons why the following reaction produces products:



Problems

8.1 The Chemical Equation

- 8.23 How many moles of phosphorus are present in
(a) 4.0 mol of tetraphosphorus hexoxide?
(b) 5.0 mol of phosphoric acid?
(c) 6.0 mol of diphosphorus pentasulfide?
- 8.24 List the number of atoms of each element in the given number of formula units:
(a) 3 KClO₃ (b) 4 H₂O₂
(c) 2 Ca(ClO₃)₂ (d) 3 CuSO₄·5H₂O
(e) 6 (NH₄)₃PO₄

- 8.25 How many atoms of oxygen are present in
(a) Three molecules of ozone, O₃?
(b) Four formula units of Mg(HCO₃)₂?
(c) Two formula units of Mn(C₂H₃O₂)₂?
- 8.26 (a) If two molecules of H₂O react with sodium metal according to the following equation, how many molecules of H₂ will be produced?
$$2 \text{Na(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{NaOH(aq)} + \text{H}_2\text{(g)}$$
- (b) If 2.00 mol of H₂O reacts with sodium metal according to the equation, how many moles of H₂ will be produced?

- 8.27 (a) If one molecule of P₄ reacts with chlorine gas according to the following equation, how many molecules of PCl₅ will be produced?
$$\text{P}_4\text{(s)} + 10 \text{Cl}_2\text{(g)} \rightarrow 4 \text{PCl}_5\text{(s)}$$
- (b) If 1.00 mol of P₄ reacts with chlorine gas according to the equation, how many moles of PCl₅ will be produced?

8.2 Balancing Equations

- 8.28 Write a balanced chemical equation for each of the following reactions:
(a) Aqueous potassium hydroxide plus phosphoric acid yields potassium phosphate plus water.
(b) Aqueous sodium sulfate plus barium bromate yields barium sulfate plus sodium bromate.
(c) Aqueous calcium hydrogen carbonate plus hydrochloric acid yields calcium chloride plus carbon dioxide plus water.
(d) Solid sulfur plus fluorine gas yields liquid sulfur hexafluoride.

- 8.29 Write a balanced equation for the reaction of oxygen gas and nitrogen monoxide gas to form gaseous N₂O₃.

8.30 Balance the equation for each of the following reactions:

- (a) Cu₂S(s) + O₂(g) → Cu(s) + SO₂(g)
(b) CO₂(g) + H₂(g) $\xrightarrow{\text{Heat}}$ CO(g) + H₂O(g)
(c) ZnS(s) + O₂(g) → ZnO(s) + SO₂(g)
(d) H₂O(ℓ) + SCl₄(ℓ) → HCl(aq) + H₂SO₃(aq)
(e) O₂(g) + MnO(s) → Mn₃O₄(s)
(f) C₇H₁₄O(ℓ) + O₂(g) → CO₂(g) + H₂O(g)

8.31 Balance the equation for each of the following reactions:

- (a) AlCl₃(aq) + NaOH(aq) → NaAl(OH)₄(aq) + NaCl(aq)
(b) H₃PO₄(aq) + NaOH(aq) → Na₃PO₄(aq) + H₂O(ℓ)
(c) C₂H₆(g) + O₂(g) → CO₂(g) + H₂O(ℓ)
(d) MnO₂(s) + H₂C₂O₄(aq) → CO₂(g) + MnO(s) + H₂O(ℓ)
(e) As₂S₃(s) + O₂(g) → As₂O₃(s) + SO₂(g)
(f) C₂H₄O(ℓ) + O₂(g) → CO₂(g) + H₂O(g)
(g) CuSO₄·5H₂O(s) + NH₃(aq) → CuSO₄·4NH₃(aq) + H₂O(ℓ)
(h) Na₂SO₃(aq) + S(s) → Na₂S₂O₃(aq)
(i) Zn(s) + NaOH(aq) + H₂O(ℓ) → Na₂Zn(OH)₄(aq) + H₂(g)
(j) BiCl₃(aq) + H₂O(ℓ) → Bi(O)Cl(s) + HCl(aq)
(k) NaAl(OH)₄(aq) + HCl(aq) → AlCl₃(aq) + H₂O(ℓ) + NaCl(aq)
(l) C₆H₁₂(ℓ) + O₂(g) → CO(g) + H₂O(g)
(m) Mn₃O₄(s) + O₂(g) → Mn₂O₃(s)

- 8.32 Write a balanced equation for the reaction of aqueous copper(II) nitrate with aqueous sodium iodide to produce solid copper(I) iodide plus aqueous iodine plus aqueous sodium nitrate.

8.33 Balance the equation for each of the following reactions:

- (a) Al₂O₃(in solution) + C(s) $\xrightarrow[\text{Heat}]{\text{Electricity}}$ Al(ℓ) + CO(g)
(b) N₂(g) + O₂(g) $\xrightarrow{\text{Lightning}}$ NO(g)
(c) C₃O₂(s) + O₂(g) → CO₂(g)
(d) B₂H₆(g) + O₂(g) → B₂O₃(s) + H₂O(ℓ)
(e) C(s) + O₂(g) → CO₂(g)
(f) NO₂(g) $\xrightarrow{\text{Cool}}$ N₂O₄(ℓ)
(g) Ba(s) + O₂(g) $\xrightarrow{\text{Heat}}$ BaO(s)
(h) Na(s) + Cl₂(g) → NaCl(s)
(i) P(s) + O₂(g) → P₂O₅(s)

■ Problems

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- 8.34 Write a balanced chemical equation for each of the following reactions:
- Aqueous lithium hydroxide reacts with gaseous carbon dioxide to produce aqueous lithium hydrogen carbonate.
 - Solid calcium sulfite decomposes on heating to produce solid calcium oxide and sulfur dioxide gas.
 - Pentene gas (C_5H_{10}) burns in excess oxygen to produce carbon dioxide and water.
 - Water reacts with sodium metal to produce aqueous sodium hydroxide and hydrogen gas. (*Caution: This reaction is potentially explosive.*)
 - Lithium metal when heated with nitrogen gas reacts to produce solid lithium nitride.
- 8.35 Balance the equation for each of the following reactions:
- $Li(s) + O_2(g) \rightarrow Li_2O(s)$
Oxide
 - $Na(s) + O_2(g) \rightarrow Na_2O_2(s)$
Peroxide
 - $K(s) + O_2(g) \rightarrow KO_2(s)$
Superoxide
- 8.3 Predicting the Products of Chemical Reactions**
- 8.36 Write two balanced equations for the reaction of $(NH_4)_2CO_3$ with HCl.
- 8.37 The following reagents in aqueous solution produce the indicated product. What conclusions can you reach about the barium carbonate?
- $$Ba(NO_3)_2 + Na_2CO_3 \rightarrow BaCO_3 + 2 NaNO_3$$
- 8.38 Write a balanced equation for the reaction of (a) iron with HCl(aq) to form an iron(II) compound and (b) iron with chlorine to form an iron(III) compound.
- 8.39 Complete and balance each of the following equations:
- $NaCl(\ell) \xrightarrow{\text{Electricity}}$
 - $H_2O(\ell) \xrightarrow{\text{Electricity}} Na_2SO_4$
 - $HCl(aq) \xrightarrow{\text{Electricity}}$
- 8.40 Write two balanced equations for the possible reactions of H_2SO_3 with NaOH.
- 8.41 In which of the following systems is a reaction expected? Complete the equation for any reaction that occurs.
- $FeCl_2 + Cl_2 \rightarrow$
 - $FeCl_3 + Cl_2 \rightarrow$
- 8.42 Complete and balance each of the following equations:
- $Al(s) + FeCl_2(s) \xrightarrow{\text{Heat}}$
 - $Cl_2(g) + AlI_3(aq) \rightarrow$
 - $Ba(C_2H_3O_2)_2(aq) + Na_2CO_3(aq) \rightarrow$
 - $BaCl_2(aq) + (NH_4)_2SO_4(aq) \rightarrow$
 - $Ba(ClO_4)_2(aq) + Na_2SO_4(aq) \rightarrow$
 - $NH_3(g) + HCl(aq) \rightarrow$
- 8.43 Complete and balance an equation for each of the following reactions. If no reaction occurs, write N.R.
- $Zn(s) + HCl(aq) \rightarrow$
 - $Ag(s) + HCl(aq) \rightarrow$
 - $Au(s) + HCl(aq) \rightarrow$
- 8.44 Table 8.3 states that most sulfides are insoluble in water. Which sulfides are soluble?
- 8.45 Complete and balance chemical equations for the combustion of propane and butane:
- $C_3H_8(g) + O_2(g, \text{ limited supply}) \rightarrow$
 - $C_3H_8(g) + O_2(g, \text{ excess}) \rightarrow$
 - $C_4H_{10}(g) + O_2(g, \text{ limited supply}) \rightarrow$
 - $C_4H_{10}(g) + O_2(g, \text{ excess}) \rightarrow$
- 8.46 Write two balanced equations for the possible reactions of toluene, C_7H_8 , with oxygen.
- 8.47 Complete and balance each of the following equations:
- $C_7H_{16}O_2(\ell) + O_2(g, \text{ excess}) \rightarrow$
 - $C_8H_{16}O_2(\ell) + O_2(g, \text{ limited}) \rightarrow$
- 8.48 Which type of reaction involving ionic compounds is most likely to occur without any change in the charges on the ions?
- 8.49 Complete and balance an equation for each of the following chemical reactions:
- Production of copper(I) bromide from its elements
 - Production of copper(I) sulfide from its elements
 - Methane (CH_4) plus limited oxygen
 - Zinc chloride plus silver nitrate
 - Perchloric acid plus barium hydroxide
- 8.50 Complete and balance each of the following equations:
- $Ba(s) + H_2O(\ell) \rightarrow$
 - $F_2(g) + H_2O(\ell) \rightarrow$
- 8.51 In which, if any, of the following systems is a reaction expected?
- $MgCl_2(aq) + Pb(s) \rightarrow$
 - $Au(s) + HCl(aq) \rightarrow$
 - $ZnCl_2(aq) + Cl_2(g) \rightarrow$
 - $Ne(g) + O_2(g) \rightarrow$

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8.52 Consider the following pair of reactants:



- (a) Adding chromium metal to the compound is equivalent to doing what with the chlorine?
(b) What other compound of chromium and chlorine exists?
(c) Complete and balance the preceding equation.
(d) Write the symbol for chromium surrounded by the symbols for three chlorine atoms, and write a second such set to the right of the first set. Add another chromium atom between two of the chlorine atoms, and encircle three sets of atoms to make the compound in part (b).

8.53 If a compound decomposes without any external energy being added in some form, do you expect the compound to be very long-lasting? Explain.

8.54 Complete and balance each of the following equations:

- (a) $\text{C}_5\text{H}_{10}\text{O}(\ell) + \text{O}_2(\text{g}, \text{limited}) \rightarrow$
(b) $\text{C}_5\text{H}_{12}\text{O}_2(\ell) + \text{O}_2(\text{g}, \text{excess}) \rightarrow$

8.55 Complete and balance each of the following equations:

- (a) $\text{CrO}(\text{s}) + \text{O}_2(\text{g}) \rightarrow$
(b) $\text{AsCl}_5(\ell) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{AsO}_4(\text{aq}) +$
(c) $\text{PCl}_3(\ell) + \text{Cl}_2(\text{g}) \rightarrow$
(d) $\text{Mg}(\text{s}) + \text{N}_2(\text{g}) \rightarrow$

8.56 Complete and balance each of the following equations:

- (a) $\text{Fe}_2(\text{SO}_4)_3(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow$
(b) $\text{FeSO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow$
(c) $(\text{NH}_4)_2\text{SO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow$

8.57 Write a balanced equation for the reaction of chlorine with (a) an alkali metal and (b) an alkaline earth metal.

8.4 Acids and Bases

8.58 Complete and balance each of the following equations:

- (a) $\text{H}_3\text{PO}_4(\text{aq}) + \text{KOH}(\text{aq}, \text{excess}) \rightarrow$
(b) $\text{Ba}(\text{OH})_2(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow$
(c) $\text{Na}_2\text{HPO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
(d) $\text{Ba}(\text{OH})_2(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}, \text{limited}) \rightarrow$

8.59 Solid MgCO_3 “dissolves” in excess $\text{HCl}(\text{aq})$. Write an equation for the reaction. Describe what we would expect to see during this reaction.

8.60 Complete and balance each of the following equations:

- (a) $\text{K}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq}, \text{limited}) \rightarrow$
(b) $\text{K}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq}, \text{excess}) \rightarrow$
(c) $\text{Na}_2\text{O}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow$
(d) $\text{NaOH}(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow$

CHAPTER 8 ■ Chemical Reactions

8.61 Complete and balance each of the following equations:

- (a) $\text{NH}_4\text{Cl}(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow$
(b) $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HClO}_3(\text{aq}) \rightarrow$

8.62 Write an equation for the reaction of carbon dioxide and water with calcium carbonate to produce a soluble product.

8.63 Write balanced equations for two possible reactions of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) with sodium hydroxide (limited and excess).

8.64 State four different ways that CaCl_2 can be prepared, starting with $\text{HCl}(\text{aq})$ plus other reagents.

8.65 Complete and balance each of the following equations:

- (a) $\text{HClO}_3(\text{aq}) + \text{ZnO}(\text{s}) \rightarrow$
(b) $\text{N}_2\text{O}_3(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow$
(c) $\text{SO}_3(\text{g}) + \text{LiOH}(\text{aq}) \rightarrow$

8.66 Complete and balance the following equations:

- (a) $\text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow$ (b) $\text{Cl}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow$
(c) $\text{Cl}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow$ (d) $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow$

8.67 Complete and balance each of the following equations:

- (a) $\text{SO}_3(\text{g}) + \text{K}_2\text{O}(\text{s}) \rightarrow$
(b) $\text{SO}_2(\text{g}) + \text{KOH}(\text{aq}) \rightarrow$
(c) $\text{SO}_2(\text{g}) + \text{K}_2\text{O}(\text{s}) \rightarrow$

8.68 Complete and balance the following equations:

- (a) $\text{KOH} + \text{KHCO}_3 \rightarrow$
(b) $\text{HCl} + \text{KHCO}_3 \rightarrow$
(c) $\text{K}_2\text{O} + \text{CO}_2 \rightarrow$
(d) $\text{KOH} + \text{CO}_2 \rightarrow$

8.69 Complete and balance each of the following equations, assuming that an excess of the second reactant is present. Comment on why each reaction proceeds.

- (a) $\text{NaH}_2\text{BO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow$
(b) $\text{MgCO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow$
(c) $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow$
(d) $\text{Na}_2\text{O}(\text{s}) + \text{HClO}_3(\text{aq}) \rightarrow$
(e) $\text{Ba}(\text{OH})_2(\text{aq}) + \text{HClO}_3(\text{aq}) \rightarrow$
(f) $\text{Mg}(\text{OH})_2(\text{s}) + \text{HNO}_3(\text{aq}) \rightarrow$

8.70 Complete and balance each of the following equations:

- (a) $\text{H}_3\text{PO}_4(\text{aq}) + \text{NaOH}(\text{aq}, \text{limited quantity}) \rightarrow$
(b) $\text{HClO}_3(\text{aq}, \text{excess}) + \text{BaCO}_3(\text{s}) \rightarrow$
(c) $\text{HCl}(\text{aq}) + \text{Mg}(\text{HCO}_3)_2(\text{aq}) \rightarrow$

8.71 What are the products of the reaction of

- (a) An acid and a base?
(b) An acid and a metal oxide?
(c) An acid and a carbonate?
(d) What is the major difference among these?

■ General Problems

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General Problems

- 8.72** Explain the difference among the following questions:
- What is the product of the electrolysis of water containing dilute NaCl to carry the current?
- What is the product of the electrolysis of water containing dilute NaCl?
- What is the product of the electrolysis of dilute aqueous NaCl?
- 8.73** Consider the following pairs of reactants. For each, determine the possible reaction type, and write correct formulas for the products that could be produced. If the reaction can proceed, write a balanced equation.
- CO(g) and O₂(g)
 - HCl(aq) and Al(s)
 - KNO₃(aq) and AgCl(s)
- 8.74** Give one example of each type of reaction in Problem 8.1.
- 8.75** (a) Which class of reaction requires only one reactant?
 (b) Does the addition of a catalyst change the answer to part (a)?
 (c) How can we recognize a substance as a catalyst?
- 8.76** Is each of the following equations balanced? Is each correct?
- AgCl(s) + HNO₃(aq) → HCl(aq) + AgNO₃(aq)
 - ZnCl₂(aq) + Fe(s) → FeCl₂(aq) + Zn(s)
 - KCl(aq) + NaNO₃(aq) → NaCl(aq) + KNO₃(aq)
- 8.77** What is unusual about the following decomposition reactions?
- NH₄HCO₃(s) $\xrightarrow{\text{Heat}}$
 - Ca(HCO₃)₂(s) $\xrightarrow{\text{Heat}}$
- 8.78** Complete and balance each of the following equations:
- HCl(aq) + NaHCO₃(aq) →
 - NaOH(aq) + NaHSO₃(aq) →
 - HNO₃(aq) + Ba(OH)₂(aq) →
 - KF(aq) + HCl(aq) →
- 8.79** Balance the following equation:
- $$\text{Cu}(\text{NO}_3)_2(\text{aq}) + \text{KI}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + \text{KNO}_3(\text{aq}) + \text{CuI}(\text{s})$$
- 8.80** How can we distinguish a combustion reaction from a displacement reaction, considering that each may involve an element and a compound?
- 8.81** Addition of aqueous ammonia to a solution of Ca(HCO₃)₂(aq) causes a white solid to form. What is the formula of the solid? Write an equation for the reaction.
- 8.82** Neither N₂O nor CO reacts with water under normal conditions. What is unusual about that lack of reactivity?
- 8.83** Complete and balance each of the following equations:
- C₅H₁₀O₂(ℓ) + O₂(g, excess) →
 - C₃H₈(g) + O₂(g, excess) →
 - C₁₂H₂₆(ℓ) + O₂(g, limited) →
Kerosene
 - C₁₂H₂₆(ℓ) + O₂(g, excess) →
Kerosene
- 8.84** Explain why the Solvay process is used instead of the following reaction:
- $$\text{CaCO}_3 + 2\text{NaCl} \rightarrow \text{CaCl}_2 + \text{Na}_2\text{CO}_3$$
- 8.85** Complete and balance each of the following equations:
- CrCl₂(aq) + AgNO₃(aq) →
 - CrCl₃(aq) + AgNO₃(aq) →
- 8.86** Inexpensive metal forks corrode rapidly if used in a delicatessen to remove pickles from the juice in which they are shipped. Explain the probable cause.
- 8.87** Assuming that water containing Ca(HCO₃)₂ deposits 1 mg of CaCO₃ per minute on the ceiling of a limestone cavern, how long will it take to produce a stalactite with a mass of 75 metric tons (1 metric ton = 1 × 10⁶ g)?
- 8.88** What products are expected from the reaction of ammonium chloride and potassium hydroxide? Write an equation for the reaction.
- 8.89** Complete and balance each of the following equations:
- CrBr₃(s) + Cl₂(g) →
 - CrCl₂(s) + Cl₂(g) →
 - CrBr₂(s) + Cl₂(g, excess) →
- 8.90** Balance the following equation:
- $$\text{NaI}(\text{aq}) + \text{Cr}(\text{NO}_3)_3(\text{aq}) \rightarrow \text{CrI}_2(\text{aq}) + \text{NaNO}_3(\text{aq}) + \text{I}_2(\text{aq})$$
- 8.91** A certain double substitution reaction produced sodium sulfate, carbon dioxide, and water. Write four balanced chemical equations that could have occurred.
- 8.92** Balance the equation for each of the following reactions:
- Lithium metal plus oxygen produces lithium oxide.
 - Sodium metal plus oxygen gas produces sodium peroxide.
 - Potassium metal plus oxygen produces potassium superoxide.
- 8.93** A student bubbled an excess of fluorine gas into aqueous sodium iodide, producing sodium fluoride and sodium periodate. What additional products did she obtain?

9

Net Ionic Equations

- 9.1 Properties of Ionic Compounds in Aqueous Solution
- 9.2 Writing Net Ionic Equations



Conversion of Cu^{2+} to a more complex ion by the addition of ammonia is evidenced by the color change

Review Clues

- Section 9.1** Sections 5.2, 5.4, 8.3, 8.4
Section 9.2 Chapter 8

Objectives

- 9.1** To recognize that each type of ion in an aqueous solution of an ionic compound is not affected by the properties of the other type(s) of ion(s) in the solution
To write formulas for the ions present in solution when an ionic compound or a strong acid is dissolved in water
- 9.2** To write net ionic equations for reactions in aqueous solution and to interpret such equations

9.1 ■ Properties of Ionic Compounds in Aqueous Solution**241**

Section 9.1 describes the properties of ionic compounds in aqueous solution. Section 9.2 then explains how to write net ionic equations for many reactions in aqueous solution. These equations show the actual reactions that occur; ions that do not change at all during the reaction are not included. Each net ionic equation can summarize many equations involving complete compounds.

Net ionic equations are used in discussions of limiting quantities problems (Chapter 10), molarities of ions (Chapter 11), balancing oxidation-reduction equations (Chapter 16), acid-base theory (Chapter 19), and many other areas beyond the scope of this book. They make possible writing equations for half-reactions at the electrodes in electrochemical experiments (Chapter 17), which have electrons included explicitly in them. They make understandable the heat effects of many reactions such as those of strong acids with strong bases.

9.1 Properties of Ionic Compounds in Aqueous Solution

The properties of ionic compounds in solution are actually the properties of the individual ions themselves (Figure 9.1). These compounds are called **strong electrolytes** because their solutions conduct electricity well. For example, an aqueous solution of sodium chloride consists essentially of sodium ions and chloride ions in water. A similar solution of calcium chloride consists of calcium ions and chloride ions in water. If either solution is treated with a solution containing silver ions, the chloride ions will form silver chloride, which is insoluble. The chloride ions act independently of the cation that is also present, regardless of whether it is sodium ion, calcium ion, or any other ion. Because the properties of the compound are the properties of the component ions, we need to learn to write equations for only the ions that react, omitting the ions that remain unchanged throughout the reaction (Section 9.2).

Strong acids, strong bases (Table 9.1), and salts all provide ions in solution. They are all strong electrolytes, but the process by which these types of compounds form ions in solution differs. When they are pure, strong acids are covalent compounds, but they undergo a chemical reaction with water to form ions in solution. This process, called *ionization*, will be discussed in more detail

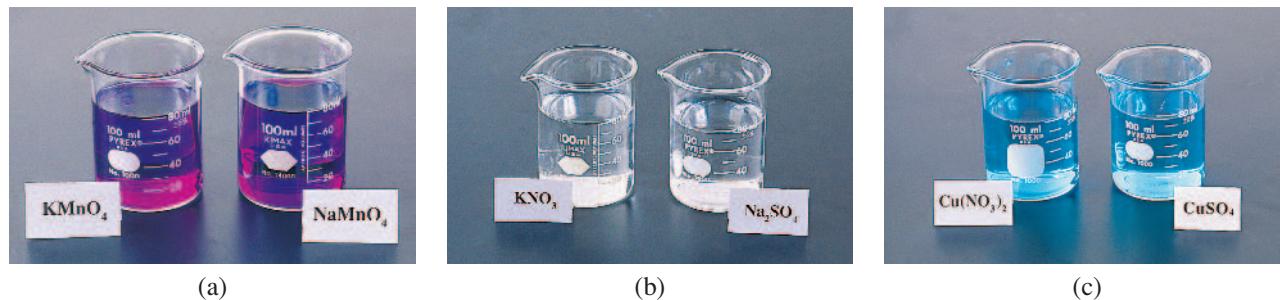


Figure 9.1 Properties of Ions

(a) The purple color of these two solutions is due to the permanganate ion. (b) Solutions of potassium and sodium ions with different anions than the permanganate ion show that these cations are colorless. (c) The blue color of these solutions is characteristic of the copper(II) ion; the nitrate ion and the sulfate ion are colorless, as shown in part (b).

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CHAPTER 9 ■ Net Ionic Equations

Table 9.1 Strong Acids and Bases

Strong Acids	Strong Bases
HCl	All soluble metal hydroxides,
HBr	such as NaOH,
HI	KOH, and
HClO ₃	Ba(OH) ₂ *
HClO ₄	
HNO ₃	
H ₂ SO ₄	

*Note that Ba(OH)₂ has limited solubility.

Table 9.2 Electrolytic Properties of Various Types of Compounds*Electrolytes*

Strong electrolytes

Salts

Strong acids

Strong bases

Weak electrolytes

Weak acids

Weak bases

Nonelectrolytes

Covalent compounds other than acids or bases

in Chapter 19. Salts and strong bases are ionic even when they are pure, and their interaction with water is more a physical process than a chemical reaction. The solution process for them is called *dissociation* because the ions dissociate from each other; that is, they get out of each other's sphere of influence and are able to move relatively independently of ions of the opposite charge.

Weak acids and bases ionize only slightly in aqueous solution. Because their solutions conduct electricity poorly, they are called **weak electrolytes**. Compounds whose solutions do not conduct electricity at all are called **non-electrolytes**. An outline of the electrolytic properties of compounds is presented in Table 9.2.

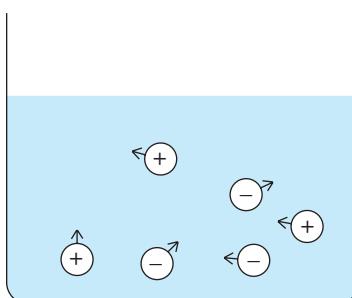
A strong electrolyte *in aqueous solution* may be represented as separate ions because the ions of each type are free to move about independently of the ions of the other type. However, an ionic solid that is not dissolved in water is not written as separate ions; the oppositely charged ions in the solid lattice of an ionic compound are not independent of each other (Figure 9.2).

Thus, compounds must be both soluble and ionic to be written in the form of their separate ions. A listing of water-soluble compounds was given in Table 8.3. In addition to the compounds listed there, all strong acids are water soluble. In summary strong electrolytes—compounds that dissociate or ionize extensively in aqueous solution—include the following:

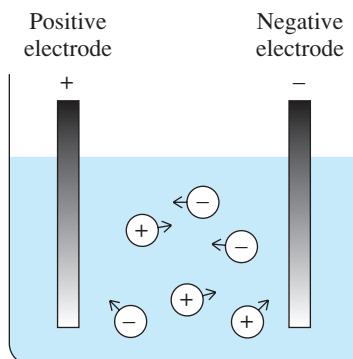
1. All soluble metal hydroxides
2. All salts (other compounds containing metal or ammonium ions) that are soluble
3. Strong acids (HCl, HClO₃, HClO₄, HBr, HI, HNO₃, H₂SO₄)

All other compounds (for example, gases, other covalent compounds, and all solids) either contain no ions or have ions that are affected by the presence of the other ions. These weak electrolytes, nonelectrolytes, or solids (ionic or not) are written using their regular formulas.

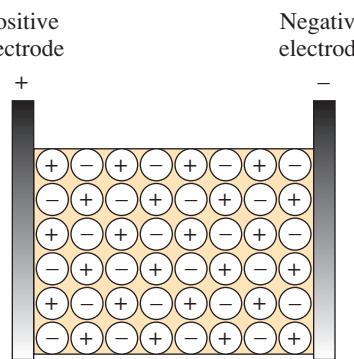
Compounds must be both soluble and ionic to be written in the form of their separate ions.



(a) Solution of ions



(b) Effect of charged electrodes



(c) Ionic solid

Figure 9.2 Mobility of Ions

(a) Ions in dilute solutions are free to move independently of other ions. In the absence of electrodes, they move in random directions. (b) Under the influence of the charges on electrodes, the ions move toward the electrode of opposite charge. (c) In contrast, even if charged electrodes are present, ions in solids cannot move because of the surrounding ions of opposite charge.

9.2 ■ Writing Net Ionic Equations**243****EXAMPLE 9.1**

Write each of the following compounds to represent best how it acts in the presence of water:

- (a) NH₄Cl(aq) (b) AgCl(s) (c) HNO₃(aq) (d) CoCl₂(aq)
 (e) CH₃OH(aq) (f) H₂O(ℓ)

Solution

- (a) NH₄⁺(aq) + Cl⁻(aq) (b) AgCl(s) (c) H⁺(aq) + NO₃⁻(aq)
 (d) Co²⁺(aq) + 2 Cl⁻(aq) (e) CH₃OH(aq) (f) H₂O(ℓ)

Practice Problem 9.1 Write each of the following compounds to represent best how it acts in the presence of water:

- (a) BaSO₄ (b) HNO₂ (c) NaOH

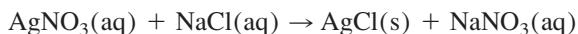
**Snapshot Review**

- Strong and weak electrolytes conduct electricity only in the liquid state. Strong and weak acids and weak bases conduct in solution only; ionic compounds conduct in solution or in the molten state.
 - Compounds that are ionic in solution are written as separate ions because they behave almost independently of the other ion(s) present. Such compounds include (a) metal-containing compounds, (b) ammonium compounds, (c) strong acids and bases.
- A. Write each of the following compounds to best represent it in the presence of water: (a) C₁₂H₂₂O₁₁ (table sugar), (b) NH₄Cl, and (c) Na₂SO₄.
- B. Which of the following conduct electricity well?
- (a) HClO₂(aq) (b) HClO₃(aq) (c) C₆H₁₂O₆(aq) (glucose)
 (d) KCl(aq) (e) KCl(ℓ) (f) KCl(s)

9.2 Writing Net Ionic Equations

We will find net ionic equations extremely useful for summarizing a great deal of information with relatively little effort. The concept behind net ionic equations is essential in writing equations for half-reactions in Chapters 16 and 17. We will also find net ionic equations useful in simplifying some calculations, starting in this chapter and in much greater detail in Chapters 10, 11, 17, 19, and others.

When sodium chloride solution is added to silver nitrate solution, a precipitate of silver chloride is produced, and the solution contains sodium nitrate (Figure 9.3):



This type of equation can be called the **total equation**. (A total equation is sometimes referred to as a *molecular equation* because the compounds in it are written “as if they were molecules.”)

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CHAPTER 9 ■ Net Ionic Equations

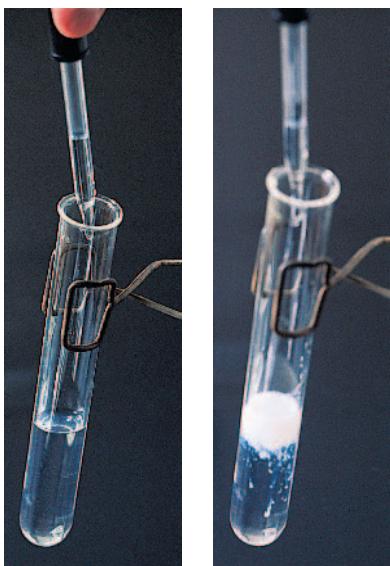
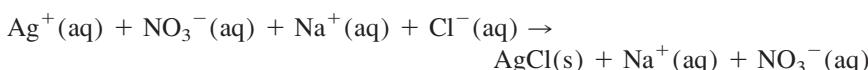
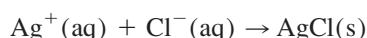


Figure 9.3 Reaction of Silver Nitrate and Sodium Chloride
NaCl solution in the medicine dropper; AgNO₃ in the test tube.

Even more informative than a total equation is an **ionic equation**. An ionic compound *in aqueous solution* may be represented as separate ions, but an ionic solid that is not dissolved in water is written as a complete compound. We can write an ionic equation for the reaction of sodium chloride with silver nitrate in aqueous solution (see Figure 9.3) as follows:



Because the Na⁺ and NO₃⁻ ions appear on both sides of this equation (unchanged by the reaction), they are called **spectator ions**. They may be eliminated from the equation:



This equation is an example of a **net ionic equation**. All the spectator ions are omitted from a net ionic equation.

While we are learning to write net ionic equations, we will use the following procedure. After we get used to working with them, we will be able to write them directly and save even more effort with their use.

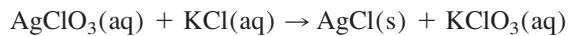
1. Start with a total equation for the reaction, making sure that it is balanced.
2. Write all compounds that are both soluble and ionic in the form of their separate ions, making sure to have the correct number of ions of each type. Write all other compounds (for example, gases, other covalent compounds, and all solids) as complete compounds.
3. Eliminate the ions that are unchanged on both sides of the equation to obtain the net ionic equation.

EXAMPLE 9.2

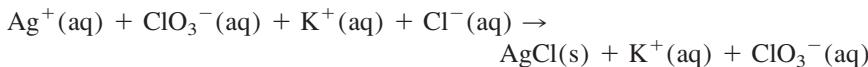
Write a net ionic equation for the reaction of silver chlorate and potassium chloride.

Solution

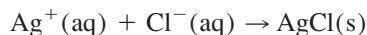
1. The total equation for the reaction is



2. The ionic equation is



3. Eliminating the K⁺ and ClO₃⁻ spectator ions produces the net ionic equation:



This is the same as the net ionic equation given previously for the reaction of sodium chloride with silver nitrate because essentially the same reaction has taken place. Whether it was the sodium ions or the potassium ions or the nitrate ions or the chlorate ions that *did not react* is not important to us. In general, we can say that soluble ionic chlorides react with soluble silver salts to produce silver chloride. This statement does not mention the other ions present in the

9.2 ■ Writing Net Ionic Equations**245**

reactant solutions and may be represented by the net ionic equation, which similarly does not mention any other ions that may be present.

Practice Problem 9.2 Write a net ionic equation for the reaction of $\text{AgC}_2\text{H}_3\text{O}_2$ with CuCl_2 .

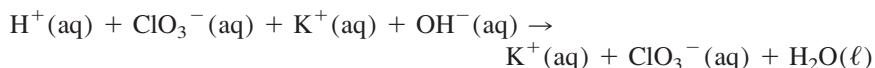
Be careful not to misinterpret the name *net ionic equation*. It is not necessarily true that all the substances appearing in such an equation are ionic. Covalent compounds often occur in net ionic equations. Also, just because the formula for a complete compound is written in such an equation does not mean that the compound is not ionic; it might simply be insoluble.

An important type of reaction is the reaction of a strong acid with a strong base (see Table 9.1) to produce a salt and water. In solution, strong acids and bases exist completely in the form of their ions. All salts, the products of reactions of acids with bases, may also be regarded as completely ionic (but not all are water soluble). We may therefore write net ionic equations for this type of reaction. The reaction of chloric acid and potassium hydroxide is typical:

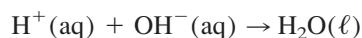


In solution, both of the reactants and the potassium chlorate are ionic, but the water is covalent, of course.

2. The ionic equation for the reaction is



3. Eliminating the spectator ions from both sides of this equation yields the net ionic equation:



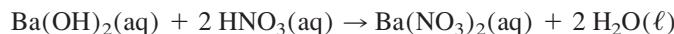
Note that water, which is molecular, not ionic, is included in this net ionic equation.

EXAMPLE 9.3

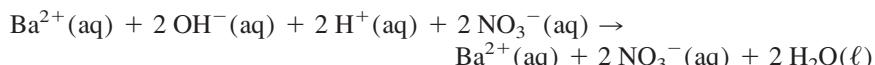
Write a net ionic equation for the reaction of aqueous $\text{Ba}(\text{OH})_2$ with aqueous HNO_3 .

Solution

1. The total equation is



2. The ionic equation is



3. Eliminating the spectator ions yields



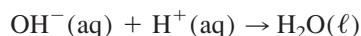
Be careful with the coefficients of the ions in the ionic equation.

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Figure 9.4 Silver Ion Test Solution

A solution that can be used to test whether another solution contains silver ions can contain any soluble ionic chloride. A bottle containing such a solution may be labeled “Cl[−] solution” or “Ag⁺ Test Reagent.” That this solution also contains Na⁺ ions or K⁺ ions does not matter, since these cations would not react with the ions in a solution containing silver ions.

This equation can be simplified by dividing each coefficient by 2:



Again, this is the same net ionic equation as that for the reaction of KOH with HClO₃. In fact, the reaction of *any* aqueous strong acid with *any* aqueous strong base yields this net ionic equation (unless some precipitation occurs).

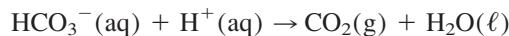
Practice Problem 9.3 Write a net ionic equation for the reaction of NaOH(aq) with aqueous solutions of each of the following:

- (a) HCl (b) HBr (c) HNO₃ (d) HClO₄

Net ionic equations can also be written for reactions in which gases are produced. For example, sodium hydrogen carbonate reacts with nitric acid to produce sodium nitrate, carbon dioxide, and water:



The net ionic equation is



What does a net ionic equation actually tell us? As an example, the net ionic equation of Example 9.3 indicates that any strong acid in water reacts with any soluble strong hydroxide to yield water as a product. The ions that do not react are not of immediate concern. However, no aqueous solution contains only H⁺ ions or only OH[−] ions. The net ionic equation does not state that these ions occur without ions of the opposite charge, only that the identities of the oppositely charged ions are not important because they do not react (Figure 9.4).

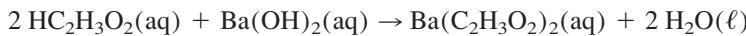
Weak acids—any acids not listed in Table 9.1—are essentially covalent in solution and should be written as complete compounds.

EXAMPLE 9.4

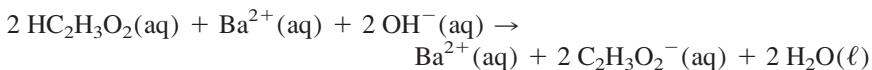
Write a net ionic equation for the reaction of acetic acid, HC₂H₃O₂, with aqueous barium hydroxide, Ba(OH)₂.

Solution

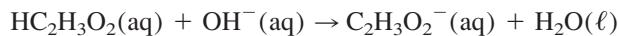
1. The total equation for the reaction is



2. To write the ionic equation, we must remember that acetic acid is a weak acid; that is, it does not ionize completely in water. It is written as a covalent compound. The ionic equation is



3. The net ionic equation is written without the barium ions or the four “2” coefficients:



9.2 ■ Writing Net Ionic Equations**247**

Note that this net ionic equation is *not* the same as the one for the reaction of a strong acid and a strong base!

Practice Problem 9.4 Write a net ionic equation for the reaction of aqueous NH_3 with aqueous HNO_3 .

EXAMPLE 9.5

Reaction of excess $\text{HClO}_4(\text{aq})$ with 1 mol of $\text{NaOH}(\text{aq})$ produces 55.2 kJ of heat. How much heat is liberated when 1 mol of $\text{Ba}(\text{OH})_2(\text{aq})$ is treated with excess $\text{HClO}_4(\text{aq})$? How can we tell?

Solution

The same net ionic equation describes both reactions:

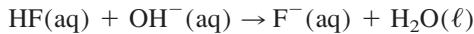


Because 55.2 kJ of heat is liberated per mole of water formed, as shown by the NaOH reaction, the same quantity of heat is produced *per mole* of water formed by the $\text{Ba}(\text{OH})_2$. Thus $2 \text{ mol} \times 55.2 \text{ kJ/mol} = 110 \text{ kJ}$ is produced.

Practice Problem 9.5 Explain why 1 mol of NaOH plus excess $\text{HC}_2\text{H}_3\text{O}_2$ does *not* produce 55.2 kJ of heat.

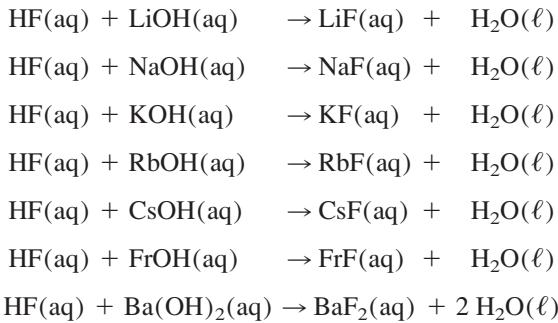
EXAMPLE 9.6

Write seven total equations corresponding to the following net ionic equation:



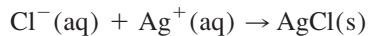
Solution

Any soluble, ionic hydroxide may be used. We know that barium hydroxide (to a limited extent) and the six alkali metal hydroxides are soluble:



EXAMPLE 9.7

Explain how we can write 90 or more complete equations for which the net ionic equation is



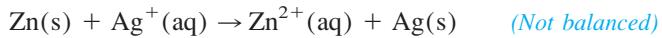
That is, which chlorides should we select? Which silver salts?

Solution

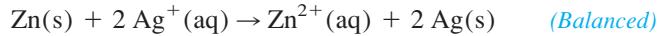
We should choose reagents that we know are both ionic and soluble. The chlorides that we know have these properties are HCl and NH₄Cl, the 12 alkali metal and alkaline earth metal chlorides, about 16 transition metal chlorides (for example, FeCl₂, FeCl₃, and CdCl₂), and chlorides of some other main group metals like AlCl₃ and SnCl₂. Each of these chlorides can react with silver nitrate, silver acetate, or silver chlorate (which we know are ionic and soluble), producing the required number of complete equations.

Practice Problem 9.7 Why can we not use PbCl₂ as an answer in Example 9.7? Comment on one important reason to learn to use net ionic equations.

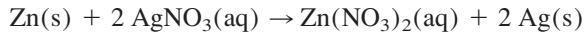
For a net ionic equation to be balanced, both the numbers of each type of atom and the net charge must be the same on the two sides of the equation. For example, we know that zinc is more active than silver is (Table 8.2) and will replace silver from its compounds. We could start to write the net ionic equation for the reaction in solution as follows:



This net ionic equation is balanced only with regard to the numbers of zinc and silver atoms. Because the charge is not balanced, however, the equation is not balanced. We can balance it by doubling the charge on the left side (with a 2 before the Ag⁺) and keeping the number of silver atoms balanced (with a 2 before the Ag):

**EXAMPLE 9.8**

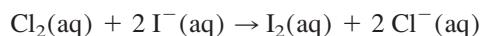
Write a total equation corresponding to the net ionic equation for the reaction of silver ions and zinc, using nitrate ions as the spectator ions. Explain why the charges in the net ionic equation have to be balanced.

Solution

9.2 ■ Writing Net Ionic Equations**249**

Each positive charge in the net ionic equation represents one nitrate ion in this total equation. The charges must be balanced in the net ionic equation because the nitrate ions must be balanced in the total equation.

Practice Problem 9.8 Write a balanced total equation that is represented by the following net ionic equation:

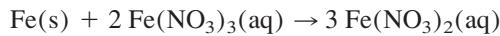


EXAMPLE 9.9

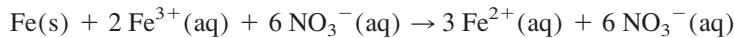
Write a net ionic equation for the reaction of iron metal with aqueous iron(III) nitrate to produce aqueous iron(II) nitrate.

Solution

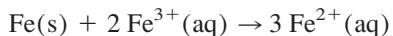
1. The total equation is



2. The ionic equation is

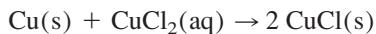


3. Eliminating the nitrate ions from each side yields the net ionic equation:



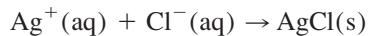
Note that the cations are *not* eliminated because they are not the same on each side. There has been a change from iron(III) to iron(II). The uncharged metal atom has also changed and cannot be eliminated as a spectator ion. The net ionic equation indicates that iron metal will react with *any* soluble iron(III) compound as long as the corresponding iron(II) compound is soluble.

Practice Problem 9.9 Write a net ionic equation for the following reaction:

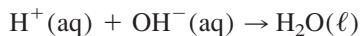


Be sure the total equation is balanced before attempting to write the ionic equation.

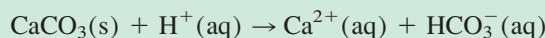
The advantage of using net ionic equations becomes even greater when we become familiar enough with the process to avoid having to write out total equations at all. We know that alkali metal ions are almost always spectator ions. Such ions as nitrate ions are spectator ions almost as often. Thus when confronted with a reaction such as RbCl plus AgNO_3 , we can just ignore the probable spectator ions and write the net ionic equation directly:



Similarly, when we see a strong acid and a strong base, we can write directly



In some cases, the net ionic equation is significantly simpler than the full equation. For example, consider the reaction of solid calcium carbonate with a limited quantity of hydrochloric acid. (In this case, these substances react in a 1:1 ratio.) Assuming that the chloride ion is a spectator ion allows us to write the net ionic equation directly:



The full equation is



The net ionic equation is obviously much simpler.

Net ionic equations are also useful in quantitative calculations, as will be introduced here and used extensively in Chapters 11, 17, and 19. For example, we can calculate the numbers of moles of individual ions in solution using net ionic equations.

EXAMPLE 9.10

Calculate the number of moles of sodium ion present in a solution containing 1 mol of sodium sulfate.

Solution

$$1 \text{ mol Na}_2\text{SO}_4 \left(\frac{2 \text{ mol Na}^+}{1 \text{ mol Na}_2\text{SO}_4} \right) = 2 \text{ mol Na}^+$$

There is 2 mol of sodium ion in this solution.

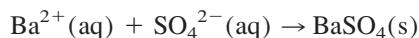
Practice Problem 9.10 Calculate the number of moles of nitrate ion in a solution containing 1 mol of aluminum nitrate.

EXAMPLE 9.11

Calculate the number of moles of sodium ion in a solution containing 1 mol of sodium sulfate to which some barium nitrate is added.

Solution

The net ionic equation for the reaction that takes place is



This equation shows that the sodium ion is a spectator ion, and does not react. Since there is 2 mol of sodium ion present initially (Example 9.10), and the sodium does not react, there will always be 2 mol of sodium ion present no matter how much barium nitrate is added.

■ Summary

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Net ionic equations are also very useful for the ions that do react, as will be shown in Chapter 11 and in later chapters.

Net ionic equations are used extensively in chemistry. For example, equilibrium expressions for acid-base reactions, as well as for the ionization of water itself, are conventionally written in the form of net ionic equations. Many complex oxidation-reduction equations are balanced using net ionic equations. These topics are introduced in Chapters 16 and 19.



Snapshot Review



ChemSkill Builder 5.3

- Only spectator ions—ions that are identical and in solution before and after the reaction—are omitted from a net ionic equation.
- A. Write a net ionic equation for each of the following:
- (NH₄)₂SO₄(aq) + Ba(NO₃)₂(aq) → BaSO₄(s) + 2 NH₄NO₃(aq)
 - 2 HClO₂(aq) + Ba(OH)₂(aq) → Ba(ClO₂)₂(aq) + 2 H₂O(ℓ)
 - 2 HClO₂(aq) + Ba(OH)₂(s) → Ba(ClO₂)₂(aq) + 2 H₂O(ℓ)
- B. Complete and balance a net ionic equation for each of the following reactions: (a) aqueous chromium(III) nitrate plus chromium metal and, (b) zinc metal plus hydrochloric acid.

Key Terms

Key terms are defined in the Glossary.

ionic equation (9.2)
net ionic equation (9.2)
nonelectrolyte (9.1)

spectator ion (9.2)
strong electrolyte (9.1)

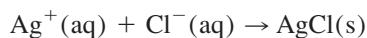
total equation (9.2)
weak electrolyte (9.1)

Summary

In aqueous solutions of ionic compounds, the ions act independently of each other. Soluble ionic compounds are written as their separate ions. We must be familiar with the solubility rules presented in Chapter 8 and recognize that the following types of compounds are strong electrolytes: strong acids in solution, soluble metallic hydroxides, and salts. (Salts, which can be formed as the products of reactions of acids with bases, include all ionic compounds except strong acids and bases and metallic oxides and hydroxides.) Compounds must be *both ionic and soluble* to be written in the form of their separate ions. (Section 9.1)

A net ionic equation describes the actual reaction between ions of compounds in aqueous solution. Ions that do not change at all during the reaction are omitted from

the equation; these ions are called spectator ions. One net ionic equation may describe the reactions of many compounds. For example, the net ionic equation



summarizes all the reactions described by the statement: “Any soluble silver salt reacts with any soluble ionic chloride to produce (the insoluble) silver chloride.” The equation also gives the mole ratios, which the statement does not.

Net ionic equations are balanced only if the numbers of atoms of each element and the net charge on each side of the equation are all balanced.

Net ionic equations also make many quantitative examples easier to solve. (Section 9.2)

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CHAPTER 9 ■ Net Ionic Equations

Items for Special Attention

- Strong acids react completely with water to form ions in solution. Metal hydroxides and salts are ionic in the solid state, as well as in solution; however, in the solid state, such compounds are written as complete compounds because the ions are not independent of each other.
- Pure HCl is classified as a strong electrolyte (even though it does not conduct electricity) because its aqueous solution conducts well.
- Most ionic compounds are composed of only one type of positive ion and one type of negative ion. (Of course, more than one of each type of ion may be present in each formula unit.)

- Don't be confused about what should be included in net ionic equations. It is easier to remember what should be left out: *Only ions in solution that remain unchanged in solution* should be left out to produce net ionic equations; all other species must be included. Thus, insoluble compounds (ionic or not), covalent compounds, elements, and ions that change in any way between reactants and products are all included. Remembering what to omit—the spectator ions—is much easier!

Answers to Snapshot Reviews

- 9.1 A. (a) $C_{12}H_{22}O_{11}$ (b) $NH_4^+ + Cl^-$
(c) $2 Na^+ + SO_4^{2-}$
B. (b) $HClO_3(aq)$, (d) $KCl(aq)$, and (e) $KCl(\ell)$
- 9.2 A. (a) $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$
(b) $HClO_2(aq) + OH^-(aq) \rightarrow$
 $ClO_2^-(aq) + H_2O(\ell)$

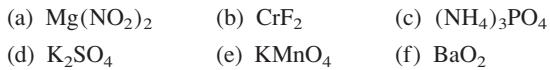
- (c) $2 HClO_2(aq) + Ba(OH)_2(s) \rightarrow$
 $2 ClO_2^-(aq) + Ba^{2+}(aq) + 2 H_2O(\ell)$
- B. (a) $2 Cr^{3+}(aq) + Cr(s) \rightarrow 3 Cr^{2+}(aq)$
(b) $Zn(s) + 2 H^+(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$

Self-Tutorial Problems

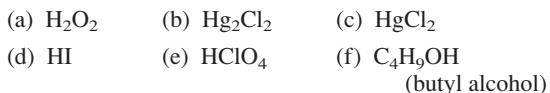
- 9.1 What is the difference in the nature of the bonding of the chlorine in the following species?



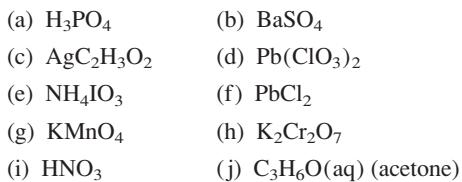
- 9.2 Write formulas for the ions that constitute each of the following compounds:



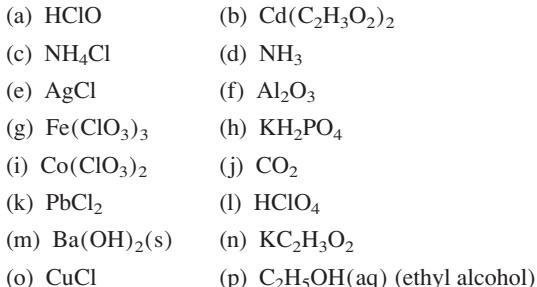
- 9.3 For each of the following compounds, determine whether it is soluble in water, whether it is ionic in the pure state or in solution, and whether it should be written as a compound or as separate ions in an ionic equation. Then write the compound as it should be written in an ionic equation.



- 9.4 Write each of the following species (in aqueous solution, if soluble) as it should appear in an ionic equation:

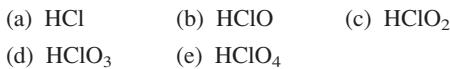


- 9.5 Write each of the following species (in aqueous solution, if soluble) as it should appear in an ionic equation:

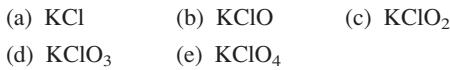


- 9.6 Which, if any, of the common acids exist as ions (a) in the pure state and (b) in aqueous solution?

- 9.7 Assuming that each of the following acids is in aqueous solution, write its formula to best represent it:



- 9.8 Assuming that each of the following compounds is in aqueous solution, write its formula to best represent it:



■ Problems

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- 9.9** Write a net ionic equation for the reaction of (a) Zn with HCl, (b) Zn with any strong acid, and (c) Zn with a strong acid.
- 9.10** Assuming that each of the following compounds is in aqueous solution, write its formula to best represent it:
- NH_4ClO_3
 - $\text{HC}_2\text{H}_3\text{O}_2$
 - CO_2
 - AlCl_3
 - CH_2O (formaldehyde)
- 9.11** Which ones of the following are strong electrolytes? Which conduct electricity?
- HCl(g)
 - KCl(s)
 - $\text{H}_2\text{SO}_3(\ell)$
- 9.12** Write a net ionic equation for each of the following reactions:
- $\text{Ba(OH)}_2(\text{aq}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\ell)$
 - $\text{Ba(OH)}_2(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\ell)$
 - Is the same quantity of heat expected in each reaction?
- 9.13** A bottle labeled “ Ag^+ Test Reagent” in a chemistry lab is used to test for the presence of silver ion. What does the bottle contain?

Problems**9.1 Properties of Ionic Compounds in Aqueous Solution**

- 9.14** Assuming that each of the following compounds is in aqueous solution, write its formula to best represent it:
- CuSO_4
 - H_2S
 - HNO_2
 - $\text{UO}_2(\text{NO}_3)_2$
 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- 9.15** Write the formula for each of the following compounds to best represent it in the presence of water:
- HClO_4
 - CuCl_2
 - HClO_2
 - Cu_2S
 - AgCl
 - $(\text{NH}_4)_2\text{SO}_3$
- 9.16** Write the formula for each of the following compounds to best represent it in the presence of water:
- ZnCl_2
 - $(\text{NH}_4)_2\text{S}_2\text{O}_3$
 - Hg_2O
 - $\text{BaCO}_3(\text{s})$
 - Li_2SO_4
 - H_3PO_4
- 9.17** (a) Would HF or NaF be better for making a solution containing fluoride ion, or doesn't it make any difference?
 (b) Would HCl or NaCl be better for making a solution containing chloride ion, or doesn't it make any difference?
- 9.18** Would an alkali metal phosphate or a transition metal phosphate be better for making a solution containing phosphate ion?

9.2 Writing Net Ionic Equations

- 9.19** Balance each of the following net ionic equations:
- $\text{Pb}(\text{s}) + \text{Cr}^{3+}(\text{aq}) \rightarrow \text{Cr}^{2+}(\text{aq}) + \text{Pb}^{2+}(\text{aq})$
 - $\text{Br}^-(\text{aq}) + \text{Ce}^{4+}(\text{aq}) \rightarrow \text{Ce}^{3+}(\text{aq}) + \text{Br}_2(\text{aq})$
 - $\text{Ag}^+(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Ag}(\text{s})$
 - $\text{Cu}_2\text{O}(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq}) + \text{H}_2\text{O}(\ell)$
 - $\text{Co}^{3+}(\text{aq}) + \text{Co}(\text{s}) \rightarrow \text{Co}^{2+}(\text{aq})$
- 9.20** Write a net ionic equation for the reaction of an insoluble metal oxide, represented as M_2O_3 , with a strong acid, H_2X .
- 9.21** Balance each of the following net ionic equations:
- $\text{Mn}(\text{s}) + \text{Co}^{3+}(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + \text{Mn}^{2+}(\text{aq})$
 - $\text{NH}_3(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$
 - $\text{Ce}^{4+}(\text{aq}) + \text{Pd}^{2+}(\text{aq}) \rightarrow \text{Pd}^{4+}(\text{aq}) + \text{Ce}^{3+}(\text{aq})$
 - $\text{PbSO}_4(\text{s}) + \text{H}_2\text{O}(\ell) \rightarrow \text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + \text{H}^+(\text{aq}) + \text{Pb}(\text{s})$
- 9.22** Write a net ionic equation for each of the following reactions:
- $\text{BaI}_2(\text{aq}) + \text{K}_2\text{CO}_3(\text{aq}) \rightarrow 2 \text{KI}(\text{aq}) + \text{BaCO}_3(\text{s})$
 - $2 \text{HNO}_3(\text{aq}) + \text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{Ba}(\text{NO}_3)_2(\text{aq}) + 2 \text{H}_2\text{O}(\ell)$
 - $\text{NaHCO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$
 - $\text{NaHCO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$
 - $\text{NaBr}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgBr}(\text{s})$
 - $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{aq}) + 2 \text{KI}(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2 \text{KC}_2\text{H}_3\text{O}_2(\text{aq})$
- 9.23** Do either part (a) or part (b).
- Write a total equation for the reaction of 15 different soluble metal chlorides with each of the following: lead(II) nitrate, lead(II) acetate, and lead(II) chlorate.
 - Write one net ionic equation representing all 45 equations of part (a).
- 9.24** Write six total equations that correspond to the following net ionic equation and have an alkali metal ion and nitrate ion as spectator ions:
- $$\text{Pb}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{PbS}(\text{s})$$
- 9.25** Write a net ionic equation for the reaction of silver acetate with each of the following in aqueous solution:
- Aluminum chloride
 - Vanadium(II) chloride
 - Cadmium chloride

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- (d) Hydrochloric acid
(e) Chromium(III) chloride
(f) Nickel(II) chloride
(g) Cobalt(III) chloride
- 9.26 Write six total equations that are represented by the following net ionic equation and have spectator ions chosen from Na^+ , NH_4^+ , ClO_3^- , NO_3^- , and $\text{C}_2\text{H}_3\text{O}_2^-$:
- $$\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$$

- 9.27 Write a net ionic equation for the reaction of aqueous barium chlorate with aqueous sodium carbonate to yield solid barium carbonate and aqueous sodium chlorate.
- 9.28 Write a net ionic equation for the reaction of aqueous silver acetate with aqueous sodium carbonate to yield solid silver carbonate and aqueous sodium acetate.

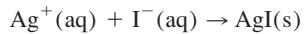
- 9.29 Write a net ionic equation for each of the following reactions:

- (a) $\text{HClO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaClO}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$
(b) $\text{HClO}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaClO}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$

- 9.30 Complete and balance the following equations:

- (a) $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow$
(b) $\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow$

- 9.31 (a) Write six total equations that correspond to the following net ionic equation and have an alkali metal ion and nitrate ion as spectator ions:



- (b) If any of three anions—acetate ion, chlorate ion, or nitrate ion—were used as a spectator ion, how many total equations could be written?
- 9.32 Balance the following equations. Then write a net ionic equation for each.
- (a) $\text{Sn}(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{SnCl}_2(\text{aq})$
(b) $\text{Sn}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{SnSO}_4(\text{aq})$
(c) $\text{Sn}(\text{s}) + \text{HClO}_3(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Sn}(\text{ClO}_3)_2(\text{aq})$

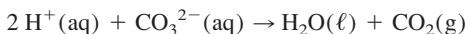
CHAPTER 9 ■ Net Ionic Equations

- 9.33 Balance the following net ionic equations:

- (a) $\text{Ce}^{4+}(\text{aq}) + \text{Pt}^{2+}(\text{aq}) \rightarrow \text{Pt}^{4+}(\text{aq}) + \text{Ce}^{3+}(\text{aq})$
(b) $\text{H}_2(\text{g}) + \text{Ag}^+(\text{aq}) \rightarrow \text{Ag}(\text{s}) + \text{H}^+(\text{aq})$
(c) $\text{I}^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{CuI}(\text{s}) + \text{I}_2(\text{aq})$

- 9.34 Write a net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium hydrogen carbonate to yield solid barium carbonate, aqueous sodium nitrate, carbon dioxide, and water.

- 9.35 Write five total equations that are represented by the following net ionic equation:



- 9.36 Write a net ionic equation for the reaction of aqueous $\text{Ba}(\text{OH})_2$ with aqueous H_2SO_4 .

- 9.37 Name one compound which could be used to provide each ion in Problem 9.30.

- 9.38 Write a net ionic equation for the reaction of

- (a) A strong acid with a strong base
(b) A strong acid with ammonia (a weak base)
(c) A weak acid, represented as HA, with a strong base

- 9.39 Write a net ionic equation for the reaction of ammonium sulfide with each of the following in aqueous solution. An insoluble sulfide is formed in each case.

- (a) Manganese(II) sulfate (b) Iron(II) sulfate
(c) Copper(II) sulfate (d) Zinc sulfate
(e) Cobalt(II) sulfate (f) Nickel(II) sulfate

- 9.40 Barium hydroxide, $\text{Ba}(\text{OH})_2$, has limited water solubility. If a small quantity of barium hydroxide is added to a given volume of water, it might dissolve. If a large quantity of barium hydroxide is added to the same volume of water, most of it will not dissolve. Thus, barium hydroxide might appear in an equation as either solid or aqueous. Write a net ionic equation for the reaction of barium hydroxide with HClO_4 for each of these cases.

General Problems

- 9.41 Complete and balance the following net ionic equations. There is a reaction in each case.

- (a) $\text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow$
(b) $\text{Ag}^+(\text{aq}) + \text{CN}^-(\text{aq}) \rightarrow$
(c) $\text{H}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow$
(d) $\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}, \text{excess}) \rightarrow$
(e) $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow$
(f) $\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow$

- 9.42 Write a balanced total equation and a balanced net ionic equation for each of the following reactions (there is a reaction in each case):

- (a) $\text{BaCO}_3(\text{s}) + \text{HNO}_3(\text{aq}) \rightarrow$
(b) $\text{H}_2\text{SO}_4(\text{aq}) + \text{BaCO}_3(\text{s}) \rightarrow$
(c) $\text{MgCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow$
(d) $\text{Ca}(\text{HCO}_3)_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow$
(e) $\text{BaO}(\text{s}) + \text{HCl}(\text{aq}) \rightarrow$

■ General Problems

9.43 Write a balanced total equation and a balanced net ionic equation for each of the following reactions (there is a reaction in each case):

- $\text{NH}_4\text{NO}_3(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow$
- $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow$
- $\text{Na}_2\text{HPO}_4(\text{aq}) + \text{HNO}_3(\text{aq}, \text{excess}) \rightarrow$

9.44 Write a balanced total equation and a balanced net ionic equation for each of the following reactions (there is a reaction in each case):

- $\text{KC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HClO}_3(\text{aq}) \rightarrow$
- $\text{NH}_4\text{Cl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
- $\text{NaH}_2\text{PO}_4(\text{aq}) + \text{HClO}_4(\text{aq}) \rightarrow$
- $(\text{NH}_4)_2\text{CO}_3(\text{aq}) + \text{HNO}_3(\text{aq}, \text{excess}) \rightarrow$

9.45 Write a balanced net ionic equation for each of the following reactions (there is a reaction in each case):

- $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{K}_3\text{PO}_4(\text{aq}) \rightarrow$
- $\text{Hg}_2(\text{NO}_3)_2(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow$
- $\text{CuCl}_2(\text{aq}) + (\text{NH}_4)_2\text{S}(\text{aq}) \rightarrow$
- $\text{ZnCl}_2(\text{aq}) + (\text{NH}_4)_2\text{S}(\text{aq}) \rightarrow$
- $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{aq}) + \text{K}_3\text{PO}_4(\text{aq}) \rightarrow$
- $\text{CaCl}_2(\text{aq}) + \text{K}_2\text{CO}_3(\text{aq}) \rightarrow$

9.46 Write a net ionic equation for the reaction of (a) a soluble carbonate with excess strong acid, (b) a soluble acid carbonate with a strong acid, (c) a soluble acid carbonate with a strong base, and (d) CO_2 with excess strong aqueous base.

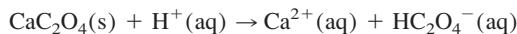
9.47 When $\text{CHCl}_3(\ell)$ (chloroform) is treated with $\text{AgNO}_3(\text{aq})$, no reaction occurs. Explain why.

9.48 Write net ionic equations for the reactions required in Problem 8.91.

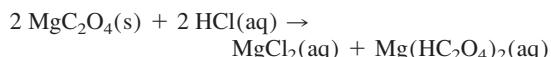
9.49 Write a net ionic equation for the reaction of sodium metal with water. What is unusual about this equation?

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9.50 Write a total equation corresponding to the following net ionic equation:



9.51 Write a net ionic equation corresponding to the following total equation:

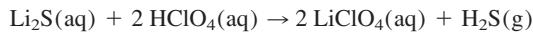
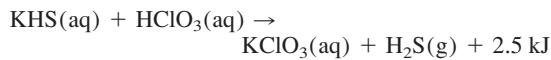
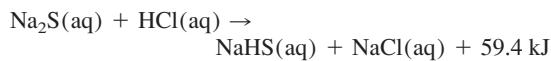


9.52 Write a net ionic equation and a full equation for each of the following reactions:

- Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) with a limited quantity of aqueous KOH
- MgO with HCl
- Solid $\text{Ca}(\text{H}_2\text{PO}_4)_2$ with a limited quantity of NaOH to give solid CaHPO_4
- Aqueous $\text{Mg}(\text{H}_2\text{PO}_4)_2$ with a limited quantity of NaOH to give aqueous MgHPO_4

9.53 Explain why the reaction of HCl with NaOH and the reaction of HNO_3 with aqueous $\text{Ba}(\text{OH})_2$ yield the same quantity of heat per mole of water produced.

9.54 When two equations are added to yield a third equation, the heats of reaction of the two may be added to obtain the heat of reaction of the third. The following reactions were carried out at 25°C under the same conditions of concentration, pressure, etc. The first two yielded 59.4 kilojoules (kJ) and 2.5 kJ of heat per mole of the first reactant, respectively. What was the heat liberated per mole of the first reactant for the third reaction? How can we tell?



10

Stoichiometry

- 10.1 Mole Calculations for Chemical Reactions
- 10.2 Mass Calculations for Chemical Reactions
- 10.3 Calculations Involving Other Quantities
- 10.4 Problems Involving Limiting Quantities
- 10.5 Theoretical Yield and Percent Yield
- 10.6 Calculations with Net Ionic Equations

Review Clues

- Section 10.1** Sections 7.3, 8.2
Section 10.2 Section 7.1, Chapter 6
Section 10.3 Section 7.3
Section 10.5 Section A1.1
Section 10.6 Section 9.2

Objectives

- 10.1** To calculate the number of moles of any other substance in a chemical reaction from the number of moles of any one of the substances
10.2 To use the mass of one substance to determine masses of other substances involved in a chemical reaction



Color testing to analyze a sample

- 10.3** To determine how much of any substance is involved in a chemical reaction, given any quantity of another substance, no matter what units are involved
10.4 To calculate the quantities of substances produced in a reaction when quantities of more than one reactant are specified
10.5 To express the quantity of product obtained from a reaction as a percentage of what the reaction is theoretically capable of producing
10.6 To calculate the numbers of moles involved in net ionic equations, to calculate the masses of complete compounds involved in such equations, and to recognize the limitations of net ionic equations in calculating masses of individual ions

10.1 ■ Mole Calculations for Chemical Reactions**257**

In Chapter 7, we learned to interpret chemical formulas in terms of the quantities of the elements involved. In Chapters 8 and 9, we learned to complete and balance chemical equations. This chapter shows how to interpret the quantities of substances involved in a chemical reaction, using the balanced chemical equation almost as the formula was used in Chapter 7.

Just as compounds have definite ratios of elements, chemical reactions have definite ratios of reactants and products. Those ratios are used in Section 10.1 to calculate the number of moles of other substances in a reaction from the number of moles of any one of the substances. Section 10.2 combines information from Section 10.1, Chapter 7, and elsewhere to explain how to calculate the mass of any substance involved in a reaction from the mass of another. Section 10.3 demonstrates how to work with quantities in units other than moles or masses when finding quantities of reactants or products. Section 10.4 shows how to calculate the quantities of substances involved in a reaction even if the quantities of reactants present are not in the mole ratio of the balanced equation. Section 10.5 covers the calculation of the percentage yield of a product from the actual yield and the theoretical yield, based on the amount(s) of reactant(s). Section 10.6 explains which of these types of calculations can and cannot be done with net ionic equations.

10.1 Mole Calculations for Chemical Reactions

Stoichiometry involves the calculation of quantities of any substances involved in a chemical reaction from the quantities of the other substances. The balanced equation gives the ratios of formula units of all the substances in a chemical reaction. It also gives the corresponding ratios of moles of the substances. These relationships are shown in Figure 10.1. For example, one reaction of phosphorus with chlorine gas is governed by the equation

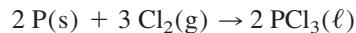
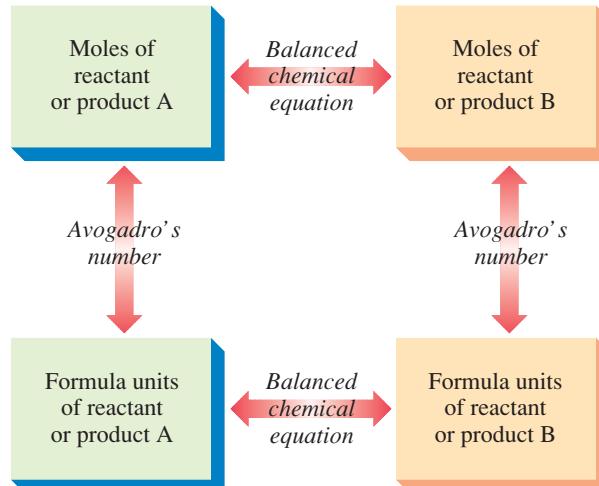


Figure 10.1 Mole Conversions for Stoichiometry Problems

The double-headed arrows indicate that the conversions can be made in either direction.



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CHAPTER 10 ■ Stoichiometry

This equation can be interpreted, as shown in Chapter 8, in two ways:

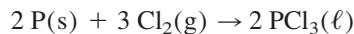
1. Two atoms of phosphorus react with three molecules of Cl_2 to produce two molecules of PCl_3 .
2. Two moles of phosphorus react with 3 mol of Cl_2 to produce 2 mol of PCl_3 .

Using Factors to Solve Mole-Mole Problems

Consider the reaction of phosphorus with chlorine as shown in the previous equation. Of course, the chemist is not required to place exactly 2 mol of P and 3 mol of Cl_2 in a reaction flask. The equation gives the **reacting ratio**. Ratios of coefficients from balanced chemical equations can be used as conversion factors for solving problems.

EXAMPLE 10.1

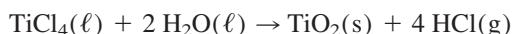
Write all the possible factors from the coefficients in the following balanced equation:



Solution

$$\frac{3 \text{ mol Cl}_2}{2 \text{ mol P}} \quad \frac{3 \text{ mol Cl}_2}{2 \text{ mol PCl}_3} \quad \frac{2 \text{ mol P}}{2 \text{ mol PCl}_3} \quad \frac{2 \text{ mol P}}{3 \text{ mol Cl}_2} \quad \frac{2 \text{ mol PCl}_3}{3 \text{ mol Cl}_2} \quad \frac{2 \text{ mol PCl}_3}{2 \text{ mol P}}$$

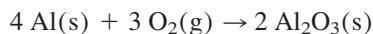
Practice Problem 10.1 Write all the possible factors from the coefficients in the following balanced equation, a reaction used to make smoke-screens in World War I:



The ratio that should be used in a particular problem will have the substance for which the number of moles is given in the denominator and the substance for which the number of moles is desired in the numerator, as introduced in Section 2.1.

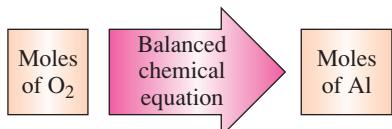
EXAMPLE 10.2

Calculate the number of moles of aluminum atoms that will react with 3.18 mol of oxygen molecules to form aluminum oxide. The balanced equation is



Solution

$$3.18 \text{ mol O}_2 \left(\frac{4 \text{ mol Al}}{3 \text{ mol O}_2} \right) = 4.24 \text{ mol Al}$$



10.1 ■ Mole Calculations for Chemical Reactions**259**

Practice Problem 10.2 Calculate the number of moles of Al_2O_3 that will be produced by the reaction in Example 10.2.

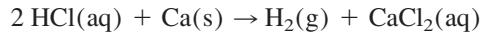
Essentially, most problems involving mole calculations are as simple as the one in Example 10.2. A problem may seem more difficult if we have to write and balance an equation, but we learned how to do that in Chapter 8.

EXAMPLE 10.3

Calculate the number of moles of hydrogen gas that can be produced by reaction of 0.750 mol of hydrochloric acid, HCl, with calcium metal.

Solution

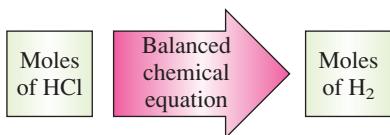
The first step, as in most stoichiometry problems, is to write a balanced equation for the reaction:



Now the stoichiometry problem can be solved, as in Example 10.2:

$$0.750 \text{ mol HCl} \left(\frac{1 \text{ mol H}_2}{2 \text{ mol HCl}} \right) = 0.375 \text{ mol H}_2$$

Practice Problem 10.3 Calculate the number of moles of aqueous NaOH that must react completely with aqueous H_2SO_4 to produce 1.24 mol of Na_2SO_4 .

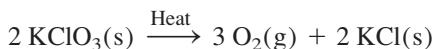


EXAMPLE 10.4

A sample of 0.1712 mol of solid KClO_3 is heated gently for a time, and 0.1146 mol of the compound decomposes. Calculate the number of moles of oxygen gas produced.

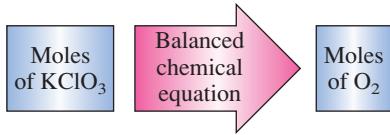
Solution

The equation (Section 8.3) is



In this experiment, even though 0.1712 mol of potassium chlorate is present, only 0.1146 mol reacts. The number of moles of oxygen gas produced depends on the number of moles of potassium chlorate that reacts:

$$0.1146 \text{ mol KClO}_3 \left(\frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \right) = 0.1719 \text{ mol O}_2$$



Practice Problem 10.4 In a certain reaction, 0.225 mol of H₂ gas reacts partially with N₂ gas to yield gaseous NH₃. If 0.033 mol of H₂ remains after the reaction is stopped, how many moles of N₂ is used up?

Tabulation Method

Many times (Section 10.4, Chapters 18 and 19) we will find it useful to tabulate the numbers of moles (or related quantities to be introduced later) of the substances undergoing reaction. For example, the data of Example 10.2 can be tabulated as follows:

Quantities must be in moles.

	4 Al(s)	+	3 O ₂ (g)	→	2 Al ₂ O ₃ (s)
<i>Initial quantities</i>	Excess		3.18 mol		0.00 mol
<i>Change due to reaction</i>	-4.24 mol		-3.18 mol		+2.12 mol

It must be noted that the magnitudes of the quantities in the “change due to reaction” line are *always* in the ratio of the coefficients in the balanced chemical equation. It will also become apparent that the numbers of moles of reactants in the “change” line are *subtracted* from the initial quantities present and the numbers of moles of products are *added* to any initial quantities present.

	4 Al(s)	+	3 O ₂ (g)	→	2 Al ₂ O ₃ (s)
<i>Initial quantities</i>	Excess		3.18 mol		0.00 mol
<i>Change due to reaction</i>	-4.24 mol		-3.18 mol		+2.12 mol
<i>Final quantities</i>	Some excess		0.00 mol		2.12 mol

EXAMPLE 10.5

Calculate the quantities of the salt and water in solution after the reaction of 1.33 mol of HCl and excess NaOH in 15.17 mol of water.

Solution

	HCl(aq)	+	NaOH(aq)	→	H ₂ O(ℓ)	+	NaCl(aq)
<i>Initial quantities</i>	1.33 mol		Excess		15.17 mol		0.00 mol
<i>Change due to reaction</i>	-1.33 mol		-1.33 mol		+1.33 mol		+1.33 mol
<i>Final quantities</i>	0.00 mol		Some excess		16.50 mol		1.33 mol



Snapshot Review



ChemSkill Builder
4.1, 4.3

- The balanced chemical equation gives the mole ratios of all the substances in the reaction, just as an empirical formula gives the ratios of atoms of the elements in a compound. As with chemical formulas, these ratios can be used as factors in calculations involving any two of the substances.

10.2 ■ Mass Calculations for Chemical Reactions**261**

- A. How many moles of hydrochloric acid does it take to prepare 1.50 mol of calcium chloride by reaction with calcium carbonate?



- B. If the equation were not given in problem A, what sections of the text would have to be reviewed to answer?

10.2 Mass Calculations for Chemical Reactions

In Section 10.1, we learned to calculate the number of moles of any substances involved in a chemical reaction from the number of moles of any other substance. We can solve problems that include mass calculations by simply changing the masses to moles or the moles to masses, as discussed in Chapter 7. In Figure 10.2, these conversions have been added to those shown in Figure 10.1.

If necessary, review Chapter 6 to solve stoichiometry problems that give the names of compounds, rather than their formulas.

EXAMPLE 10.6

Calculate the mass of chlorine gas that will react with 2.88 g of phosphorus to form phosphorus pentachloride.

Solution

First, write the balanced chemical equation:

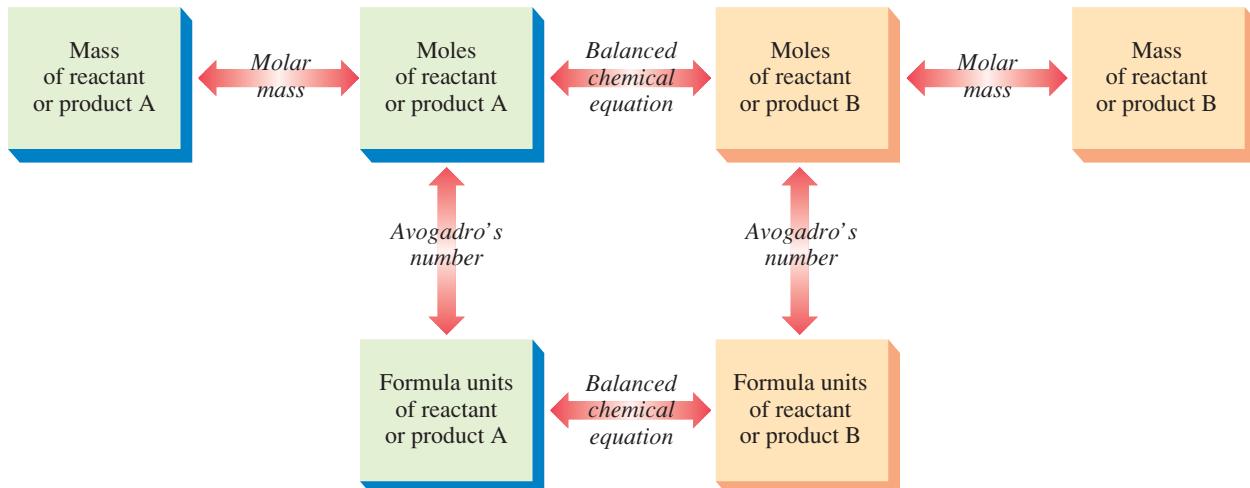


Figure 10.2 Mass and Mole Conversions for Stoichiometry Problems

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Note that the coefficient in the balanced equation has nothing to do with the molar mass.

The coefficients in the equation relate the number of moles of one substance to the number of any other substance.

The equation gives the *mole ratios*, so we need to convert the mass of phosphorus to the number of moles of phosphorus, and then we can proceed as in Section 10.1:

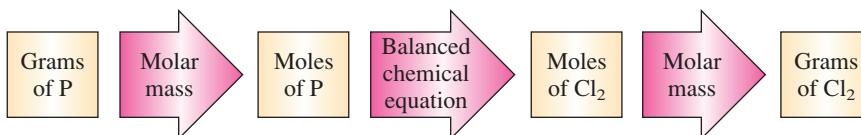
$$2.88 \text{ g P} \left(\frac{1 \text{ mol P}}{31.0 \text{ g P}} \right) = 0.0929 \text{ mol P}$$

$$0.0929 \text{ mol P} \left(\frac{5 \text{ mol Cl}_2}{2 \text{ mol P}} \right) = 0.2323 \text{ mol Cl}_2$$

Finally, convert the number of moles of chlorine to the mass of chlorine:

$$0.2323 \text{ mol Cl}_2 \left(\frac{70.9 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) = 16.5 \text{ g Cl}_2$$

As usual, we could combine all these steps into a single calculation:

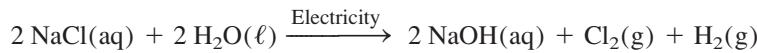
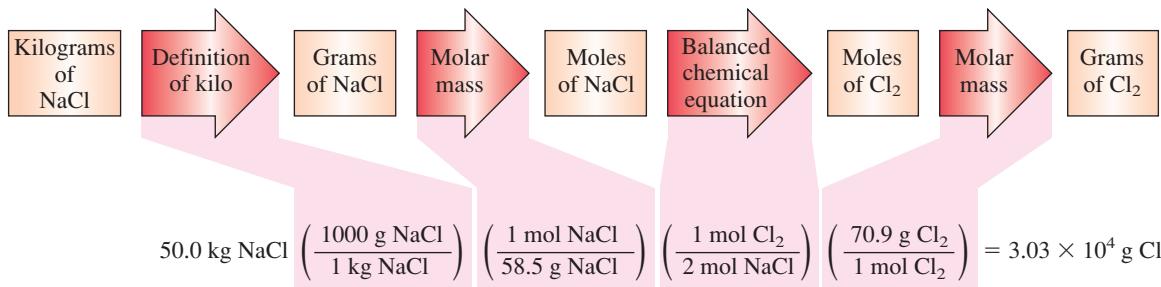


$$2.88 \text{ g P} \left(\frac{1 \text{ mol P}}{31.0 \text{ g P}} \right) \left(\frac{5 \text{ mol Cl}_2}{2 \text{ mol P}} \right) \left(\frac{70.9 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) = 16.5 \text{ g Cl}_2$$

Practice Problem 10.6 Calculate the mass of phosphorus pentachloride that will be produced by the reaction in Example 10.6.

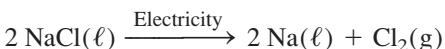
EXAMPLE 10.7

Electrolysis of concentrated aqueous sodium chloride solution (called brine) yields aqueous sodium hydroxide, hydrogen gas, and chlorine gas—three important industrial chemicals. Calculate the mass of chlorine that can be produced by electrolysis of 50.0 kg of sodium chloride in concentrated aqueous solution:

**Solution**

10.2 ■ Mass Calculations for Chemical Reactions**263**

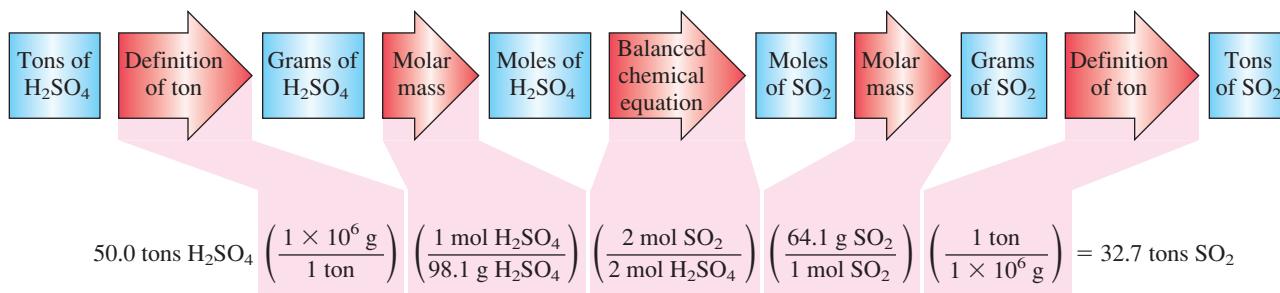
Practice Problem 10.7 The industrial process for the production of sodium metal and chlorine gas involves electrolysis of molten (melted) sodium chloride (in the absence of water). Calculate the mass of sodium that can be prepared by electrolysis of 207 kg of sodium chloride. The balanced equation is

**EXAMPLE 10.8**

Sulfuric acid, H_2SO_4 , is the chemical produced in the greatest tonnage worldwide. Calculate the number of metric tons of SO_2 gas required to prepare 50.0 metric tons of liquid H_2SO_4 (1 metric ton = 1×10^6 g). The balanced equation for the overall reaction (which is actually carried out in steps) is

**Solution**

The balanced equation can be used to calculate the quantity of a reactant from the quantity of any product, as well as vice versa. The same type of calculation is performed:

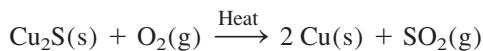


Note that the two factors for the number of grams per metric ton cancel out.

Practice Problem 10.8 Calculate the mass of chlorine gas that must be treated with chromium metal to prepare 17.6 g of solid chromium(III) chloride.

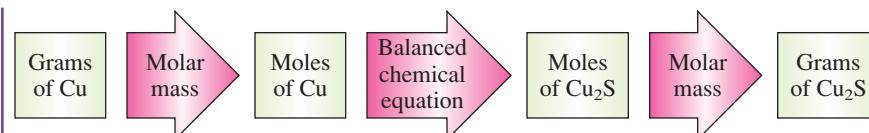
EXAMPLE 10.9

The industrial processing of copper(I) sulfide to produce copper metal involves roasting (heating) the solid ore in the presence of oxygen gas to produce the metal and sulfur dioxide gas. (The sulfur dioxide is used to make sulfuric acid.) Calculate the mass of copper(I) sulfide needed to produce 70.0 metric tons (1 metric ton = 1×10^6 g) of copper by roasting.

Solution

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CHAPTER 10 ■ Stoichiometry



$$70.0 \times 10^6 \text{ g Cu} \left(\frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \right) \left(\frac{1 \text{ mol Cu}_2\text{S}}{2 \text{ mol Cu}} \right) \left(\frac{159 \text{ g Cu}_2\text{S}}{1 \text{ mol Cu}_2\text{S}} \right) = 8.76 \times 10^7 \text{ g Cu}_2\text{S} = 87.6 \text{ metric tons Cu}_2\text{S}$$

Practice Problem 10.9 Copper(II) sulfide can also be roasted in the same way as copper(I) sulfide. Calculate the mass of copper(II) sulfide needed to produce 70.0 metric tons of copper by roasting.

EXAMPLE 10.10

Excess hydrochloric acid was added to an aqueous solution of calcium hydrogen carbonate, and the resulting solution was evaporated to dryness, which produced 2.29 g of solid product. Calculate the mass of calcium hydrogen carbonate in the original solution.

Solution

The equation is



After evaporation to dryness, the only solid remaining is calcium chloride. The carbon dioxide bubbled off during the reaction. The water produced by the reaction and the excess hydrochloric acid were evaporated, along with the water present to make the aqueous solution. Thus, the 2.29 g of solid is calcium chloride.

$$2.29 \text{ g CaCl}_2 \left(\frac{1 \text{ mol CaCl}_2}{111 \text{ g CaCl}_2} \right) \left(\frac{1 \text{ mol Ca}(\text{HCO}_3)_2}{1 \text{ mol CaCl}_2} \right) \left(\frac{162 \text{ g Ca}(\text{HCO}_3)_2}{1 \text{ mol Ca}(\text{HCO}_3)_2} \right) = 3.34 \text{ g Ca}(\text{HCO}_3)_2$$

Practice Problem 10.10 Excess hydrochloric acid was added to 1.47 g of solid barium carbonate, and the resulting solution was evaporated to dryness. What mass of solid remained?



Snapshot Review



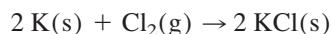
ChemSkill Builder 4.2

- This section is totally review, mostly of Sections 7.3 and 10.1. It gives some students trouble because it involves multiple steps to each problem.

- A. List the steps necessary to calculate the mass of $(\text{NH}_4)_2\text{SO}_4$ that can be prepared by reaction of 13.5 g of H_2SO_4 in water solution with excess ammonia.

10.3 ■ Calculations Involving Other Quantities**265**

B. Which one of the following is true concerning the reaction



- (a) 2 g K will react with 1 g Cl₂ or (b) 2 mol K will react with 1 mol Cl₂?

10.3 Calculations Involving Other Quantities

Not only masses but quantities of substances in any units can be used for stoichiometry purposes. The quantities given must be changed to moles. Just as a mass is a measure of the number of moles of a reactant or product, the number of individual atoms, ions, or molecules involved in a chemical reaction may be converted to moles of reactant or product and used to solve problems. The number of moles of individual atoms or ions of a given element within a compound may also be used to determine the number of moles of reactant or product. The density of a substance may be used to determine the mass of a given volume of it and the mass may be used to determine the number of moles present. Some of these additional relationships are illustrated in Figure 10.3.

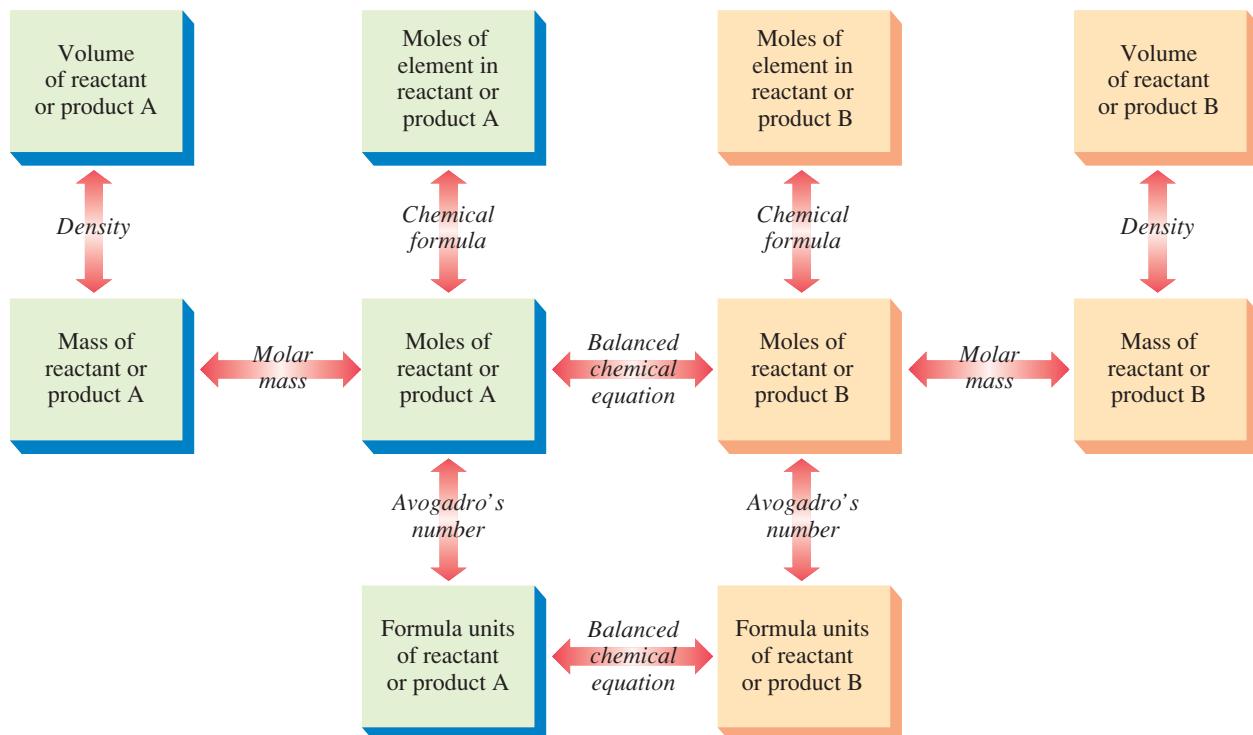
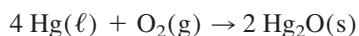


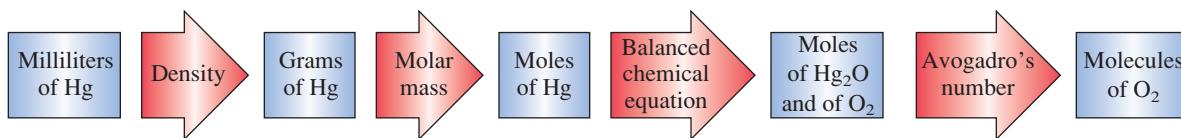
Figure 10.3 Mass, Mole, and Other Conversions

EXAMPLE 10.11

Calculate the number of moles of solid mercury(I) oxide that can be produced by the reaction of oxygen gas with 25.0 mL of liquid mercury (density = 13.6 g/mL). Also, calculate the number of molecules of oxygen required.

Solution

$$25.0 \text{ mL Hg} \left(\frac{13.6 \text{ g Hg}}{1 \text{ mL Hg}} \right) \left(\frac{1 \text{ mol Hg}}{200.6 \text{ g Hg}} \right) \left(\frac{2 \text{ mol Hg}_2\text{O}}{4 \text{ mol Hg}} \right) = 0.847 \text{ mol Hg}_2\text{O}$$



$$25.0 \text{ mL Hg} \left(\frac{13.6 \text{ g Hg}}{1 \text{ mL Hg}} \right) \left(\frac{1 \text{ mol Hg}}{200.6 \text{ g Hg}} \right) \left(\frac{1 \text{ mol O}_2}{4 \text{ mol Hg}} \right) \left(\frac{6.02 \times 10^{23} \text{ molecules O}_2}{1 \text{ mol O}_2} \right) = 2.55 \times 10^{23} \text{ molecules O}_2$$

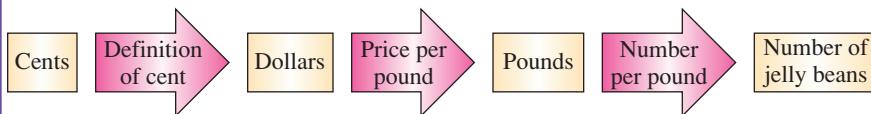
Practice Problem 10.11 Calculate the volume of liquid water (density = 1.00 g/mL) produced by burning 48.4 g of propane gas, C₃H₈, and condensing the gaseous water produced.

EXAMPLE 10.12

- (a) A girl takes 444 pennies from her piggy bank to buy jelly beans, which cost \$3.30 per pound. If there are 110 jelly beans per pound, how many jelly beans can she buy?
- (b) How many O₂ molecules does it take to produce 425 mmol of H₂O by a combination reaction with sufficient H₂ gas?

Solution

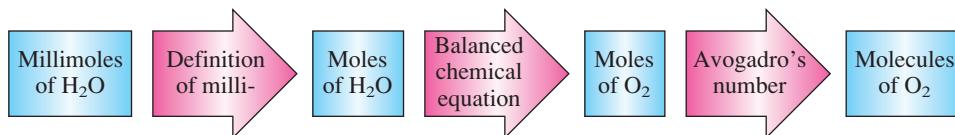
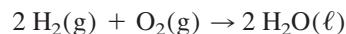
(a)



$$444 \text{ cents} \left(\frac{1 \text{ dollar}}{100 \text{ cents}} \right) \left(\frac{1.00 \text{ lb}}{3.30 \text{ dollars}} \right) \left(\frac{110 \text{ jelly beans}}{1 \text{ lb}} \right) = 148 \text{ jelly beans}$$

10.3 ■ Calculations Involving Other Quantities**267**

(b)



$$425 \text{ mmol H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{1000 \text{ mmol H}_2\text{O}} \right) \left(\frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}} \right) \left(\frac{6.02 \times 10^{23} \text{ molecules O}_2}{1 \text{ mol O}_2} \right) = 1.28 \times 10^{23} \text{ molecules O}_2$$

The main difference between parts (a) and (b) is that the values of more factors have to be stated in the problem in part (a) than in part (b).

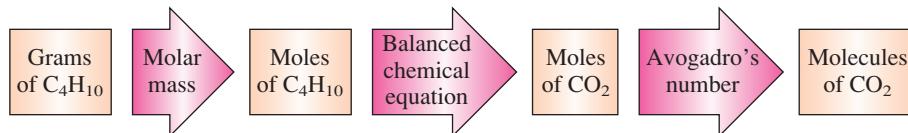
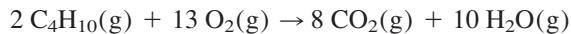
Practice Problem 10.12 How many SO₂ molecules does it take to combine with O₂ to produce 0.751 mol of SO₃?

EXAMPLE 10.13

Calculate the number of molecules of CO₂ that can be produced by complete combustion of 12.5 g of gaseous C₄H₁₀.

Solution

The balanced equation for the reaction is

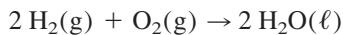


$$12.5 \text{ g C}_4\text{H}_{10} \left(\frac{1 \text{ mol C}_4\text{H}_{10}}{58.1 \text{ g C}_4\text{H}_{10}} \right) \left(\frac{8 \text{ mol CO}_2}{2 \text{ mol C}_4\text{H}_{10}} \right) \left(\frac{6.02 \times 10^{23} \text{ molecules CO}_2}{1 \text{ mol CO}_2} \right) = 5.18 \times 10^{23} \text{ molecules CO}_2$$

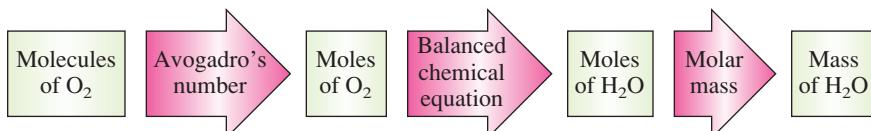
Practice Problem 10.13 Calculate the mass of H₂O produced by the complete combustion of 4.57×10^{22} molecules of C₄H₁₀.

EXAMPLE 10.14

Calculate the mass of H₂O that can be prepared by the reaction of 4.51×10^{22} O₂ molecules with hydrogen gas.

Solution

Because the equation gives the mole ratio, the number of molecules is changed to moles of O₂, then to moles of H₂O, which can then be converted to grams (mass) of H₂O:



$$4.51 \times 10^{22} \text{ O}_2 \text{ molecules} \left(\frac{1 \text{ mol O}_2}{6.02 \times 10^{23} \text{ O}_2 \text{ molecules}} \right) \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right) \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 2.70 \text{ g H}_2\text{O}$$

Practice Problem 10.14 Calculate the number of individual atoms of barium metal that can react when heated with aluminum oxide to form solid barium oxide and 7.33 g of aluminum.

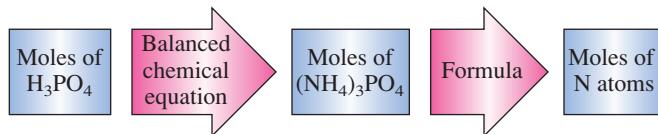
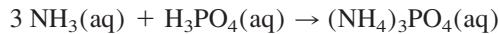
The number of moles of an element in a mole of compound can also be used to calculate the number of moles of the compound involved in a reaction. The ratio of the number of moles of an element within a compound to the number of moles of the compound is determined by the compound's chemical formula (Section 7.3). Thus, the subscripts of the formula may be used to form conversion factors.

EXAMPLE 10.15

The quantities of nitrogen, phosphorus, and potassium in a fertilizer are critical to the fertilizer's function in helping crops grow. Calculate the number of moles of nitrogen atoms in the ammonium phosphate, (NH₄)₃PO₄, produced by the reaction of excess aqueous ammonia with 227 mol of phosphoric acid.

Solution

The reaction is



$$227 \text{ mol H}_3\text{PO}_4 \left(\frac{1 \text{ mol } (\text{NH}_4)_3\text{PO}_4}{1 \text{ mol H}_3\text{PO}_4} \right) \left(\frac{3 \text{ mol N}}{1 \text{ mol } (\text{NH}_4)_3\text{PO}_4} \right) = 681 \text{ mol N}$$

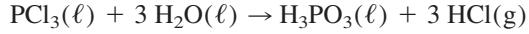
From the
chemical formula

10.4 ■ Problems Involving Limiting Quantities**269**

Practice Problem 10.15 Calculate the mass of nitrogen in the ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$, prepared by treating 6.15×10^6 g of phosphoric acid with excess aqueous ammonia.

**Snapshot Review**

- The conversions of Sections 10.1 and 10.2 are extended in this section, using Avogadro's number, density, and chemical formulas (moles of one element per mole of any other substance).
- A. Calculate the mass of PCl_3 required to prepare the quantity of HCl that contains 4.55×10^{23} chlorine atoms by the following reaction:



10.4 Problems Involving Limiting Quantities

In problems in the preceding sections, a quantity of one reactant was given, and it was assumed that enough of any other reactants was present. In Example 10.3, for instance, 0.750 mol of hydrochloric acid reacted with calcium. If no calcium is present, however, no reaction is possible—no matter how many moles of hydrochloric acid there are. In Example 10.3, we assumed that sufficient calcium was present because nothing was stated about the quantity of calcium used. In contrast, problems involving limiting quantities have the quantities of at least two reactants given. The reactant used up first limits the quantities of the products and is referred to as being present in **limiting quantity**. Any other reactant may be present in an amount that represents a number of moles equal to or greater than is required for the reaction and is said to be present in sufficient or **excess** quantity. The reaction is said to have gone to **completion** when the limiting quantity has been used up. An example from everyday life illustrates this principle.

The reactant that is present in limiting quantity determines the extent of reaction that can take place.

EXAMPLE 10.16

- If cashew nuts cost \$8.00 per pound, how many pounds of these nuts can be purchased with \$108.00?
- How many pounds of cashew nuts can be purchased with \$108.00 if the store has 12.5 lb in stock?

Solution

- Assuming that the store has sufficient nuts,

$$108.00 \text{ dollars} \left(\frac{1 \text{ lb}}{8.00 \text{ dollars}} \right) = 13.5 \text{ lb}$$



- (b) Even though the amount of money is sufficient to purchase 13.5 lb of nuts, the store does not have that much. The maximum quantity that can be purchased is the 12.5 lb on hand. The nuts are said to be available in limited quantity. No matter how much more money is available, the quantity of nuts limits the purchase.

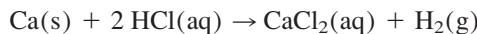
Practice Problem 10.16 How many pounds of cashew nuts, at \$8.00 per pound, can be purchased with \$150.00 if the store has 20.0 pounds of the nuts?

EXAMPLE 10.17

- (a) Calculate the quantity of calcium metal required to react with 1.50 mol of aqueous hydrochloric acid.
(b) Calculate the quantity of calcium that will react with 1.50 mol of HCl if 1.00 mol of calcium is present.
(c) Calculate the quantity of calcium that will react with 1.50 mol of HCl if 0.500 mol of calcium is present.

Solution

- (a) The quantity of calcium is determined in the same way as the quantity of hydrogen was in Example 10.3:



$$1.50 \text{ mol HCl} \left(\frac{1 \text{ mol Ca}}{2 \text{ mol HCl}} \right) = 0.750 \text{ mol Ca}$$

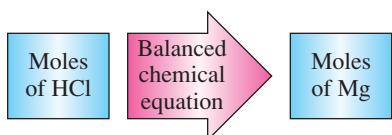
- (b) In part (a), we determined that 0.750 mol of Ca will react with 1.50 mol of HCl. Because more calcium is present in this case, 0.750 mol will be used up, and the remaining 0.25 mol will not react. Ca is *in excess*.
(c) In part (a), we showed that 0.750 mol of Ca is required to react with 1.50 mol of HCl, but in this case, not that much calcium is present. Calcium is *in limiting quantity*, and the entire 0.500 mol of Ca will react with 1.00 mol of HCl:

$$0.500 \text{ mol Ca} \left(\frac{2 \text{ mol HCl}}{1 \text{ mol Ca}} \right) = 1.00 \text{ mol HCl}$$

The hydrochloric acid is in excess. The number of moles of HCl that will be left unreacted is the difference:

$$\begin{array}{r} 1.50 \text{ mol HCl present} \\ - 1.00 \text{ mol HCl reacts} \\ \hline 0.50 \text{ mol HCl unreacted} \end{array}$$

Practice Problem 10.17 Calculate the number of moles of hydrogen gas that will be produced in each part of Example 10.17.

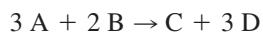


10.4 ■ Problems Involving Limiting Quantities**271**

Limiting quantities problems have the quantities of two (or more) reactants given.

The first task in doing a problem involving a limiting quantity is to recognize that it is such a problem. Fortunately, that is fairly easy: The quantities of two different reactants are given. Then, use the tabulation method outlined in Section 10.1. Do the steps given in the left column to solve the following example in the right column:

Calculate the number of moles of each of the products and of the excess reactant when 1.500 mol of A and 0.500 mol of B are allowed to react according to the following general equation:

**Steps**

- Step 1:** Write the balanced chemical equation for the reaction.
- Step 2:** Write the initial number of moles of each reactant (and product) under its formula.
- Step 3:** Determine which reactant is limiting by dividing the number of moles of each reactant given in the problem by the coefficient of that reactant in the balanced chemical equation. The smallest quotient indicates the limiting reagent. Then draw a line through the results so as not to use them later. Rewrite the number of moles present of the limiting quantity with a minus sign in a row corresponding to the change due to reaction.
- Step 4:** Complete the “change” row by writing the number of moles of each substance that would react with or be produced from the quantity in step 3. Use a minus sign with each quantity of reactant. The magnitudes in the “change” row are in the same ratio as the coefficients in the balanced chemical equation.
- Step 5:** Subtract the quantity of each reactant in the “change” row from the initial quantity and add the quantity of each product in the change row to any initial quantity to get a final quantity.

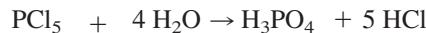
Example

	3 A	+	2 B	→	C	+	3 D
All quantities are in moles.							
Present initially	1.500		0.500		0		0
$\frac{1.500 \text{ mol A}}{3 \text{ mol A}}$	0.500		$\frac{0.500 \text{ mol B}}{2 \text{ mol B}}$	0.250			
B is limiting.							
Change due to reaction					-0.500		
Change due to reaction	-0.750		-0.500		+0.250		+0.750
Present finally	0.750		0.00		0.250		0.750

Using this method, we calculate the quantity of each product produced and the quantity of any excess reactant all in one calculation. Note that the quantities in the “initial” and “final” rows are *not* in the ratio of the balanced chemical equation; only the magnitudes of the ratios in the “change” row are in the same ratio as those in the balanced equation.

EXAMPLE 10.18

Calculate the number of moles of each of the products and of the excess reactant when 0.250 mol of PCl_5 and 1.50 mol of H_2O are allowed to react, yielding H_3PO_4 and HCl .

Solution**Step 1:**

Step 2: Present initially 0.250 1.50 0.00 0.00

Steps 3 and 4:

Change due to reaction -0.250 -1.00 +0.250 +1.25

Step 5: Present finally 0.000 0.50 0.250 1.25

Note that the ratio of the magnitudes of PCl_5 to H_2O to H_3PO_4 to HCl in the "change" row is 1 : 4 : 1 : 5, just as in the balanced chemical equation.

$$\frac{0.250 \text{ mol } \text{PCl}_5}{1 \text{ mol } \text{PCl}_5} = 0.250$$

$$\frac{1.50 \text{ mol } \text{H}_2\text{O}}{4 \text{ mol } \text{H}_2\text{O}} = 0.375$$

PCl_5 is limiting.

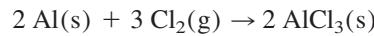
Practice Problem 10.18 Calculate the number of moles of each product produced and the number of moles of excess reagent when 0.100 mol of HCl and 0.0250 mol of $\text{Ba}(\text{OH})_2$ (aq) are allowed to react.

EXAMPLE 10.19

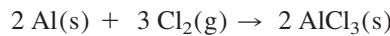
If 0.600 mol of chlorine gas is treated with 0.500 mol of aluminum metal to produce solid aluminum chloride, which reactant is in excess? How many moles of aluminum chloride can be produced?

Solution

Step 1: The balanced chemical equation is



Step 2: We tabulate these quantities, all in moles, as follows:



Present initially 0.500 0.600 0.000

Steps 3 and 4:

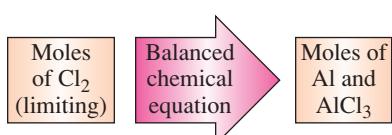
Change due to reaction -0.400 -0.600 +0.400

Step 5: Present finally 0.100 0.000 0.400

In step 3, the number of moles of Cl_2 present (the limiting quantity) was used to calculate the number of moles of Al used up and AlCl_3 produced:

$$0.600 \text{ mol Cl}_2 \left(\frac{2 \text{ mol Al}}{3 \text{ mol Cl}_2} \right) = 0.400 \text{ mol Al}$$

$$0.600 \text{ mol Cl}_2 \left(\frac{2 \text{ mol AlCl}_3}{3 \text{ mol Cl}_2} \right) = 0.400 \text{ mol AlCl}_3$$



10.4 ■ Problems Involving Limiting Quantities**273**

Remember, in such a tabulation, the magnitudes of the numbers of moles in the row showing the changes due to the reaction will always be in the same ratio as the coefficients in the balanced equation.

Practice Problem 10.19 If 1.00 mol of aluminum metal is treated with 1.75 mol of solid sulfur to produce solid aluminum sulfide, which reactant is in excess? How many moles of aluminum sulfide can be produced?

EXAMPLE 10.20

Calculate the number of moles of $\text{BaCl}_2(\text{aq})$ that will be produced by the reaction of 1.95 mol of $\text{Ba}(\text{OH})_2(\text{s})$ and 4.25 mol of $\text{HCl}(\text{aq})$.

Solution

We recognize this as a problem involving a limiting quantity because the quantities of *two* reactants are given. Because this reaction takes place in aqueous solution, the number of moles of water present before and after the reaction is unknown.

Step 1: $2 \text{ HCl}(\text{aq}) + \text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{BaCl}_2(\text{aq}) + 2 \text{ H}_2\text{O}(\ell)$

Step 2: Present initially 4.25 1.95 0.00

Steps 3 and 4:

<i>Change due to reaction</i>	−3.90	−1.95	+1.95	+3.90
-----------------------------------	-------	-------	-------	-------

Step 5: Present finally 0.35 0.00 1.95

$$\frac{4.25 \text{ mol HCl}}{2 \text{ mol HCl}} = 2.125$$

$$\frac{1.95 \text{ mol Ba(OH)}_2}{1 \text{ mol Ba(OH)}_2} = 1.95$$

$\text{Ba}(\text{OH})_2$ is limiting.

Note the difference between the water *present* and the water *produced*.

Practice Problem 10.20 Calculate the number of moles of water that will be produced by the reaction of 1.95 mol of $\text{Ba}(\text{OH})_2(\text{s})$ and 4.25 mol of $\text{HCl}(\text{aq})$.

If the number of moles present for each reactant is exactly the number required, then *both* reactants are in limiting quantity. *Either* quantity of reactant may be used to calculate the quantity of product.

EXAMPLE 10.21

Calculate the number of moles of BaCl_2 that will be produced by the reaction of 0.250 mol of $\text{Ba}(\text{OH})_2$ and 0.500 mol of HCl .

Solution

Step 1: $2 \text{ HCl}(\text{aq}) + \text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{BaCl}_2(\text{aq}) + 2 \text{ H}_2\text{O}(\ell)$

Step 2: Present initially 0.500 0.250 0.000

Steps 3 and 4:

<i>Change due to reaction</i>	−0.500	−0.250	+0.250	+0.500
-----------------------------------	--------	--------	--------	--------

Step 5: Present finally 0.000 0.000 0.250

$$\frac{0.250 \text{ mol Ba(OH)}_2}{1 \text{ mol Ba(OH)}_2} = 0.250$$

$$\frac{0.500 \text{ mol HCl}}{2 \text{ mol HCl}} = 0.250$$

Both reactants are limiting.

Practice Problem 10.21 (a) Calculate the number of millimoles of PbI_2 that can be produced by treating 2.50 mmol of $\text{Pb}(\text{NO}_3)_2$ with 5.00 mmol of NaI . (b) Calculate the number of millimoles of PbI_2 that can be produced by treating 2.00 mmol of $\text{Pb}(\text{NO}_3)_2$ with 1.00 mmol of NaI .

Some quantity of a product of a reaction might be present in a reaction mixture before the reaction occurs. The tabular method of solving makes this type of problem as easy as the others. The only difference is a nonzero value for the initial number of moles of a product.

EXAMPLE 10.22

Calculate the final number of moles of HF, NaF, and NaOH present after 0.750 mol of HF, 0.250 mol of NaF, and 0.400 mol of NaOH are placed in enough water to make 1.00 L of solution.

Solution

HF reacts with NaOH, but NaF does not react with either of the others. The equation for the reaction involves the acid reacting with the base, yielding the salt and water. Tabulating the values given, all in moles, yields:

	HF	+	$\text{NaOH} \rightarrow$	NaF	+	H_2O
Present initially	0.750			0.250		0.400
Change due to reaction	-0.250			-0.250	+0.250	
Present finally	0.500			0.000		0.650

Practice Problem 10.22 Calculate the final number of moles of each reactant and product present after 0.250 mol of HF, 0.150 mol of NaF, and 0.0550 mol of NaOH are placed in 1.000 mol of water.

Problems involving limiting quantities may be stated in terms of masses, rather than moles, and a mass of product might be required. To solve, convert the masses of reactants to moles, perform the steps given earlier in this section, and convert the final number of moles of product to a mass, if required. Figure 10.4 summarizes the conversions and procedure.

EXAMPLE 10.23

What mass of Na_2SO_4 will be formed by addition of 14.4 g of NaHCO_3 in aqueous solution to an aqueous solution containing 4.90 g of H_2SO_4 ?

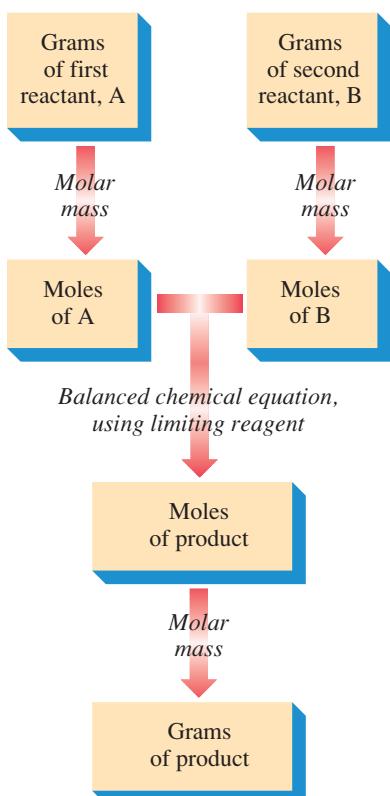
Solution

Change the given masses to moles:

$$14.4 \text{ g } \text{NaHCO}_3 \left(\frac{1 \text{ mol } \text{NaHCO}_3}{84.0 \text{ g } \text{NaHCO}_3} \right) = 0.1714 \text{ mol } \text{NaHCO}_3 \text{ present}$$

$$4.90 \text{ g } \text{H}_2\text{SO}_4 \left(\frac{1 \text{ mol } \text{H}_2\text{SO}_4}{98.1 \text{ g } \text{H}_2\text{SO}_4} \right) = 0.04995 \text{ mol } \text{H}_2\text{SO}_4 \text{ present}$$

Figure 10.4 Procedure for Solving Problems Involving Limiting Quantities When Masses Are Given and Required



10.4 ■ Problems Involving Limiting Quantities**275**

Then proceed as before:



Step 2:

Present initially	0.1714	0.04995	0.000	0.000
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Steps 3 and 4:

*Change due to
reaction*

0.0999	-0.04995	+0.04995	+0.0999
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Step 5:

Present finally	0.0715	0.000	0.04995	0.0999
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Change the number of moles of Na_2SO_4 to grams:

$$0.04995 \text{ mol Na}_2\text{SO}_4 \left(\frac{142 \text{ g Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4} \right) = 7.09 \text{ g Na}_2\text{SO}_4$$

Practice Problem 10.23 What mass of NaBr will be formed by addition of 12.3 g of NaHCO_3 to 25.0 g of HBr, both in aqueous solution?

EXAMPLE 10.24

What mass of sodium chlorate will result from the reaction of 15.5 g of aqueous sodium carbonate with 42.3 g of aqueous chloric acid? What mass of excess reagent will remain unreacted?

Solution

First convert the masses to moles:

$$15.5 \text{ g Na}_2\text{CO}_3 \left(\frac{1 \text{ mol Na}_2\text{CO}_3}{106 \text{ g Na}_2\text{CO}_3} \right) = 0.1462 \text{ mol Na}_2\text{CO}_3 \text{ present}$$

$$42.3 \text{ g HClO}_3 \left(\frac{1 \text{ mol HClO}_3}{84.5 \text{ g HClO}_3} \right) = 0.5006 \text{ mol HClO}_3 \text{ present}$$

Then proceed as before:



Step 2:

Present initially	0.5006	0.1462	0.000	0.000
-------------------	--------	--------	-------	-------

Steps 3 and 4:

*Change due to
reaction*

-0.2924	-0.1462	+0.2924	+0.1462
---------	---------	---------	---------

Step 5:

Present finally	0.2082	0.000	0.2824	0.1462
-----------------	--------	-------	--------	--------

Converting to mass:

$$0.2924 \text{ mol NaClO}_3 \left(\frac{106.5 \text{ g NaClO}_3}{1 \text{ mol NaClO}_3} \right) = 31.1 \text{ g NaClO}_3$$

$$0.2802 \text{ mol HClO}_3 \left(\frac{84.5 \text{ g HClO}_3}{1 \text{ mol HClO}_3} \right) = 23.7 \text{ g HClO}_3$$

Practice Problem 10.24 What mass of Na₂SO₄(aq) will result from the reaction of 22.7 g of NaOH(aq) and 10.0 g of H₂SO₄(aq)?

EXAMPLE 10.25

Calculate the quantity of H₂O present after the reaction of 0.425 mol HCl and 0.100 mol Al(OH)₃(s) in 12.00 mol of water.

Solution

Step 1: 3 HCl(aq) + Al(OH)₃(s) → AlCl₃(aq) + 3 H₂O(ℓ)

Step 2:

Present initially 0.425 mol 0.100 mol 0.00 mol 12.00 mol

Steps 3 and 4:

Change due
to reaction -0.300 mol -0.100 mol +0.100 mol +0.300 mol

Step 5:

Present finally 0.125 mol 0.000 mol 0.100 mol 12.30 mol

$$\frac{0.425 \text{ mol HCl}}{3 \text{ mol HCl}} = 0.1417$$

$$\frac{0.100 \text{ mol Al}}{1 \text{ mol Al}} = 0.100$$

Al is limiting.

The fact that some water was present initially does not affect the solution method.

Practice Problem 10.25 Calculate the number of moles of sodium acetate present after a solution containing 0.400 mol of acetic acid, HC₂H₃O₂, and 0.100 mol of sodium acetate, NaC₂H₃O₂, in 10.00 mol of water, is treated with 0.300 mol of NaOH.



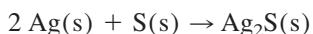
Snapshot Review



ChemSkill Builder 4.4

- When a reaction of two or more substances has proceeded until one of the reactants has been used up, the reaction stops. To determine which reactant is limiting, divide the number of moles of each by its coefficient in the balanced equation. The lowest quotient is that of the limiting quantity. Do not use these quotients for any further calculations.

- A. For each part determine which reactant in the following equation is limiting:



- (a) 2 mol Ag and 1.5 mol S
 - (b) 4 mol Ag and 1 mol S
 - (c) 2 mol Ag and 2 mol S
- B. (a) How much Ag would react with 2.5 mol S?
(b) How much S would react with 4.0 mol Ag?
(c) How much Ag and how much S react when 2.5 mol S and 4.0 mol Ag are heated together?

10.5 Theoretical Yield and Percent Yield

When a quantity of product is calculated from a quantity or quantities of reactants, as was done in Sections 10.1 through 10.4 of this chapter, that quantity of product is called the **theoretical yield**. When a reaction is run, however, less product than the calculated amount is often obtained: Some of the product may stay in the solution in which the reaction was run; some side reaction may use up some of the reactants; or the reaction may be stopped before it is completed. No matter why, the fact is that many reactions produce less product than the calculated quantity; that is, the actual yield is less than the theoretical yield. No reaction can produce more than the theoretical yield. The **percent yield** is defined as 100% times the ratio of the actual yield to the theoretical yield:

$$\text{Percent yield} = \left(\frac{\text{Actual yield}}{\text{Theoretical yield}} \right) \times 100\%$$

Example 10.26

Calculate the percent yield of a reaction if calculations indicated that 7.44 g of product could be obtained, but only 7.02 g of product was actually obtained.

Solution

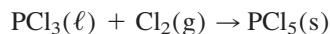
$$\text{Percent yield} = \left(\frac{\text{Actual yield}}{\text{Theoretical yield}} \right) \times 100\% = \left(\frac{7.02 \text{ g}}{7.44 \text{ g}} \right) \times 100\% = 94.4\%$$

Example 10.27

Calculate the percent yield if 14.1 g of solid PCl_5 is obtained in a certain experiment in which 10.0 g of liquid PCl_3 is treated with excess gaseous Cl_2 .

Solution

The theoretical yield in grams is calculated as discussed in Section 10.2:



$$10.0 \text{ g PCl}_3 \left(\frac{1 \text{ mol PCl}_3}{138 \text{ g PCl}_3} \right) \left(\frac{1 \text{ mol PCl}_5}{1 \text{ mol PCl}_3} \right) \left(\frac{209 \text{ g PCl}_5}{1 \text{ mol PCl}_5} \right) = 15.14 \text{ g PCl}_5$$

The percent yield is

$$\left(\frac{\text{Actual yield}}{\text{Theoretical yield}} \right) \times 100\% = \left(\frac{14.1 \text{ g}}{15.14 \text{ g}} \right) \times 100\% = 93.1\%$$

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CHAPTER 10 ■ Stoichiometry

Practice Problem 10.27 Calculate the percent yield if 14.1 g of PCl_5 is obtained from treatment of 10.0 g of PCl_3 with 6.00 g of gaseous Cl_2 .

EXAMPLE 10.28

Ozone, O_3 , is produced when O_2 molecules are subjected to electrical discharge or the action of cosmic rays in the upper atmosphere.

- Calculate the mass of ozone that could theoretically be produced by conversion of 1.47 g of O_2 .
- If 0.111 g of O_3 is actually produced, what is the percent yield?

Solution

(a)
$$3 \text{ O}_2(\text{g}) \rightarrow 2 \text{ O}_3(\text{g})$$

$$1.47 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) \left(\frac{2 \text{ mol O}_3}{3 \text{ mol O}_2} \right) \left(\frac{48.0 \text{ g O}_3}{1 \text{ mol O}_3} \right) = 1.47 \text{ g O}_3$$

This part of the problem could have been solved by simply applying the law of conservation of mass.

- (b) The percent yield is

$$\left(\frac{0.111 \text{ g}}{1.47 \text{ g}} \right) \times 100\% = 7.55\% \text{ yield}$$



Snapshot Review



ChemSkill Builder 4.4

- The calculated quantity of product (Sections 10.1–10.4) is the largest possible quantity that can ever be expected, but many factors may reduce the actual yield of product. Competing reactions, solute remaining in solution, and reactions not going to completion (Chapters 18 and 19) all lead to less product than calculated. The percent yield is 100% times the ratio of the actual yield divided by the theoretical yield.

- A. If 12.1 g of a certain reactant is calculated to yield 15.5 g of a product, but only 10.9 g of product is obtained, what is (a) the theoretical yield? (b) the actual yield? (c) the percent yield?

10.6 Calculations with Net Ionic Equations

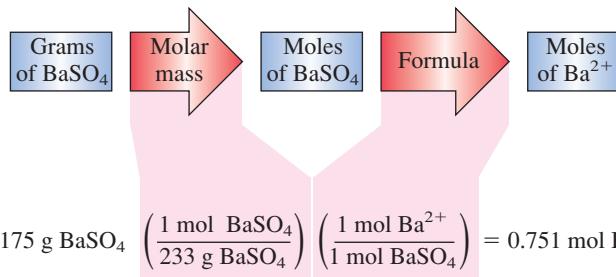
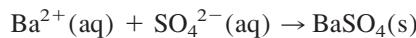
Net ionic equations (Chapter 9), like all other balanced chemical equations, give the mole ratios of reactants and products. Therefore, any calculations that require mole ratios may be done with net ionic equations as well as with total equations. However, a net ionic equation does not yield mass data directly because part of each soluble ionic compound is not given. For example, we can tell how many moles of silver ion are required to produce a certain number of moles of a product,

10.6 ■ Calculations with Net Ionic Equations**279**

but it is impossible to weigh out just the silver ions. The compound must contain some anions, too. The net ionic equation indicates that we are not interested in the anions because they do not react. However, the anions have some mass. We cannot tell how much of the mass of the compound is composed of silver ions and how much is composed of anions if we do not specify which anions are present. Thus, net ionic equations are often not directly useful for mass computations.

EXAMPLE 10.29

How many moles of barium ions is required to produce 175 g of barium sulfate?

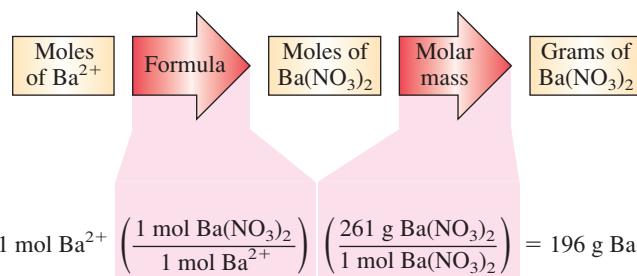
Solution

We cannot weigh out 0.751 mol of Ba^{2+} if we do not know what anion is included in the compound. Even though the anion does not react, it still has some mass.

EXAMPLE 10.30

To provide 0.751 mol of Ba^{2+} takes how many grams of (a) $\text{Ba}(\text{NO}_3)_2$? (b) $\text{Ba}(\text{ClO}_3)_2$?

(a)



$$(b) 0.751 \text{ mol Ba}^{2+} \left(\frac{1 \text{ mol Ba}(\text{ClO}_3)_2}{1 \text{ mol Ba}^{2+}} \right) \left(\frac{304 \text{ g Ba}(\text{ClO}_3)_2}{1 \text{ mol Ba}(\text{ClO}_3)_2} \right) = 228 \text{ g Ba}(\text{ClO}_3)_2$$

Practice Problem 10.30 How many moles of barium ions and how many grams of barium chloride would be required to produce 6.11 g of barium sulfate?

ITEM OF INTEREST

The masses of individual ions are important in food chemistry. For example, too much sodium in the diet may be harmful to our health. Since it doesn't matter much what anion is present, the quantity of sodium is given on package labels. The general public, however, is not familiar with moles, so the mass of sodium is stated as part of the nutritional information on packaged foods.

The mass of a metal ion is essentially that of the atom, since the electrons have such a small fraction of the mass of the atom.

EXAMPLE 10.31

- (a) Calculate the percent difference between the mass of a sodium atom and a sodium ion.
 - (b) Compare this percentage to those for a lithium atom and ion as well as for a beryllium atom and ion.

Solution

- (a) The difference is the mass of an electron, 0.000549 amu.

$$\frac{0.000549 \text{ amu}}{23.0 \text{ amu}} \times 100\% = 0.00239\%$$

- (b) For lithium:

$$\frac{0.000549 \text{ amu}}{6.94 \text{ amu}} \times 100\% = 0.00791\%$$

For beryllium, which has lost two electrons:

$$\frac{2 \times 0.000549 \text{ amu}}{9.01 \text{ amu}} \times 100\% = 0.0122\%$$

The difference is very small indeed.



Snapshot Review



ChemSkill Builder 5.3

- The mass of only the cations or only the anions in a compound cannot be measured on a balance.
 - The mass of an ionic compound cannot be calculated from its number of moles unless the identity of both ions is known.

■ Items for Special Attention

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fraction of a mole of AgCl precipitated? (c) What mass of AgCl was produced? (d) Is it possible to tell what mass of the original compound chloride was present? (e) If the original solution contained MgCl₂, could its mass be calculated?

Key Terms

Key terms are defined in the Glossary.

completion (10.4)

excess (10.4)

limiting quantity (10.4)

percent yield (10.5)

reacting ratio (10.1)

stoichiometry (10.1)

theoretical yield (10.5)

Summary

The ratios of the numbers of moles of reactants and products involved in any chemical reaction are given by the coefficients in the balanced equation for the reaction. Each ratio of moles may be used as a factor to convert the number of moles of one reactant or product to the number of moles of any other (Section 10.1).

If the quantity of any substance is given in terms of mass instead of in moles, the mass must be changed to moles before calculating the number of moles of another substance in the reaction. If the mass of a substance is required as an answer to a problem, its number of moles must be converted to a mass. (Conversions between mass and moles are presented in Chapter 7.) (Section 10.2) If some other measure of the quantity of a substance is given or required (for example, the number of molecules of a substance), an appropriate conversion factor is needed to convert to or from moles (Section 10.3).

For problems in which the quantities of two (or more) reactants are given, we must determine if one of the reactants is present in a quantity less than, equal to, or greater than that required to react with *all* the other reactants. Determine which reactant is in limiting quantity and use that quantity to calculate the quantities of the substances that will be used up and produced. A table of reactant and product quantities is useful. If masses are

given, rather than moles, they must be converted to moles first (Section 10.4).

The theoretical yield is the quantity of product calculated from the quantity of reactant used (or the limiting quantity if more than one quantity is given). In some reactions, not all of the calculated product can be collected. The percent yield is the ratio of the actual yield to the theoretical yield, converted to a percentage:

$$\text{Percent yield} = \left(\frac{\text{Actual yield}}{\text{Theoretical yield}} \right) \times 100\%$$

(Section 10.5)

Net ionic equations can be used to calculate mole ratios but often cannot be used directly with masses. Although spectator ions do not react, they do have mass, and the molar mass of the compound cannot be determined if all the ions are not specified (Section 10.6).

The small number of key terms for this chapter suggests that this chapter does not introduce many new concepts. However, this chapter may seem difficult because it draws extensively on background material from earlier chapters. The concepts presented in this chapter are extremely important because they are applied in later chapters on gas laws, electrochemistry, and equilibrium, among others.

Items for Special Attention

- The balanced chemical equation gives the *mole ratios* of reactants and products *involved in the reaction*, not the mass ratios and not the numbers of moles *present*.
- Include the formulas of the substances involved with the units when applying the factor label method to solve stoichiometry problems. For example, write “g NaCl” or “mol NaCl,” rather than just “g” or “mol.”
- The coefficient in the balanced chemical equation is *not* used in conversions between grams and moles of a substance.
- The substance present in limiting quantity may be present in a greater number of moles than the substance in excess (but always less than would be required to react with all of the substance in excess).

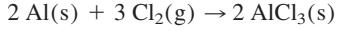
Answers to Snapshot Review

- 10.1 A. $1.50 \text{ mol CaCl}_2 \left(\frac{2 \text{ mol HCl}}{1 \text{ mol CaCl}_2} \right) = 3.00 \text{ mol HCl}$
 B. Sections 6.2 and 6.3 for writing formulas from names and Sections 8.2 and 8.4 to complete and balance the equation.
- 10.2 A. Write a balanced chemical equation.
 Convert the 13.5 g of H_2SO_4 to moles, using the molar mass.
 Convert the moles of H_2SO_4 to moles of $(\text{NH}_4)_2\text{SO}_4$, using the ratio from the balanced chemical equation.
 Convert the moles of $(\text{NH}_4)_2\text{SO}_4$ to mass of $(\text{NH}_4)_2\text{SO}_4$, using its molar mass.
- B. Only (b) is true. The equation is a mole ratio, not a mass ratio.

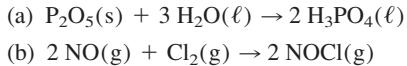
- 10.3 A. $4.55 \times 10^{23} \text{ Cl} \left(\frac{1 \text{ mol Cl}}{6.02 \times 10^{23} \text{ Cl}} \right) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol Cl}} \right) \times \left(\frac{1 \text{ mol PCl}_3}{3 \text{ mol HCl}} \right) \left(\frac{137 \text{ g PCl}_3}{1 \text{ mol PCl}_3} \right) = 34.5 \text{ g PCl}_3$
- 10.4 A. (a) Ag (b) S (c) Ag
 B. (a) 5.0 mol Ag reacts with 2.5 mol S.
 (b) 2.0 mol S reacts with 4.0 mol Ag.
 (c) 2.0 mol S reacts with 4.0 mol Ag.
 (It takes 5.0 mol of Ag to react with all the S.)
- 10.5 A. (a) 15.5 g (b) 10.9 g (c) 70.3%
 10.6 A. (a) 0.387 mol (b) 0.387 mol (c) 55.5 g
 (d) We cannot tell, because we have no way of knowing the molar mass of the metal chloride or its number of chloride ions per formula unit. (e) Yes

Self-Tutorial Problems

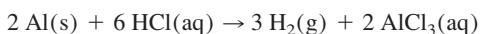
- 10.1 Write all the possible conversion factors using the coefficients from the following equation:



- 10.2 Write all of the possible conversion factors using the coefficients from each of the following equations:



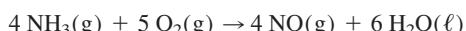
- 10.3 Consider the following reaction:



Because 2 Al atoms react with 6 molecules of HCl, how many HCl molecules will react with each of the following?

- 12 atoms of Al
- 24 atoms of Al
- 100 atoms of Al
- 1 dozen atoms of Al
- 1 mol of Al
- 3 mol of Al

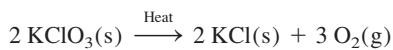
- 10.4 Consider the following reaction:



Because 4 NH_3 molecules react with 5 O_2 molecules, how many O_2 molecules will react with each of the following quantities of NH_3 ?

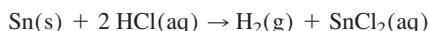
- 12 NH_3 molecules
- 1 dozen NH_3 molecules
- 4 dozen NH_3 molecules
- 4 mol NH_3
- 1 mol NH_3

- 10.5 For the reaction



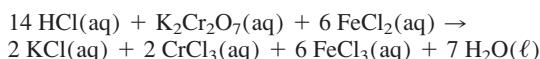
one student placed 2.00 mol of KClO_3 in a flask, a second student placed 0.750 mol of KClO_3 in a flask, and a third student placed 0.250 mol of KClO_3 in a flask. Which student(s) could carry out the reaction specified in the equation?

- 10.6 For the reaction



one student placed 1.00 mol of tin plus excess HCl in a flask, a second student placed 2.50 mol of tin plus excess HCl in a flask, and a third student placed 5.00 mol of tin plus excess HCl in a flask. Which student(s) could carry out the reaction specified in the equation?

- 10.7 Consider the following balanced equation:



What is the ratio of moles of HCl to moles of CrCl_3 ?

- 10.8 Calculate the number of moles of each of the following that is necessary to produce 2.20 mol of AgCl by reaction with $\text{AgC}_2\text{H}_3\text{O}_2$:

- CoCl_2
- CrCl_2
- CaCl_2

- 10.9 Calculate the number of moles of each of the following that is necessary to produce 0.700 mol of AgCl by reaction with $\text{AgC}_2\text{H}_3\text{O}_2$:

- NH_4Cl
- ZnCl_2
- AlCl_3

- 10.10 (a) How many (two-slice) sandwiches can you make with 24 slices of bread?

- (b) How many sandwiches can you make with 24 slices of bread and 14 hamburger patties?

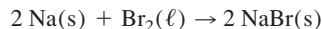
- (c) How many sandwiches can you make with 24 slices of bread and 11 hamburger patties?

- (d) How can you recognize when a problem involves a limiting quantity?

■ Problems

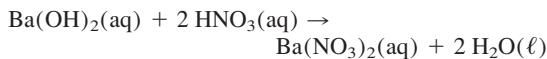
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- 10.11** How many moles of NaBr will be produced by the following reaction in each case?



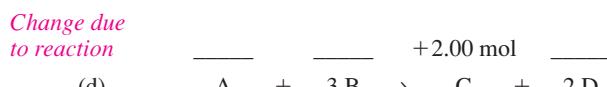
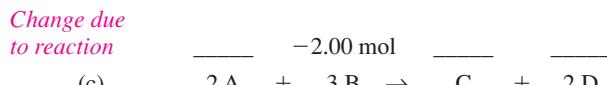
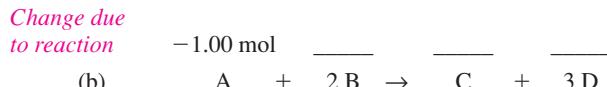
- (a) 1 mol Na and 0 mol Br₂
- (b) 2 mol Na and 1 mol Br₂
- (c) 3 mol Na and 1 mol Br₂

- 10.12** Consider the following reaction:

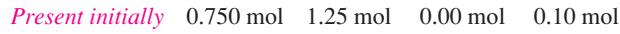
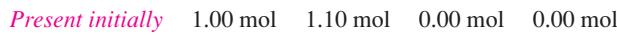


- (a) How many moles of Ba(NO₃)₂ can be made with 2.50 mol of HNO₃?
- (b) How many moles of Ba(NO₃)₂ can be made with 2.50 mol of HNO₃ and 1.10 mol of Ba(OH)₂?
- (c) How many moles of Ba(NO₃)₂ can be made with 2.50 mol of HNO₃ and 2.00 mol of Ba(OH)₂?

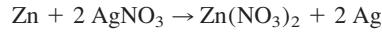
- 10.13** Complete the “Change due to reaction” line for each of the following reactions:



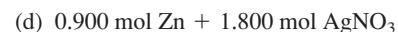
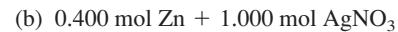
- 10.14** Complete each table below:



- 10.15** For the reaction

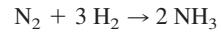


calculate the number of moles of products as well as the number of moles of excess reagent after the following pairs of reagents are combined:



- 10.16** Explain why limiting quantities problems do not usually involve decomposition reactions.

- 10.17** Consider three different experiments involving the reaction of nitrogen and hydrogen:

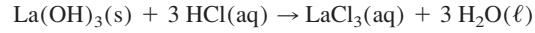


- (a) If 6.00 mol of H₂ reacts, how much N₂ reacts?

- (b) If 6.00 mol of H₂ is placed in a vessel with N₂, can you tell how much N₂ reacts?

- (c) If 3.00 mol of NH₃ is produced, can you tell how much H₂ reacts?

- 10.18** Consider the following reaction:



- (a) How many moles of LaCl₃ can be made with 9 mol of HCl?

- (b) How many moles of LaCl₃ can be made with 9 mol of HCl and 5 mol of La(OH)₃?

- (c) How many moles of LaCl₃ can be made with 9 mol of HCl and 2 mol of La(OH)₃?

Problems

10.1 Mole Calculations for Chemical Reactions

- 10.19** Calculate the number of moles of H₃PO₄ that will react with 1.29 mol of NaOH in aqueous solution to form Na₃PO₄.

- 10.20** Calculate the number of moles of H₃PO₄ that will react with 0.800 mol of Ba(OH)₂ to form solid Ba₃(PO₄)₂.

- 10.21** Calculate the number of moles of Ba(OH)₂ that will react with 0.600 mol of H₃PO₄ to form solid BaHPO₄.

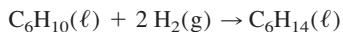
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- 10.22 Calculate the number of moles of $\text{Ba}(\text{OH})_2$ that will react with 0.600 mol of H_3PO_4 to form $\text{Ba}(\text{H}_2\text{PO}_4)_2$.

- 10.23 Which of the following samples of metal can produce the most hydrogen by reaction with HCl?

0.500 mol Zn 0.500 mol Al 0.500 mol Mg

- 10.24 How many moles of C_6H_{14} can be produced by the reaction of 4.86 mol of H_2 and sufficient C_6H_{10} ? The balanced equation is



- 10.25 How many moles of oxygen gas are required for the combustion of 7.04 mol of octane, C_8H_{18} , to yield CO_2 and water?

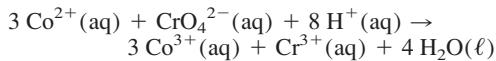
- 10.26 How many moles of oxygen gas are required for the incomplete combustion of 7.80 mol of octane, C_8H_{18} , yielding CO and H_2O ?

- 10.27 How many moles of oxygen gas are required for the complete combustion of 6.16 mol of butane, C_4H_{10} ?

- 10.28 How many moles of AlCl_3 are also produced along with 2.46 mol of H_2O from the reaction of $\text{Al}(\text{OH})_3$ and HCl?

- 10.29 How many moles of MgCl_2 are produced along with 0.750 mol of CO_2 from the reaction of $\text{Mg}(\text{HCO}_3)_2$ and HCl?

- 10.30 (a) Calculate the number of millimoles of CrO_4^{2-} that reacts with 7.00 mmol of Co^{2+} according to the following equation:



- (b) How many millimoles of water are produced?

- 10.31 Part of an 8.00-mmol sample of HgO was decomposed by heating, and 1.50 mmol of O_2 was produced.

- (a) Write the balanced equation for the reaction.
(b) Which of the numbers of millimoles given in the problem is governed by the balanced equation?
(c) Calculate the percentage of HgO that decomposed.

10.2 Mass Calculations for Chemical Reactions

- 10.32 Calculate the number of moles of H_2 that are produced by the reaction of aqueous HCl with 2.48 g of metallic

- (a) Zn.
(b) Cd.

- (c) Explain why the numbers of moles of H_2 produced in parts (a) and (b) differ greatly, even though the same number of grams of metal is used in each case.

- 10.33 (a) Butane, C_4H_{10} , burns in excess oxygen to produce carbon dioxide and water. Write a balanced equation for the reaction.

- (b) Calculate the number of moles of carbon dioxide in 14.9 g of carbon dioxide.

CHAPTER 10 ■ Stoichiometry

- (c) Calculate the number of moles of butane required to produce that number of moles of carbon dioxide.

- (d) Calculate the mass of butane in that number of moles.

- (e) Combine the calculations for parts (b)–(d) into one factor label solution.

- 10.34 (a) In an internal combustion engine, octane, C_8H_{18} , burns in limited oxygen supply to produce carbon monoxide and water. Write a balanced equation for the reaction.

- (b) Calculate the number of moles of carbon monoxide in 75.7 g of carbon monoxide.

- (c) Calculate the number of moles of octane required to produce that number of moles of carbon monoxide.

- (d) Calculate the mass of octane in that number of moles.

- (e) Combine the calculations for parts (b)–(d) into one factor label solution.

- 10.35 Calculate the mass of each of the following that is necessary to produce 4.00 mol of AgCl by reaction with $\text{AgC}_2\text{H}_3\text{O}_2$. (Compare with Problem 10.9.)

- (a) CoCl_3 (b) CaCl_2 (c) KCl

- 10.36 Calculate the mass of each of the following reagents that is necessary to produce 1.75 mol of AgCl by reaction with AgNO_3 .

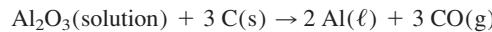
- (a) PtCl_2 (b) SrCl_2 (c) NiCl_2

- 10.37 Calculate the mass of product produced by each of the following combinations:

- (a) 15.0 g of sodium with excess bromine
(b) 25.0 g of magnesium with excess oxygen
(c) 35.0 g of aluminum with excess sulfur

- 10.38 Excess $\text{AgNO}_3(\text{aq})$ was added to a sample of $\text{FeCl}_3(\text{aq})$, and 12.1 g of $\text{AgCl}(\text{s})$ was produced. What mass of FeCl_3 was present initially?

- 10.39 Aluminum is produced commercially by high-temperature electrolysis of aluminum oxide dissolved in a nonaqueous melt. The electrodes are carbon.



Calculate the mass of Al_2O_3 used to produce 10.0 metric tons (10.0×10^6 g) of aluminum by this process.

- 10.40 *Caution:* The following reactions can proceed explosively! Calculate the number of moles of hydrogen that can be produced by reaction with water of (a) 0.600 g of lithium and (b) 0.600 g of barium. (c) Explain the difference.

- 10.41 Silver can be prepared from aqueous silver nitrate by reaction with zinc metal. Zinc nitrate is formed.

- (a) Write a balanced equation for the reaction.
(b) Calculate the number of moles of zinc in 12.10 g of zinc.

■ Problems

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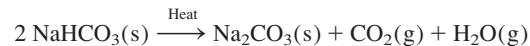
- (c) Calculate the number of moles of silver that can be produced from that number of moles of zinc.

- (d) Calculate the mass of that number of moles of silver.

- (e) Combine the calculations for parts (b)–(d) into a factor label solution to determine the mass of silver that can be produced using 12.10 g of zinc.

10.42 How many moles of KOH are required to completely neutralize 71.3 g of $\text{H}_2\text{C}_2\text{O}_4$?

10.43 Consider the following reaction:



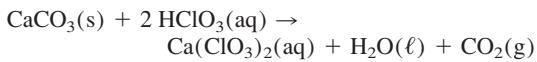
Heating 12.2 g of NaHCO_3 until no further reaction takes place can produce

- (a) what mass of Na_2CO_3 ?

- (b) what mass of solid product(s)?

- (c) What is the difference, if any, in parts (a) and (b)?

10.44 What mass of CaCO_3 can be “dissolved” by 82.3 g of HClO_3 ?

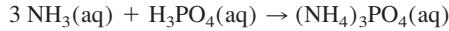


10.45 (a) Calculate the mass of NaCl that can be prepared with 7.11 g of Cl_2 and sufficient Na.

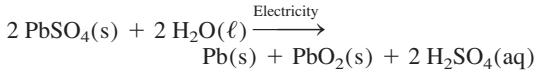
(b) Calculate the mass of NaCl that can be prepared with 7.11 g of HCl and sufficient NaOH.

(c) Which of parts (a) and (b) can be solved without any of the calculations presented in this chapter? Explain why the other part cannot be solved in the same manner.

10.46 The compound $(\text{NH}_4)_3\text{PO}_4$ is used as a fertilizer. Calculate the mass of $(\text{NH}_4)_3\text{PO}_4$ that can be produced by the reaction of 2.00 metric tons (2.00×10^6 g) of NH_3 with sufficient H_3PO_4 .

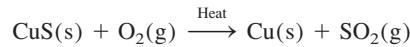


10.47 The recharge of a lead storage cell in an automobile battery can be represented by the following equation:

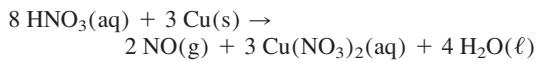


Calculate the mass of elemental lead produced when 49.7 g of lead(II) sulfate reacts.

10.48 Calculate the mass of gaseous SO_2 that will be produced along with 1.500 kg of copper from the roasting of copper(II) sulfide. (Hint: See Practice Problem 10.9 and Example 10.9, if necessary.)



10.49 Calculate the mass of NO that can be produced by the reaction of 14.0 g of Cu according to the following balanced equation:

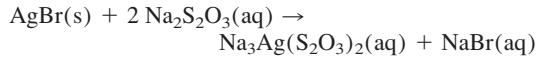


10.50 Excess $\text{Ba}(\text{NO}_3)_2(\text{aq})$ was added to a sample of $\text{NaHCO}_3(\text{aq})$, and 7.27 g of $\text{BaCO}_3(\text{s})$ was produced (along with CO_2 , H_2O , and NaNO_3). What mass of NaHCO_3 was present initially?

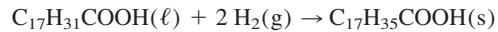
10.51 Sulfur dioxide in the atmosphere contributes to acid rain. One method of controlling sulfur dioxide emission is to absorb the sulfur dioxide into a solution of a base. Calculate the mass of SO_2 that can be absorbed by 125 kg of $\text{Ca}(\text{OH})_2$ to make CaSO_3 .

10.52 Calculate the mass of Cl_2 required to convert 115 g of AuCl to AuCl_3 .

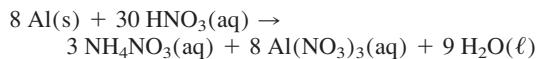
10.53 Silver bromide can be “dissolved” by the action of aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (called “hypo”) after any silver that has been “activated” by exposure to light is reduced to metallic silver by another reagent. This process is the basis for the development of black-and-white film. Calculate the mass of hypo necessary to dissolve 2.66 g of AgBr . The equation for the dissolving process is



10.54 How many grams of steric acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, a fatty acid, can be produced by the reaction of 1110 g of H_2 and sufficient $\text{C}_{17}\text{H}_{31}\text{COOH}$, a component of an oil? The balanced equation is

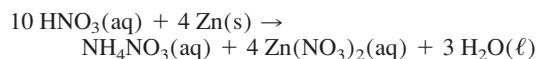


10.55 What mass of HNO_3 does it take to “dissolve” 14.4 g of aluminum?

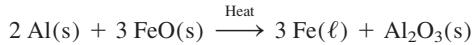


10.56 Calculate the mass of silver metal that can be produced by the action of 12.2 g of cadmium metal on excess aqueous silver nitrate.

10.57 Calculate the mass of zinc that must be used to produce 7.33 g of NH_4NO_3 according to the equation:



10.58 Powdered aluminum metal can be used to reduce iron(II) oxide to molten iron, usable for spot welding. Calculate the mass of iron that can be produced by the reaction of 775 g of aluminum.



10.59 What mass of P_4O_{10} results from the combustion of 45.7 g of P_4S_6 ? SO_2 is the other product.

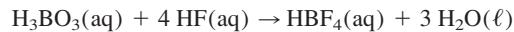
10.60 In the softening of temporary hard water—water containing magnesium hydrogen carbonate—the acid salt is converted to magnesium carbonate, carbon dioxide, and water by heating.



Calculate the mass of MgCO_3 that can be produced from 175 g of $\text{Mg}(\text{HCO}_3)_2$.

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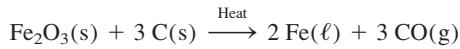
- 10.61 HBF₄ is a useful reagent, especially in organic chemistry. Calculate the mass of HF required to make 125 g of HBF₄ by the following reaction:



- 10.62 What mass of P₄O₁₀ can be prepared by combustion of 41.7 g of P₄O₆?

- 10.63 What mass of tin can be prepared by the reaction of 72.9 g of zinc and excess aqueous tin(II) nitrate?

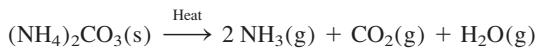
- 10.64 Iron ore is reduced to iron with coke (impure carbon). Calculate the mass of Fe that can be produced from Fe₂O₃ with 15.00 kg of carbon. The reaction may be represented as follows:



- 10.65 What mass of silver can be prepared by the reaction of 144 g of copper metal and excess aqueous silver nitrate?

- 10.66 Calculate the number of moles of oxygen gas required to convert SO₂ to 2.77 g of SO₃.

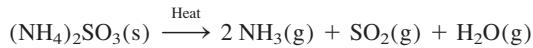
- 10.67 Calculate the mass of NH₃ that can be prepared by heating 122 g of solid (NH₄)₂CO₃. The balanced equation is



- 10.68 What mass of HClO₃ is required to completely neutralize 12.8 g of Ca(OH)₂(s).

- 10.69 What mass of P₄S₆ can be prepared by treatment of 6.19 g of sulfur with excess P₄?

- 10.70 Calculate the number of moles of NH₃ that can be prepared by heating 122 g of solid (NH₄)₂SO₃. The balanced equation is



- 10.71 (a) Calculate the number of moles of H₂ that can be produced by the reaction of aqueous HCl with 2.48 g of metallic indium, In, forming InCl₃.

- (b) Compare the value with the result of Problem 10.32(b), and explain the difference.

- 10.72 What are the differences among the following problems?

- (a) Calculate the total mass of the acids produced by the reaction of excess water with 20.83 g of phosphorus pentachloride.

- (b) Calculate the total mass of the acids produced by the reaction of excess H₂O with 20.83 g of PCl₅.

- (c) Calculate the total mass of the HCl and H₃PO₄ produced by the reaction of excess H₂O with 20.83 g of PCl₅.

- (d) PCl₅ + 4 H₂O → 5 HCl + H₃PO₄

Calculate the total mass of the acids produced by the reaction of excess water with 20.83 g of phosphorus pentachloride.

- (e) PCl₅ + 4 H₂O → 5 HCl + H₃PO₄

CHAPTER 10 ■ Stoichiometry

Calculate the total mass of the acids produced by the reaction of excess water with 20.83 g of phosphorus pentachloride (MM = 208.3 g/mol).

- (f) Calculate the mass of water that reacts with 20.83 g of phosphorus pentachloride. Use this value to calculate the total mass of the acids produced.

10.3 Calculations Involving Other Quantities

- 10.73 (a) How many moles of chlorine atoms does 2.35×10^{23} chlorine atoms represent?

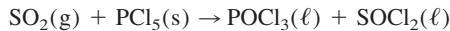
- (b) How many moles of PCl₃ contain that number of chlorine atoms?

- (c) How many moles of PCl₅ can be prepared by treatment of that much PCl₃ with Cl₂?

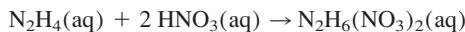
- (d) What mass of PCl₅ is that?

- 10.74 Calculate the number of moles of fluorine atoms in 61.7 mL of CHClF₂ (density = 1.49 g/mL).

- 10.75 What mass of SOCl₂ can be prepared by heating SO₂ gas with the quantity of PCl₅ that contains 3.01×10^{23} Cl atoms? The balanced equation for the reaction is

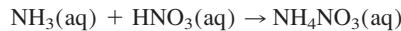


- 10.76 How many nitrogen atoms are contained in the N₂H₆(NO₃)₂ prepared by treatment of 4.14 g of aqueous hydrazine, N₂H₄, with excess dilute nitric acid?



- 10.77 What mass of diphosphorus trisulfide can be prepared by heating sulfur with the quantity of phosphorus that contains 1.50×10^{23} P atoms?

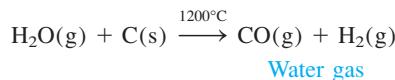
- 10.78 What mass of nitrogen is contained in the ammonium nitrate prepared by treatment of 6.69 g of aqueous ammonia with excess dilute nitric acid?



- 10.79 Calculate the number of oxygen atoms in the chromium(III) oxide prepared by treating chromium(II) oxide with 1.72 g of oxygen gas.

- 10.80 Calculate the number of moles of hydrogen atoms in 45.3 mL of pure H₂O₂ (density = 1.44 g/mL).

- 10.81 A solid combustible material can sometimes be changed into a more useful fuel if it is converted to a gas before burning. The following reaction, known as the water gas reaction, can be used to provide gaseous fuels:



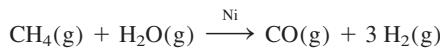
- (a) Calculate the number of moles of water required to convert 1.00×10^{26} carbon atoms to carbon monoxide and hydrogen.

- (b) What are the products of the complete combustion of water gas?

■ Problems

- 10.82** Calculate the number of fluorine atoms in the sulfur hexafluoride prepared by treating sulfur difluoride with 6.11 g of fluorine gas.

- 10.83** The hydrogen used for about 90% of the industrial synthesis of ammonia comes from the following reaction at high temperature:



Calculate the number of molecules of CH_4 required to produce 1.25 metric tons (1.25×10^6 g) of H_2 .

10.4 Problems Involving Limiting Quantities

- 10.84** The director of a summer baseball camp has five home plates and 12 bases. One home plate and three bases are needed for each baseball field.

- (a) How many baseball fields can the director equip?
 (b) How many extra pieces of equipment will there be?

- 10.85** (a) Calculate the number of moles of MgCl_2 that will react with 5.00 mol of AgNO_3 .

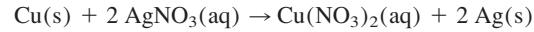
- (b) Calculate the number of moles of MgCl_2 that will react if 2.00 mol of MgCl_2 is treated with 5.00 mol of AgNO_3 .

- (c) Calculate the number of moles of MgCl_2 that will react if 4.00 mol of MgCl_2 is treated with 5.00 mol of AgNO_3 .

- 10.86** Calculate the number of moles of AgCl that is produced in each part of Problem 10.85.

- 10.87** Calculate the mass of hydrogen produced when 12.7 g of zinc is treated with 22.7 g of hydrobromic acid.

- 10.88** For the reaction



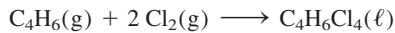
calculate the number of moles of products as well as the number of moles of excess reagent after 0.272 mol of Cu and 0.576 mol of AgNO_3 are combined.

- 10.89** Calculate the number of moles of H_2O produced and the number of moles of excess reactant when 0.444 mol of $\text{Mg}(\text{OH})_2$ is treated with 6.66×10^{23} molecules of HNO_3 .

- 10.90** Calculate the number of moles of unreacted starting material that will be present when 15.50 g of HNO_3 (in aqueous solution) is treated with 5.05 g of solid CaCO_3 .

- 10.91** Calculate the number of moles of each solute in the final solution after 1.75 mol of aqueous BaCl_2 and 2.70 mol of aqueous AgNO_3 are mixed.

- 10.92** Consider the following equation:



- (a) Calculate the mass of $\text{C}_4\text{H}_6\text{Cl}_4$ that can be prepared from 35.0 g of C_4H_6 and 105.0 g of Cl_2 .

- (b) Explain why this problem cannot be solved by applying the law of conservation of mass.

- 10.93** Calculate the number of moles of unreacted starting material that will be present when 41.2 g of HCl is treated with 25.0 g of solid $\text{Mg}(\text{HCO}_3)_2$.

- 10.94** Calculate the mass of solid Cu produced when 4.33×10^6 g of Cu_2S is treated with 2.00×10^6 g of O_2 . SO_2 is the other product.

- 10.95** Calculate the mass of unreacted starting material when 17.3 g of H_2SO_4 is treated with 42.7 g of NaOH.

- 10.96** Calculate the mass of solid Ag_2SO_4 produced when 5.79 g of Na_2SO_4 is treated with 3.48 g of AgNO_3 .

- 10.97** Calculate the number of moles of H_2O produced by the reaction of 6.02 g of HClO_3 and 4.95×10^{22} formula units of NaOH.

- 10.98** Calculate the mass of unreacted starting material when 91.1 g of H_3PO_4 is treated with 145 g of NaOH.

- 10.99** Calculate the number of moles of H_2O that will be produced by the reaction of 40.7 mol of HClO_3 and 1.25 kg of $\text{Ca}(\text{OH})_2$.

- 10.100** How many molecules of NO can be produced by the reaction of 65.00 g of NH_3 with 150.0 g of O_2 according to the following balanced equation?



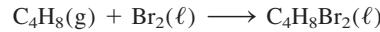
10.5 Theoretical Yield and Percent Yield

- 10.101** Calculate (a) the theoretical yield and (b) the percent yield, if 0.151 mol of liquid SO_2Cl_2 is obtained from the reaction of 0.160 mol of gaseous SO_2 and excess gaseous Cl_2 .

- 10.102** Calculate (a) the theoretical yield and (b) the percent yield, if 12.4 g of liquid SO_2Cl_2 is obtained from the reaction of 6.11 g of gaseous SO_2 and excess gaseous Cl_2 .

- 10.103** Calculate the percent yield for an experiment in which 29.8 g of PCl_5 was obtained by treatment of 4.50 g of P with sufficient Cl_2 .

- 10.104** Calculate the percent yield of a reaction which produced 36.0 g of $\text{C}_4\text{H}_8\text{Br}_2$ from 10.0 g of C_4H_8 and excess Br_2 .



- 10.105** Calculate the percent yield for an experiment in which 46.9 g of SO_3 was obtained by treatment of 51.2 g of SO_2 with 25.0 g of O_2 .

10.6 Calculations with Net Ionic Equations

- 10.106** (a) Calculate the number of moles of Na^+ present in 0.750 mol of NaOH.

- (b) How many moles of NaCl will be produced by the reaction of that quantity of NaOH with 0.600 mol of HCl?

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- (c) How many moles of NaOH will be present after the reaction?
- (d) How many moles of Na^+ will be present in the final solution?
- (e) Does your answer to part (d) confirm that Na^+ is a spectator ion?
- 10.107 How many moles of carbonate ion can be converted to carbon dioxide and water with 4.42 mol H^+ ?
- 10.108 Calculate the mass of solid Ag_2S that can be produced by the reaction of 0.300 mol of S^{2-} with excess Ag^+ .
- 10.109 How many moles of sulfite ion can be converted to sulfur dioxide and water with 0.650 mol H^+ ?
- 10.110 Calculate the number of moles of each ion in the final solution after 1.75 mol of aqueous BaCl_2 and 2.70 mol of aqueous AgNO_3 are mixed.

CHAPTER 10 ■ Stoichiometry

- 10.111 Calculate the number of moles of SO_2 that will be produced by the reaction of 1.00 mol of SO_3^{2-} with 2.76 mol of H^+ .
- 10.112 Calculate the number of moles of CO_2 that will be produced by the reaction of 2.20 mol of HCO_3^- with 1.80 mol of H^+ .
- 10.113 Calculate the mass of CO_2 that will be produced by the reaction of 0.550 mol of CO_3^{2-} with 1.25 mol of H^+ .
- 10.114 Calculate the mass of BaSO_4 that can be produced by the reaction of 0.234 mol of SO_4^{2-} with 0.125 mol of Ba^{2+} .
- 10.115 Calculate the mass of PbI_2 that can be produced by the reaction of 0.105 mol of Pb^{2+} with 0.400 mol of I^- .

General Problems

- 10.116 List the steps necessary to do each of the following stoichiometry problems:
- Calculate the number of moles of aluminum metal required to prepare 6.11 mol of solid Al_2O_3 .
 - Calculate the number of grams of $\text{Ca}(\text{OH})_2(s)$ required to prepare 0.885 mol of $\text{Ca}(\text{ClO}_4)_2(aq)$ by reaction with $\text{HClO}_4(aq)$.
 - Calculate the number of grams of $\text{CO}_2(g)$ that can be prepared from 6.16 g of $\text{CO}(g)$ and 3.60 g of $\text{O}_2(g)$.
- 10.117 Calculate the number of moles of each substance except water in solution after 3.11 mol of $\text{NaOH}(aq)$ is added to 3.82 mol of $\text{HC}_2\text{H}_3\text{O}_2(aq)$. Why was water excluded?
- 10.118 In each case, calculate the mass of the product other than water:
- 75.0 g of sulfuric acid is treated with sufficient aqueous potassium hydroxide so that the acid is completely neutralized
 - 75.0 g of aqueous sodium hydroxide is treated with excess chloric acid
 - 75.0 g of solid magnesium oxide is treated with excess hydrochloric acid
 - 75.0 g of gaseous dinitrogen trioxide is treated with excess aqueous sodium hydroxide
- 10.119 Rewrite Problem 10.33 as a single-step problem.
- 10.120 (a) Write three stepwise equations for the reaction of NaOH and H_3PO_4 , using only 1 mol of NaOH in each step. (b) If we add 1.50 mol of NaOH to 1.00 mol of NaH_2PO_4 , how many moles of Na_2HPO_4 and Na_3PO_4 will be present at the end of all reaction?

- 10.121 How many moles of H_2 can be prepared using 0.500 mol of silver and excess H_3PO_4 ?
- 10.122 What mass of barium carbonate can be produced by treatment in aqueous solution of 31.2 g of sodium hydrogen carbonate with 30.0 g of barium nitrate? (CO_2 is also produced.)
- 10.123 Heating of solid sodium hydrogen carbonate is one step in the industrial process for production of washing soda—sodium carbonate. Carbon dioxide and water are also produced. Calculate the mass of solid produced when a 2.11-kg sample of sodium hydrogen carbonate is heated.
- 10.124 (a) After 2.06 g of solid KClO_3 is heated for a brief time, 1.18 g of KCl has been produced. What mass of O_2 has been produced?
(b) What mass of KClO_3 remained undecomposed?
- 10.125 (a) A 1.221-g sample of a mixture of $\text{KClO}_3(s)$ and $\text{MnO}_2(s)$ was heated for a brief time, after which 0.998 g of solid remained. Write the balanced equation for the reaction, indicating which of the substances is the catalyst and including the states of all reactants and products.
(b) How many grams of oxygen were produced?
(c) How many grams of KClO_3 decomposed?
(d) How many grams of KCl were produced?
(e) What is the minimum mass of KClO_3 that was present originally?
- 10.126 After 0.0800 mol of solid KClO_3 has been heated for a period of time, 0.0188 mol remains. Calculate the mass of each product.

■ General Problems

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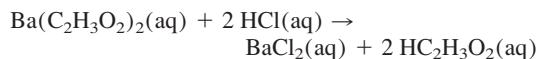
10.127 What mass of nitrogen is contained in the ammonium nitrate that can be prepared by treatment of 20.2 g of aqueous ammonia with 41.6 g of nitric acid?

10.128 A 60.0-mmol sample of solid KClO_3 was partially decomposed by heating, and 75.0 mmol of O_2 was produced. Calculate the percentage of KClO_3 that decomposed.

10.129 A 2.172-g sample of a mixture of $\text{KClO}_3(s)$ and $\text{MnO}_2(s)$ was heated for a brief time, after which 1.951 g of solid remained. How many grams of KCl is present in the final mixture?

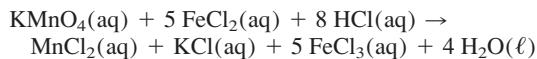
10.130 What mass of barium sulfate can be produced by treatment in aqueous solution of 11.6 g of ammonium sulfate with 25.5 g of barium fluoride?

10.131 Calculate the number of moles of each substance in solution after 0.150 mol of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2(aq)$ is added to 0.500 mol of $\text{HCl}(aq)$. The balanced equation is



10.132 For a store's going-out-of-business sale, a set consisting of a card table and four chairs is advertised at \$233. The store has 31 tables and 98 chairs. An outlet manager arrives with \$5000. What is the maximum number of sets the outlet manager can buy?

10.133 Determine the number of moles of MnCl_2 that can be prepared by the reaction of 0.300 mol KMnO_4 , 1.08 mol of FeCl_2 , and 3.10 mol of HCl , according to the following balanced equation:



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Molarity

- 11.1 Definition and Uses of Molarity
- 11.2 Molarities of Ions
- 11.3 Titration



Titration

Review Clues

- Section 11.1** Sections 1.1, 2.2, 7.3
Section 11.2 Sections 5.1, 5.5, 9.2, 10.3
Section 11.3 Sections 7.3, 10.6

Objectives

- 11.1** To define molarity—the most often used chemical measure of concentration—and to use molarity to solve problems
11.2 To extend the concept of molarity to the individual ions in solutions of ionic substances
11.3 To determine the concentration, or the number of moles present, of a substance by an experimental technique called titration

11.1 ■ Definition and Uses of Molarity**291**

Solutions were introduced in Chapter 1, and quantities of substances in moles were presented in Section 7.3. We can easily measure the quantity of a solute in solution by measuring the volume of a solution if we can determine the concentration of the solute. In this chapter, we will limit our discussions to aqueous solutions.

Molarity, the most common measure of concentration used by chemists, is introduced in Section 11.1 and used to solve problems involving numbers of moles and volumes. The concentrations of individual ions in aqueous solutions of ionic substances are discussed in Section 11.2. The technique of titration, used to determine experimentally the unknown concentrations of solutions or unknown numbers of moles of a substance, is presented in Section 11.3.

11.1 Definition and Uses of Molarity

A **solute** is the substance dissolved in a **solvent**, the substance doing the dissolving. Most often, the solvent is the component present in greatest quantity, and the solutes are present in lower quantities. However, when water is a component, it is often regarded as the solvent, even if more of another component is present. For example, in an alcohol-water solution, the alcohol is regarded as the solute, and the water the solvent no matter how much of each is present.

Everyone is familiar with the concept of concentration. **Concentration** is quantity of solute in a given quantity of solvent or solution. For example, if a person usually drinks coffee with 2 teaspoons (tsp) of sugar per cup, how much sugar would he use in half a cup of coffee to get the usual sweetness? The sweetness depends on the concentration—the amount of sugar *per given volume of solution*. He would use 1 tsp of sugar (half of the normal amount) in half a cup of coffee (half of the normal amount).

EXAMPLE 11.1

If someone absentmindedly stirs more sugar than he likes into a cup of coffee, how can he make it less sweet?

Solution

Taking some sugar out of the solution is difficult, once the sugar has dissolved. The easy way to make the drink less sweet is to add more liquid. Increasing the volume makes less sugar *per unit volume*, so the coffee tastes less sweet.

EXAMPLE 11.2

Two cubes of sugar are dissolved in some water and then more water is added to fill a cup. A second cup has one lump of sugar dissolved in enough water to half fill the cup.

- Which cup, if either, contains more sugar?
- Which cup, if either, contains the sweeter-tasting solution?
- What is the difference between *quantity* and *concentration*?

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CHAPTER 11 ■ Molarity

Solution

- (a) The first cup contains more sugar—two lumps is more than one.
- (b) The contents of both cups taste equally sweet—both solutions have the same concentration.
- (c) Concentration is a quantity of solute in a given volume of solution.

Basic Problems

Molarity is defined as the *number of moles of solute per liter of solution*:

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

This definition is often shortened to “moles per liter,” but condensing it in this way does not change the fact that it is really the number of moles of *solute* per liter of *solution*. The unit of molarity is **molar**, symbolized M. An italic capital *M* is sometimes used as a symbol for molarity; note that a nonitalic capital M means molar.

EXAMPLE 11.3

Calculate the molarity of a solution containing 7.50 mol of CH₂O in enough water to make 1.50 L of solution.

Solution

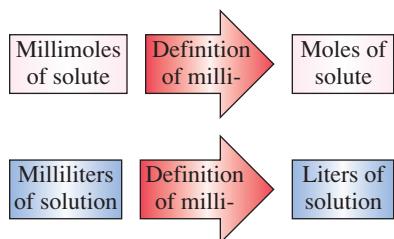
$$\text{Molarity} = \frac{7.50 \text{ mol}}{1.50 \text{ L}} = \frac{5.00 \text{ mol}}{1 \text{ L}} = 5.00 \text{ M}$$

There are at least three different ways of stating this concentration:

- It is a 5.00 molar (5.00 M) solution.
- The CH₂O is 5.00 M.
- The concentration is 5.00 M.

Practice Problem 11.3 A solution is prepared using 3.55 L of water and 2.10 mol of a certain solute. The total volume is 3.75 L, and there is 19.7 mol of water. What is the molarity of the solute?

$$M = \frac{\text{no. of moles of solute}}{\text{liter of solution}} \\ = \frac{\text{no. of millimoles of solute}}{\text{mL of solution}}$$



Molarity can also be defined as the number of *millimoles* (mmol) of solute per *milliliter* of solution.

EXAMPLE 11.4

Calculate the molarity of 60.0 mL of solution containing 1.25 mmol of solute.

Solution

$$\frac{1.25 \text{ mmol} \left(\frac{1 \text{ mol}}{1000 \text{ mmol}} \right)}{60.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)} = \frac{1.25 \text{ mol}}{60.0 \text{ L}} = 0.0208 \text{ M}$$

11.1 ■ Definition and Uses of Molarity**293**

Note that the number of millimoles per milliliter is equal to the number of moles per liter, and thus millimoles per milliliter is another way to define molarity. This equivalent definition makes many problems easier because quantities used in chemical laboratories are often measured in millimoles and milliliters.

Practice Problem 11.4 Calculate the molarity of a solution containing 4.50 mmol of NaCl in 3.80 mL of solution.

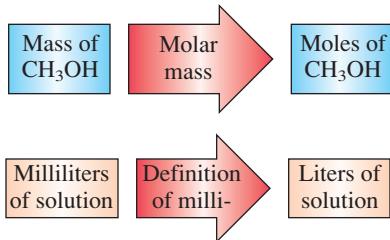
If quantities of solute and solution are given in units other than moles and liters or millimoles and milliliters, respectively, they can be changed to one of these sets of units to calculate the molarity.

EXAMPLE 11.5

Calculate the molarity of 50.0 mL of solution containing 7.50 g of CH₃OH.

Solution

Because molarity is defined in terms of moles of solute and liters of solution, the given quantities can be converted to moles and liters, respectively:



$$7.50 \text{ g CH}_3\text{OH} \left(\frac{1 \text{ mol CH}_3\text{OH}}{32.0 \text{ g CH}_3\text{OH}} \right) = 0.2344 \text{ mol CH}_3\text{OH}$$

$$50.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.0500 \text{ L}$$

$$M = \frac{0.2344 \text{ mol CH}_3\text{OH}}{0.0500 \text{ L}} = 4.69 \text{ M CH}_3\text{OH}$$

Alternatively, the number of moles can be changed to millimoles.

$$0.2344 \text{ mol} \left(\frac{1 \text{ mmol}}{0.001 \text{ mol}} \right) = 234.4 \text{ mmol}$$

$$M = \frac{234.4 \text{ mmol CH}_3\text{OH}}{50.0 \text{ mL}} = 4.69 \text{ M CH}_3\text{OH}$$

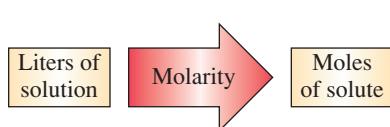
Practice Problem 11.5 Calculate the molarity of 11.6 mL of solution containing 0.750 g of CaCl₂.

Because molarity is a ratio, like speed and density, it can be used as a conversion factor. Wherever it appears, the symbol M can be replaced by the ratio moles per liter (mol/L) or millimoles per milliliter (mmol/mL). For example, a concentration of 3.11 M can be used as any of the following factors:

$$\frac{3.11 \text{ mol}}{1 \text{ L}} \quad \frac{1 \text{ L}}{3.11 \text{ mol}} \quad \frac{3.11 \text{ mmol}}{1 \text{ mL}} \quad \frac{1 \text{ mL}}{3.11 \text{ mmol}}$$

In this way we can calculate the number of moles of solute present in 3.00 L of 1.50 M solution:

$$3.00 \text{ L} \left(\frac{1.50 \text{ mol}}{1 \text{ L}} \right) = 4.50 \text{ mol}$$



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In this solution, the total quantity of solute is easy to visualize, as shown in Figure 11.1.

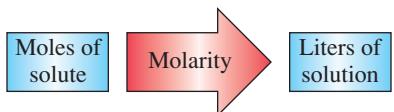
EXAMPLE 11.6

Calculate the number of liters necessary to contain 0.853 mol of 0.415 M solute.

Solution

$$0.853 \text{ mol} \left(\frac{1 \text{ L}}{0.415 \text{ mol}} \right) = 2.06 \text{ L}$$

Practice Problem 11.6 Calculate the number of millimoles of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, in 29.21 mL of 6.013 M solution.



Dilution Problems

We can calculate the concentration of a solution that has been prepared by diluting a more concentrated solution by using the basic definition of molarity. For example, what concentration results when 0.750 L of 1.60 M NaCl is diluted with water to make 3.00 L of solution? When the solution is diluted with water, the *concentration* of NaCl is reduced, but the *quantity* of NaCl remains the same. (See Example 11.2.) We first calculate the original number of moles of NaCl and use that to calculate the final concentration:

$$0.750 \text{ L} \left(\frac{1.60 \text{ mol}}{1 \text{ L}} \right) = 1.20 \text{ mol}$$

Because only water—and no more solute—is added, there is 1.20 mol of solute in the final solution. Thus, the concentration of the final solution is

$$M = \frac{1.20 \text{ mol}}{3.00 \text{ L}} = 0.400 \text{ M}$$

It is easy to understand that when the volume is quadrupled, the concentration is divided by four, from 1.60 M to 0.400 M.

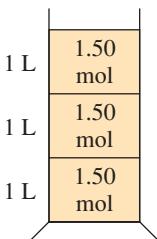


Figure 11.1 Moles and Concentration of Solute in a Solution

It is easy to see that 3.00 L of 1.50 M solution contains 4.50 mol of solute.

EXAMPLE 11.7

Calculate the final concentration of NaCl after 1.25 L of 0.500 M NaCl is diluted (a) to 2.50 L with water and (b) with 2.50 L of water.

Solution

The fraction of a mole of NaCl in the original solution is

$$1.25 \text{ L} \left(\frac{0.500 \text{ mol}}{1 \text{ L}} \right) = 0.625 \text{ mol}$$

The number of moles of NaCl is not changed by the addition of water.

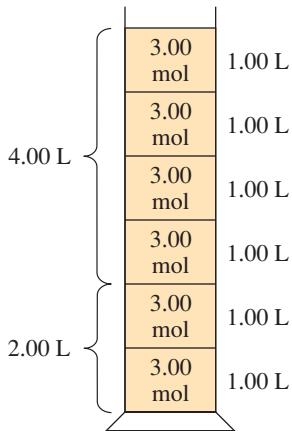
11.1 ■ Definition and Uses of Molarity**295**

Figure 11.2 Combination of Two Solutions of Equal Concentration

- (a) In this case, the final volume is 2.50 L, so the final concentration is

$$M = \frac{0.625 \text{ mol}}{2.50 \text{ L}} = 0.250 \text{ M}$$

- (b) In this case, the final volume is almost exactly $1.25 \text{ L} + 2.50 \text{ L} = 3.75 \text{ L}$, so the final concentration is

$$M = \frac{0.625 \text{ mol}}{3.75 \text{ L}} = 0.167 \text{ M}$$

Practice Problem 11.7 A nurse must prepare 4.00 L of 0.250 M saline solution (NaCl). What volume of 6.00 M stock solution should the nurse dilute?

Combining two solutions is only a little more complicated.

EXAMPLE 11.8

Calculate the final concentration of a solution prepared by adding 2.00 L of 3.00 M sugar solution to 4.00 L of 3.00 M sugar solution.

Solution

Because the concentration of each solution is the same, the concentration of the combined solution is also 3.00 M (Figure 11.2). (The solutions would taste as sweet before and after mixing.)

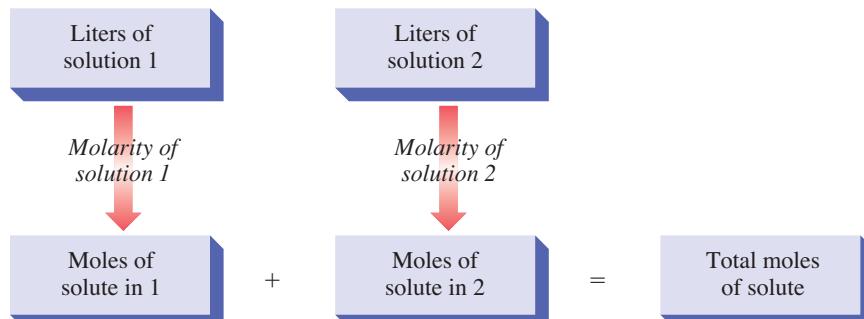
Practice Problem 11.8 Show by calculation of the total number of moles of sugar in the combined solution of Example 11.8 that the concentration is still 3.00 M.

EXAMPLE 11.9

Calculate the final concentration after 1.25 L of 2.25 M NaCl is added to 3.50 L of 2.45 M NaCl and the resulting solution is diluted to 5.00 L.

Solution

The molarity of the final solution is equal to the total number of moles of solute divided by the final volume. Solute is contained in each solution, but not in the



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CHAPTER 11 ■ Molarity

water used to dilute to 5.00 L. The number of moles of NaCl in the final solution is the sum of the numbers of moles in the two initial solutions:

$$1.25 \text{ L} \left(\frac{2.25 \text{ mol}}{1 \text{ L}} \right) = 2.813 \text{ mol} \quad 3.50 \text{ L} \left(\frac{2.45 \text{ mol}}{1 \text{ L}} \right) = 8.575 \text{ mol}$$

The total number of moles of NaCl is $2.813 \text{ mol} + 8.575 \text{ mol} = 11.388 \text{ mol}$. The final volume is 5.00 L, and the final concentration is

$$\frac{11.388 \text{ mol}}{5.00 \text{ L}} = 2.28 \text{ M}$$

Practice Problem 11.9 Calculate the final concentration after 87.3 mL of 1.71 M sugar solution is combined with 71.7 mL of 3.11 M sugar solution and the resulting solution is diluted to 275 mL.

Numbers of Moles in Chemical Reactions

Molarities and volumes may be used to calculate the numbers of moles involved in chemical reactions (Chapter 10). The conversions used are shown in Figure 11.3, where they have been added to those of Figure 10.2.

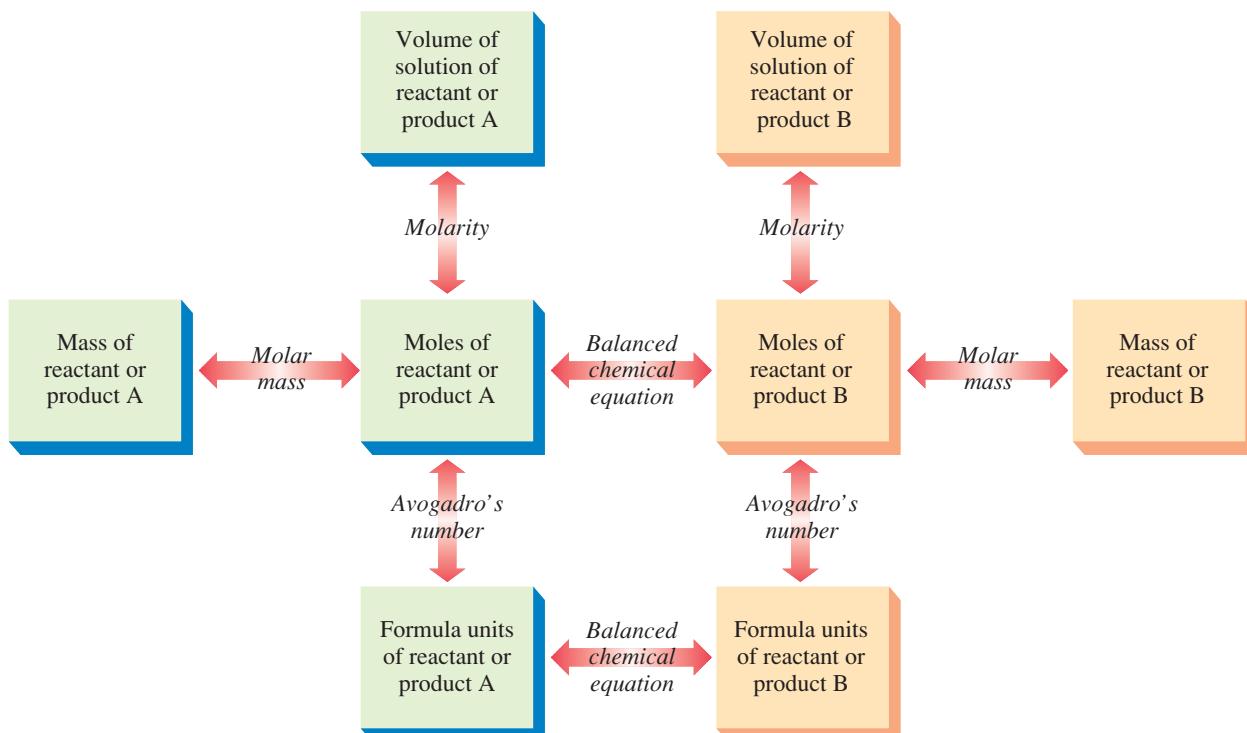


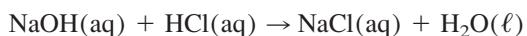
Figure 11.3 Conversions Including Those Involving Molarity

11.1 ■ Definition and Uses of Molarity**297****EXAMPLE 11.10**

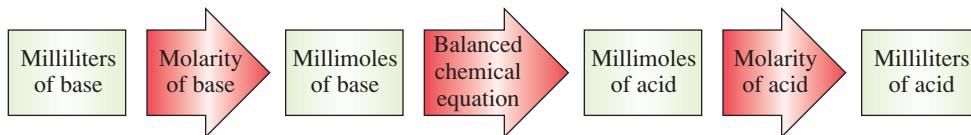
What volume of 1.50 M HCl is required to react with 34.6 mL of 2.44 M NaOH?

Solution

The reaction is



Molarity can be expressed as millimoles per milliliter.



The number of millimoles of base is

$$34.6 \text{ mL} \left(\frac{2.44 \text{ mmol NaOH}}{1 \text{ mL NaOH}} \right) = 84.42 \text{ mmol NaOH}$$

That number of millimoles of base is equal to the number of millimoles of acid, according to the balanced equation given previously. The volume of acid required is therefore

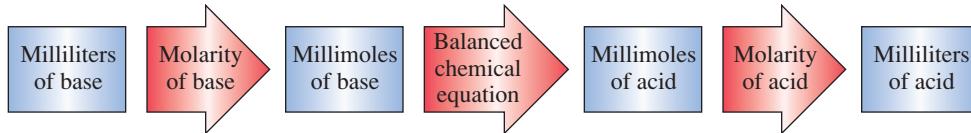
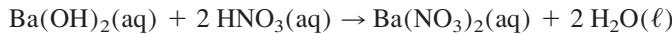
$$84.42 \text{ mmol HCl} \left(\frac{1 \text{ mL HCl}}{1.50 \text{ mmol HCl}} \right) = 56.3 \text{ mL HCl}$$

EXAMPLE 11.11

What volume of 0.5000 M HNO₃ is required to react with 41.77 mL of 0.1603 M Ba(OH)₂?

Solution

The equation is



$$41.77 \text{ mL Ba(OH)}_2 \left(\frac{0.1603 \text{ mmol Ba(OH)}_2}{1 \text{ mL}} \right) = 6.6957 \text{ mmol Ba(OH)}_2 \text{ present}$$

$$6.6957 \text{ mmol Ba(OH)}_2 \left(\frac{2 \text{ mmol HNO}_3}{1 \text{ mmol Ba(OH)}_2} \right) = 13.39 \text{ mmol HNO}_3 \text{ required}$$

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The volume of 0.5000 M HNO₃ required is therefore

$$13.391 \text{ mmol HNO}_3 \left(\frac{1 \text{ mL HNO}_3}{0.5000 \text{ mmol HNO}_3} \right) = 26.78 \text{ mL HNO}_3$$

Practice Problem 11.11 What volume of 0.1212 M Ba(OH)₂ is required to react with 41.74 mL of 0.2500 M HNO₃?

EXAMPLE 11.12

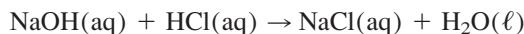
Calculate the number of moles of NaCl produced by reaction of 0.0452 L of 4.20 M HCl and 0.120 L of 2.17 M NaOH.

Solution

Because the quantities of two reactants are given, this problem involves a limiting quantity.

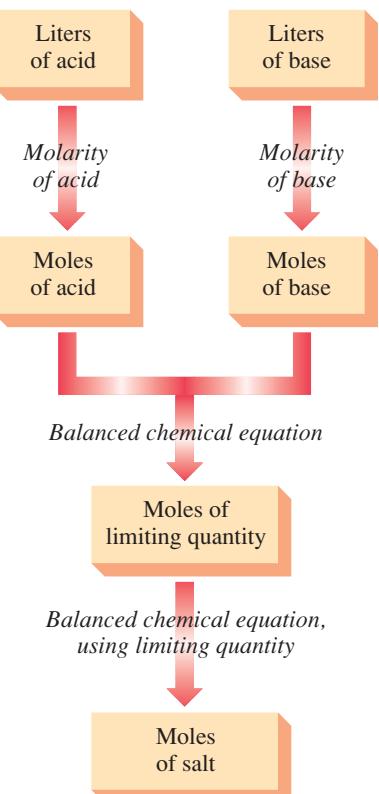
$$0.0452 \text{ L HCl} \left(\frac{4.20 \text{ mol HCl}}{1 \text{ L HCl}} \right) = 0.1898 \text{ mol HCl}$$

$$0.120 \text{ L NaOH} \left(\frac{2.17 \text{ mol NaOH}}{1 \text{ L NaOH}} \right) = 0.2604 \text{ mol NaOH}$$



Because the reactants react in a 1:1 mole ratio, NaOH is in excess, HCl is in limiting quantity, and 0.190 mol of NaCl will be produced.

Practice Problem 11.12 Calculate the number of milligrams of NaCl that can be produced by the reaction of 22.4 mL of 2.00 M HCl and 1.74 g of NaOH.



The maximum molarity possible in an aqueous solution of an ionic compound is about 40 M (with LiClO₃ as the solute). Pure water itself contains 55.6 mol/L. Sometimes, knowing the maximum molarity is important for determining whether a calculated answer is reasonable, or for other purposes.

EXAMPLE 11.13

Two ionic solutes, called A and B, are dissolved in the same solvent. The ratio of the molarity of A to the molarity of B is 10⁵. What can be deduced from this fact?

Solution

Chemists customarily represent the concentration of a substance by enclosing its formula or symbol in square brackets. For example, [A] represents the molarity of A. Then

$$\frac{[A]}{[B]} = 1 \times 10^5$$

11.2 ■ Molarities of Ions**299**

The concentration of B in its solution must be very low because the concentration of A cannot be much greater than 10^1 , at most.

Practice Problem 11.13 The ratio of molarities of A to B is 10^{-5} . What can be deduced from this fact?

**Snapshot Review**

ChemSkill Builder 6.1

- Molarity, the number of moles of solute per liter of solution, can be used as a factor to find the volume of a solution from the number of moles of solute or vice versa.
 - Molarity may also be defined as the number of millimoles per milliliter of solution (but not the number of moles per milliliter of solution or the number of millimoles per liter of solution).
 - If two or more substances are dissolved in the same solution, they may react or not. The numbers of moles of each solute in the final solution will be different in these two cases.
- A. Calculate the concentration of a solution containing
 - (a) 0.125 mol of solute in 0.375 L of solution.
 - (b) 125 mmol of solute in 375 mL of solution.
 - (c) 0.125 mol of solute in 375 mL of solution.
 - B. Calculate the number of millimoles of solute in 15.0 mL of 2.00 M solute.
 - C. Calculate the concentration of a solution prepared by adding 75.0 mmol of CH_3OH in 25.0 mL of aqueous solution to 45.0 mmol of CH_3OH in 25.0 mL and diluting to 200.0 mL.

11.2 Molarities of Ions

As shown in Section 11.1, the molarities of ionic compounds can be calculated just as the molarities of covalent compounds are. The molarity of an ionic compound is the number of moles of the *compound* per liter of solution. However, as discussed in Chapter 9, it is often useful to describe ionic compounds in solution as the separate ions. The molarity of any ion is simply the number of moles of *that ion* per liter of solution.

EXAMPLE 11.14

- (a) Calculate the molarity of AlCl_3 if 0.220 mol of that compound is dissolved in enough water to make 0.500 L of solution.
- (b) Calculate the concentration of each type of ion in that solution.

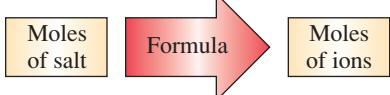
Solution

(a)

$$\frac{0.220 \text{ mol } \text{AlCl}_3}{0.500 \text{ L}} = 0.440 \text{ M AlCl}_3$$

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- (b) The AlCl_3 is composed of Al^{3+} ions and Cl^- ions. The formula indicates that there are three times as many Cl^- ions as Al^{3+} ions. Thus,



$$0.220 \text{ mol AlCl}_3 \left(\frac{1 \text{ mol Al}^{3+}}{1 \text{ mol AlCl}_3} \right) = 0.220 \text{ mol Al}^{3+}$$

$$0.220 \text{ mol AlCl}_3 \left(\frac{3 \text{ mol Cl}^-}{1 \text{ mol AlCl}_3} \right) = 0.660 \text{ mol Cl}^-$$

The concentrations of the ions are

$$\frac{0.220 \text{ mol Al}^{3+}}{0.500 \text{ L}} = 0.440 \text{ M Al}^{3+}$$

$$\frac{0.660 \text{ mol Cl}^-}{0.500 \text{ L}} = 1.32 \text{ M Cl}^-$$

Practice Problem 11.14

- (a) Calculate the molarity of $\text{Al}_2(\text{SO}_4)_3$ if 0.150 mol of that compound is dissolved in enough water to make 2.70 L of solution.
(b) Calculate the concentration of each ion in that solution.

When two different compounds containing an ion in common are placed in the same solution, if no reaction occurs, the numbers of moles of the common ion are added.

EXAMPLE 11.15

Calculate the concentration of each ion in a solution made by adding 41.4 mL of 1.03 M NaCl to 66.2 mL of 0.818 M CaCl_2 and diluting to 150.0 mL.

Solution

When these two solutions are combined, no chemical reaction takes place, but the final chloride ion concentration includes the chloride ions provided by both salts. The cation concentrations are not added because the cations are different.

The number of moles of each ion is calculated as follows:

$$41.4 \text{ mL NaCl} \left(\frac{1.03 \text{ mmol NaCl}}{1 \text{ mL NaCl}} \right) = 42.64 \text{ mmol NaCl}$$

$$66.2 \text{ mL CaCl}_2 \left(\frac{0.818 \text{ mmol CaCl}_2}{1 \text{ mL CaCl}_2} \right) = 54.15 \text{ mmol CaCl}_2$$

In 42.64 mmol of NaCl, there are

$$42.64 \text{ mmol Na}^+ \text{ and } 42.64 \text{ mmol Cl}^-$$

In 54.15 mmol of CaCl_2 , there are

$$108.3 \text{ mmol Cl}^- \text{ and } 54.15 \text{ mmol Ca}^{2+}$$

Because no reaction takes place,
the numbers of moles of Cl^- ion
are merely added.

11.2 ■ Molarities of Ions**301**

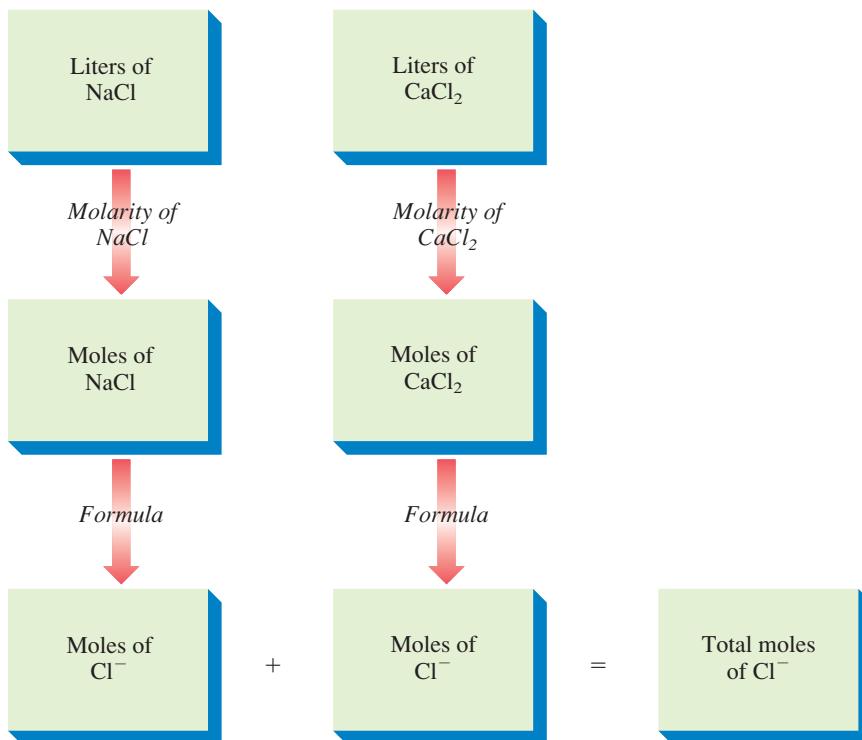
The total numbers of millimoles are

$$42.64 \text{ mmol Na}^+, \quad 150.9 \text{ mmol Cl}^-, \text{ and } 54.15 \text{ mmol Ca}^{2+}$$

The final concentrations are

$$\frac{42.64 \text{ mmol Na}^+}{150.0 \text{ mL}} = 0.284 \text{ M Na}^+ \quad \frac{150.9 \text{ mmol Cl}^-}{150.0 \text{ mL}} = 1.01 \text{ M Cl}^-$$

$$\frac{54.15 \text{ mmol Ca}^{2+}}{150.0 \text{ mL}} = 0.361 \text{ M Ca}^{2+}$$



Practice Problem 11.15 Calculate the concentration of each ion in a solution made by adding 10.0 mL of 0.800 M $(\text{NH}_4)_3\text{PO}_4$ to 14.9 mL of 1.44 M NH_4Cl and diluting to 50.0 mL.

We can calculate the concentrations of ions in solution after a chemical reaction takes place. In doing so, we often use net ionic equations (Chapter 9).

EXAMPLE 11.16

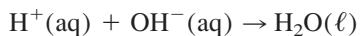
Calculate the concentration of each ion in a solution made by adding 24.0 mL of 1.50 M HCl to 42.7 mL of 0.212 M $\text{Ba}(\text{OH})_2$ and diluting to 100.0 mL.

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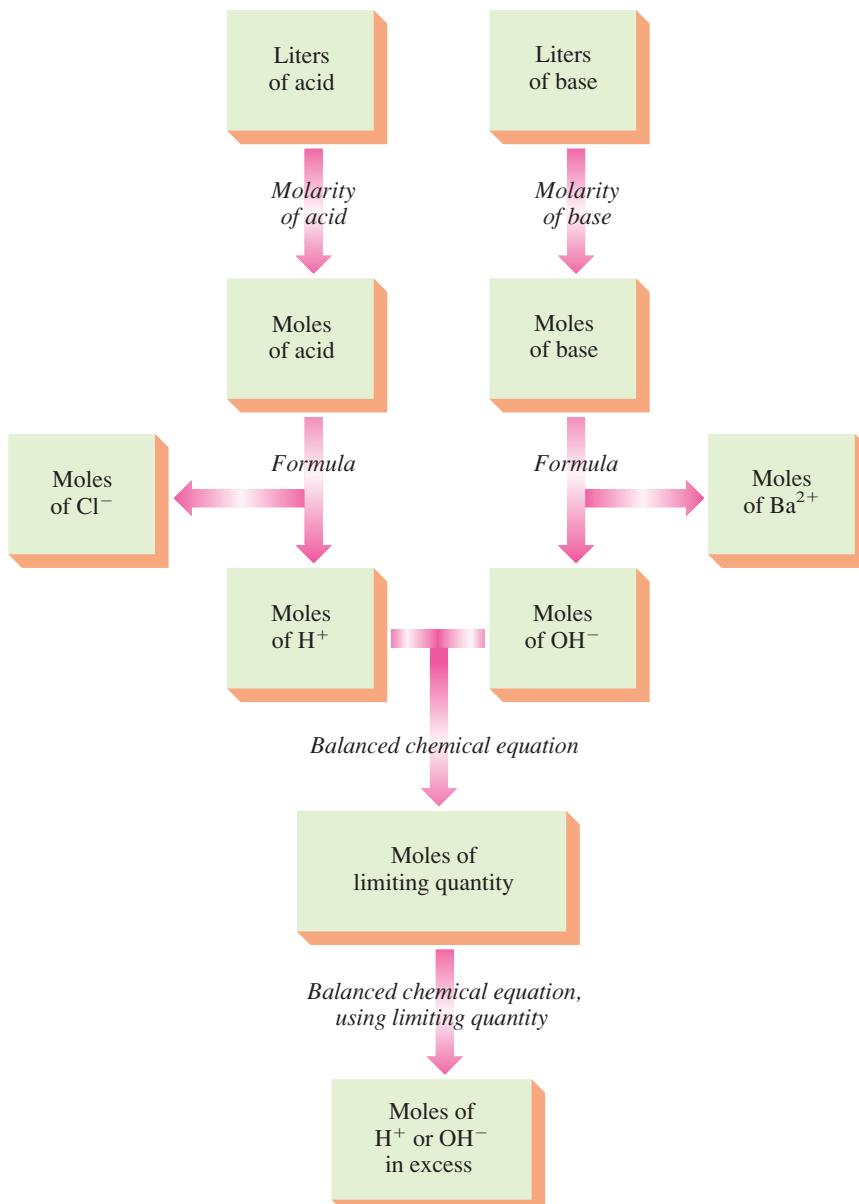
CHAPTER 11 ■ Molarity

Solution

When these two solutions are combined, a chemical reaction does take place. The net ionic equation for the reaction is



The numbers of moles of H^+ and OH^- in the two initial solutions are 36.0 mmol H^+ and 18.10 mmol OH^- (determined by calculations similar to those in Example 11.15). Because the OH^- ion is in limiting quantity, the 18.1 mmol of OH^- will react with 18.1 mmol of H^+ , leaving 17.9 mmol of H^+ in



11.3 ■ Titration**303**

solution. The number of moles of water is of no interest; water is the solvent. The volume of water produced in the reaction is also of no interest. First, the volume of water produced is not significantly different from the sum of the volumes of H^+ and OH^- used up. Then, the final solution is diluted with water to 100.0 mL. The Cl^- and Ba^{2+} ions are spectator ions; their numbers of moles do not change when the initial solutions are combined. Thus, there are 9.052 mmol of Ba^{2+} and 36.0 mmol of Cl^- in the final solution, along with the excess 17.9 mmol of H^+ . The concentrations are

$$\frac{17.9 \text{ mmol H}^+}{100.0 \text{ mL}} = 0.179 \text{ M H}^+ \quad \frac{36.0 \text{ mmol Cl}^-}{100.0 \text{ mL}} = 0.360 \text{ M Cl}^-$$

$$\frac{9.052 \text{ mmol Ba}^{2+}}{100.0 \text{ mL}} = 0.0905 \text{ M Ba}^{2+}$$

Practice Problem 11.16 Calculate the concentration of each ion in a solution made by adding 15.5 mL of 2.50 M HCl to 12.6 mL of 3.13 M NaOH and diluting to 50.0 mL.



Snapshot Review



ChemSkill Builder 6.4

- The molarities of individual ions of an ionic solute are calculated using the numbers of moles of the individual ions.
- Similar to the principle in Section 11.1, if more than one ionic solute is present, the ions may or may not react.

A. Calculate the concentration of hydroxide ion in a solution prepared by adding 5.00 mL of 2.50 M HNO_3 to 20.0 mL of 0.750 M NaOH and diluting to 100.0 mL

11.3 Titration

Titration is a technique for determining either the concentration of a solution of unknown molarity or the number of moles of a substance in a given sample. A chemical reaction is used for this purpose, and the reaction must be fast, be complete, and have a determinable end point. The reactions of strong acids and bases generally meet these criteria, and acid-base titrations are among the most important examples of this technique.

An **indicator** is used to signal the point at which the titration is stopped. An acid-base indicator is a weak acid or base that has a different color from its salt. At least one of them—the indicator or its salt—must be intensely colored so that it can be seen even in very dilute solution. The color of the solution is thus different depending on the acidity or basicity of the solution it is in, and when the acidity of a solution changes sufficiently, a color change will occur. For example, the indicator called litmus is blue in basic solution and red in acidic solution. If we place a drop of a solution on a piece of paper treated with litmus and the paper turns red, the solution is acidic.

EXAMPLE 11.17

A common indicator, phenolphthalein, is colorless in acidic solution and red in basic solution. Describe the color changes when two drops of phenolphthalein solution are added to 100 mL of a colorless acidic solution and then the acid is gradually neutralized by adding drops of base to the continuously stirred solution.

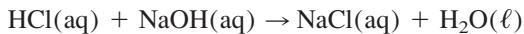
Solution

The acidic solution is initially colorless and remains so when the indicator is added. As most of the base is added, no permanent color change takes place. When one drop or less of *excess* base is added, the solution will change to pink. The indicator, usually red in a basic solution, is present in very low concentration, and its red color looks pink in such a relatively large volume of solution.

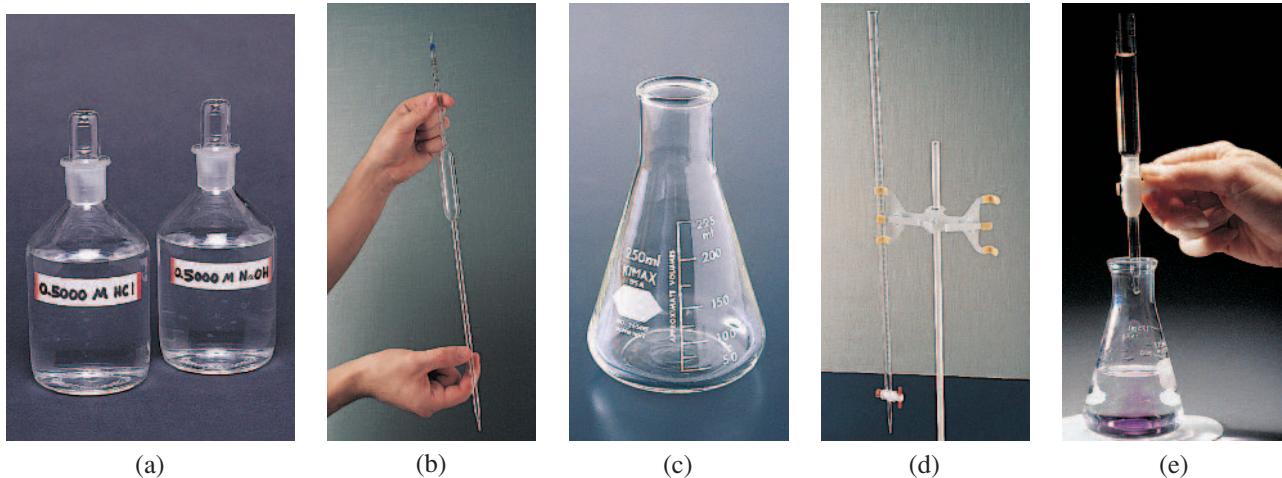
Practice Problem 11.17 What happens to the color of the solution in Example 11.17 if acid is added after the last drop of base has been added?

The purpose of a typical titration is the determination of the concentration of a solution such as HCl, using a solution of NaOH of known concentration. Assume that 1 L of each solution is available (Figure 11.4a). Exactly 25.00 mL of the HCl solution is transferred with a **pipet** (Figure 11.4b) to a clean **Erlenmeyer flask** (Figure 11.4c), and two drops of an indicator are added to the solution. The indicator will show when the reaction is complete by changing color; that is, it will indicate when the **end point** has been reached. The end point is the point in the titration at which the mole ratio of reactants added is exactly equal to their mole ratio in the balanced chemical equation. That is the point at which we wish to stop the titration.

The NaOH solution is placed in a **buret** (Figure 11.4d). The tip of the buret is filled by allowing a small portion of the solution to run out the bottom, and then the level of the solution in the buret is read and recorded. Next, the NaOH solution is added from the buret to the Erlenmeyer flask—rapidly at first, then slowly as the reaction nears completion. When the last drop or half drop of NaOH solution completes the reaction, addition is stopped, and the final buret level is read and recorded. At this point, the number of moles of HCl originally in the solution and the number of moles of NaOH added to that solution are equal, just as they are in the balanced equation:



The indicator enables us to tell when the reaction is complete because it has one color in the HCl solution and another in the NaOH solution (or it may be colorless in one solution and have a color in the other). As we add the NaOH solution from the buret, the color characteristic of that solution appears where the drop enters the HCl solution. As we swirl the flask rapidly to ensure mixing, that color disappears (Figure 11.4e). As the reaction proceeds further toward completion, it takes longer for the color due to the added base to disappear, even though we are adding smaller portions of NaOH solution. When we add the last drop of NaOH solution, the associated color remains for at least 1 min. We know then that the end point of the titration has been reached.

11.3 ■ Titration**305****Figure 11.4** Apparatus for Performing an Acid-Base Titration (not shown to scale)

(a) Stock solutions of hydrochloric acid and sodium hydroxide. (b) A pipet is a piece of glassware shaped like a straw with an enlarged middle section. There is a mark about halfway up the top section. When the pipet is filled to the mark and then allowed to drain, the liquid delivered from the pipet will have the volume marked on the side. Common volumes are 5.000 mL, 10.00 mL, and 25.00 mL. The enlarged midsection allows more solution to be held, and the small top and bottom sections allow more exact volumes to be delivered. (c) An Erlenmeyer flask is shaped so that the contents do not spill out when the flask is swirled. (d) A buret is a uniform-bore tube with volume calibrations marked on its side. Readings are taken at the bottom of the meniscus, the curved surface of the liquid in the buret. The volume delivered from a buret is equal to the difference between the initial and final readings. The portion below the stopcock must be filled with liquid both before and after the titration to get an accurate volume. (e) One reagent is added from the buret to a measured volume of the other reagent in the Erlenmeyer flask.

In titrations, it is the concentration of the *original* solutions that is of interest, not the concentrations in the *final* solution.

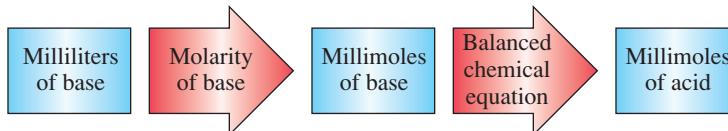
We can now calculate the concentration of the HCl solution. The volume of NaOH solution used is the difference between the initial and final buret readings. The concentration of NaOH is known, and thus the number of millimoles (or moles) of NaOH can be calculated. From the way a titration is run and the fact that the mole ratio of HCl to NaOH in the balanced equation is 1:1, the number of millimoles of HCl is equal to the number of millimoles of NaOH. The concentration of the HCl solution is calculated by dividing that number of millimoles by the number of milliliters of the HCl solution.

EXAMPLE 11.18

An acid-base titration is performed as just described. Calculate the concentration of the HCl solution if the concentration of the NaOH solution is 2.000 M, the volume of HCl solution is 25.00 mL, the initial buret reading for the NaOH solution is 2.17 mL, and the final buret reading is 39.42 mL. (The lower numbers are toward the top of the buret.)

Solution

The volume of NaOH solution used is $39.42 \text{ mL} - 2.17 \text{ mL} = 37.25 \text{ mL}$. The number of millimoles of NaOH is

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$$37.25 \text{ mL} \left(\frac{2.000 \text{ mmol}}{1 \text{ mL}} \right) = 74.50 \text{ mmol NaOH}$$

The number of millimoles of HCl is also 74.50 mmol because the titration was stopped when the numbers of millimoles of the two reactants were equal. The HCl concentration is therefore

$$\frac{74.50 \text{ mmol HCl}}{25.00 \text{ mL HCl}} = 2.980 \text{ M HCl}$$

Practice Problem 11.18 A titration is done to determine the concentration of NH₃ in a certain sample of household ammonia solution. The concentration of the HCl solution used is 1.500 M, the volume of HCl solution is 25.00 mL, the initial buret reading for the NH₃ solution is 1.73 mL, and the final buret reading is 42.36 mL. Calculate the molarity of the base.

The indicator for an acid-base titration is an intensely colored dye, which is itself an acid or a base. It must be intensely colored in at least one of the two solutions so that its color is visible when it is present in a very low concentration. We should not use too much of the indicator because it, rather than the acid or base of interest, would react with the other reagent; its quantity must be negligible, relative to the quantity of either reactant.

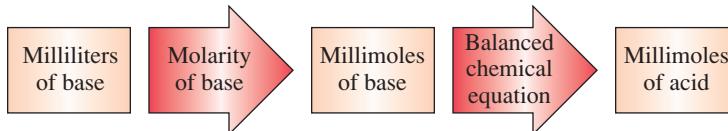
Why would we want to determine the concentration of an acid solution such as that of Example 11.18 when the acid gets converted to a salt in the process? The portion of acid used for the titration is indeed no longer useful, but the greater portion left in the stock bottle (see Figure 11.4a) is the same concentration as that initially present in the flask. Thus, the titration allows us to determine the concentration of the major portion of the original solution.

EXAMPLE 11.19

Calculate the concentration of H₂SO₄ solution that is completely neutralized in an acid-base titration if the concentration of NaOH solution is 1.500 M, the volume of H₂SO₄ solution is 25.00 mL, the initial buret reading for the NaOH solution is 1.28 mL, and the final buret reading is 45.19 mL.

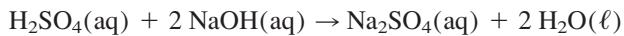
Solution

The volume of NaOH solution used is 45.19 mL – 1.28 mL = 43.91 mL. The number of millimoles of NaOH is

11.3 ■ Titration**307**

$$43.91 \text{ mL} \left(\frac{1.500 \text{ mmol NaOH}}{1 \text{ mL}} \right) = 65.865 \text{ mmol NaOH}$$

The balanced equation for this reaction is



The number of millimoles of H_2SO_4 is

$$65.865 \text{ mmol NaOH} \left(\frac{1 \text{ mmol H}_2\text{SO}_4}{2 \text{ mmol NaOH}} \right) = 32.933 \text{ mmol H}_2\text{SO}_4$$

The concentration of the H_2SO_4 solution is

$$\frac{32.933 \text{ mmol H}_2\text{SO}_4}{25.00 \text{ mL}} = 1.317 \text{ M H}_2\text{SO}_4$$

EXAMPLE 11.20

Two different indicators are used to show the two end points (one for each ionizable hydrogen atom) when H_2SO_3 is titrated with NaOH . In one laboratory, the labels fell off the indicator bottles. To determine which indicator was which, a student titrated 25.00 mL of 1.317 M H_2SO_3 with 21.96 mL of 1.500 M NaOH , using one of the indicators. Write the equation for the chemical reaction that occurred.

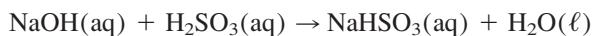
Solution

The numbers of millimoles of acid and base are calculated from the volumes and molarities given:

$$25.00 \text{ mL H}_2\text{SO}_3 \left(\frac{1.317 \text{ mmol H}_2\text{SO}_3}{1 \text{ mL H}_2\text{SO}_3} \right) = 32.925 \text{ mmol H}_2\text{SO}_3$$

$$21.96 \text{ mL NaOH} \left(\frac{1.500 \text{ mmol NaOH}}{1 \text{ mL NaOH}} \right) = 32.94 \text{ mmol NaOH}$$

Because the numbers of millimoles of acid and base are equal, the acid and base react with each other in a 1:1 ratio. The balanced equation is therefore



Practice Problem 11.20 What volume of 1.500 M NaOH would be required to completely neutralize 25.00 mL of 4.176 M H_2SO_4 ?

EXAMPLE 11.21

Calculate the number of millimoles of Na_2CO_3 present in a sample if it takes 27.17 mL of 2.500 M HCl to convert the sample to NaCl, CO_2 , and H_2O .

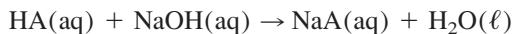
Solution

$$27.17 \text{ mL HCl} \left(\frac{2.500 \text{ mmol HCl}}{1 \text{ mL HCl}} \right) \left(\frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol HCl}} \right) = 33.96 \text{ mmol Na}_2\text{CO}_3$$

Practice Problem 11.21 Calculate the number of millimoles of NaHCO_3 in a sample if it takes 27.17 mL of 2.500 M HCl to convert the sample to NaCl, CO_2 , and H_2O .

EXAMPLE 11.22

An unknown acid with only one ionizable hydrogen atom per formula unit, represented as HA, is prepared in the laboratory. Calculate the molar mass of the acid if it takes 33.48 mL of 0.5000 M NaOH to neutralize a solution prepared by dissolving 3.172 g of the acid in water. The reaction may be represented as follows:

**Solution**

The number of moles of base is calculated first:

$$33.48 \text{ mL NaOH} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.5000 \text{ mol NaOH}}{1 \text{ L NaOH}} \right) = 0.01674 \text{ mol NaOH}$$

The number of moles of acid is

$$0.01674 \text{ mol NaOH} \left(\frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} \right) = 0.01674 \text{ mol HA}$$

The molar mass is the number of grams per mole:

$$\frac{3.172 \text{ g HA}}{0.01674 \text{ mol HA}} = 189.5 \text{ g/mol}$$

**Snapshot Review**

- A titration is a controlled reaction used to determine the number of moles of one substance by treatment with a known number of moles of a second substance. The known number of moles is calculated as a volume times a molarity of the solution of known concentration. The

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number of moles of the other substance may be used to calculate its concentration, its molar mass, or other quantities.

- A. A titration of HCl and NaOH used 10.00 mL of 3.000 M HCl and 29.42 mL of NaOH. (a) How many millimoles of HCl was used? (b) How many millimoles of NaOH did that HCl react with? (c) What was the original concentration of the NaOH?

Key Terms

Key terms are defined in the Glossary.

buret (11.3)
concentration (11.1)
end point (11.3)
Erlenmeyer flask (11.3)

indicator (11.3)
molar (11.1)
molarity (11.1)
pipet (11.3)

solute (11.1)
solvent (11.1)
titration (11.3)

Symbols/Abbreviations

M (molar) (11.1)

M (molarity) (11.1)

Summary

The concentration of a solute depends on the quantities of both the solute and the solution (or solvent). Molarity is defined as the number of moles of solute per liter of solution. Molarity is calculated by dividing the number of moles of solute by the volume of the solution in liters, or alternatively, by dividing the number of millimoles of solute by the milliliters of solution. Because molarity is a ratio, it can be used as a conversion factor to change the volume of solution into the number of moles of solute, or vice versa.

If an aqueous solution is diluted with water, the number of moles of solute does not change, but the molarity does. The final concentration of such a solution is calculated by dividing the number of moles of solute by the final volume. (The number of moles might have to be calculated from the initial volume and concentration.) If two solutions of the same solute are mixed, the total number of moles present in the final solution is the sum of the numbers of moles in the two original solutions. The *molarities* are not added.

The number of moles of a reactant involved in a reaction can be calculated from molarity and volume; that number of moles can then be used to calculate the number

of moles of product. The number of moles of product can then be changed to a final molarity if a final volume is known (Section 11.1).

The individual ions of an ionic compound may be regarded as separate solutes. The number of moles of each ion is calculated from the number of moles of the compound and the formula of the compound. If solutions of two compounds containing one ion in common are mixed, the number of moles of that ion is determined by adding the numbers of moles of the ion in the original solutions. In contrast, if solutions of ions that react with each other are mixed, the numbers of moles of the ions that react are subtracted from the original numbers of moles present, as in a problem involving a limiting quantity. The molarities of the ions in the final solution will be related to the numbers of moles of the ions remaining in that solution (Section 11.2).

The experimental technique of titration is often used to determine the number of moles of a reactant in a given sample of an unknown, using a measured volume of a (standard) solution of known concentration. The color change of an indicator shows when the reaction has been completed. The concentration and volume of the standard

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solution give the number of moles of solute in the standard solution, and then the number of moles of the unknown substance may be calculated from the balanced chemical equation. If an unknown substance is dissolved

CHAPTER 11 ■ Molarity

in a measured volume of solution, its molarity can be calculated from its volume and the calculated number of moles (Section 11.3).

Items for Special Attention

- Do not confuse quantities and concentrations.
- Be sure to use mol as an abbreviation for mole—not M or m, which are used for other quantities related to moles.
- Remember that the volume of *solution*, not the volume of solvent, is used in the definition of molarity.

- Concentrations are *not* added when solutions are mixed.
- In molarity problems involving two compounds, be sure to distinguish between those in which a reaction does not occur and those in which one does occur.

Answers to Snapshot Reviews

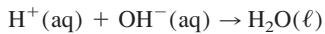
11.1 A. (a), (b), and (c) All three solutions contain the same quantity of solute and all have the same volume. Their concentration is 0.333 M.

$$\text{B. } 15.0 \text{ mL} \left(\frac{2.00 \text{ mmol}}{1 \text{ mL}} \right) = 30.0 \text{ mmol}$$

C. There is a total of 120.0 mmol in the final solution.

$$\frac{120.0 \text{ mmol}}{200.0 \text{ mL}} = 0.6000 \text{ M}$$

11.2 A. The substances react according to the net ionic equation



There are present

$$5.00 \text{ mL} \left(\frac{2.50 \text{ mmol H}^+}{1 \text{ mL}} \right) = 12.5 \text{ mmol H}^+$$

$$20.0 \text{ mL} \left(\frac{0.750 \text{ mmol OH}^-}{1 \text{ mL}} \right) = 15.0 \text{ mmol OH}^-$$

The 12.5 mmol H⁺ reacts with 12.5 mmol OH⁻, leaving 2.5 mmol OH⁻ in solution. The concentration of OH⁻ is (2.5 mmol)/(100.0 mL) = 0.025 M.

11.3 A. (a) 30.00 mmol HCl (b) 30.00 mmol NaOH
(c) $\frac{30.00 \text{ mmol}}{29.42 \text{ mL}} = 1.020 \text{ M}$

Self-Tutorial Problems

- 11.1 (a) If exactly one-thousandth of a 2.000-L sample of 3.000 M solution is poured into a small beaker, what is the concentration of the solution in the beaker?
(b) How many milliliters of solution are in the beaker?
(c) How many millimoles of solute are in the beaker?
(d) What is the concentration in millimoles per milliliter in the beaker?

- 11.2 Calculate the molarity of a solution of 1.70 mol of solute in
(a) 1.00 L of solution (b) 2.00 L of solution
(c) 5.00 L of solution (d) 0.500 L of solution

- 11.3 What is the difference between (a) “dilute the solution to 40.0 mL with water” and (b) “dilute the solution with 40.0 mL of water”?

- 11.4 What is the final concentration when 25.0 mL of 1.22 M sugar solution is added to 35.0 mL of 1.22 M sugar solution?

- 11.5 Calculate the concentration of each of the following solutes:
(a) 0.365 mol solute in 0.4000 L of solution
(b) 365 mmol solute in 0.4000 L of solution
(c) 0.365 mol solute in 400.0 mL of solution
(d) 365 mmol solute in 400.0 mL of solution

- 11.6 If 3.13 mL of a solution is poured from 100.0 mL of a 0.693 M sample, what is the concentration of the 3.13-mL portion?

■ Problems

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- 11.7** (a) If two dozen couples get married at city hall on a certain weekend, how many brides are there? How many grooms?
- (b) What is the concentration of the cation in a 2.0 M solution of NH_4NO_3 ? What is the concentration of the anion?
- 11.8** What is the concentration of each ion in the following solutions?
- | | |
|--|--|
| (a) 1.0 M NaCl | (b) 1.0 M MgCl_2 |
| (c) 1.0 M CrCl_3 | (d) 1.0 M LiNO_3 |
| (e) 1.0 M $\text{Co}(\text{NO}_3)_2$ | (f) 1.0 M $\text{Al}(\text{NO}_3)_3$ |
| (g) 1.0 M $\text{Al}_2(\text{SO}_4)_3$ | (h) 1.0 M $(\text{NH}_4)_2\text{SO}_4$ |
- 11.9** What is the final volume of solution if 2.2 L of solution is diluted (a) with 3.3 L of solvent or (b) to 3.3 L with solvent?
- 11.10** Which of the following combinations of solutions will result in a chemical reaction, which will result in a combination of the number of moles of a common ion, and which will result in a mere dilution?
- | |
|---|
| (a) $\text{Na}_2\text{SO}_4(\text{aq}) + \text{Ba}(\text{NO}_3)_2(\text{aq})$ |
| (b) $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{KNO}_3(\text{aq})$ |
- (c) $\text{KCl}(\text{aq}) + \text{AlCl}_3(\text{aq})$
- (d) $\text{Na}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq})$
- (e) $\text{LiOH}(\text{aq}) + \text{KNO}_3(\text{aq})$
- (f) $\text{KOH}(\text{aq}) + \text{LiOH}(\text{aq})$
- 11.11** (a) A chemist titrates 25.00 mL of NaHCO_3 with 31.77 mL of 2.000 M HCl. What is the purpose of the titration? What answer does she get?
- (b) A chemist titrates 4.13 g of an acid, HA, with 35.72 mL of 2.000 M NaOH. What is the purpose of the titration? What answer does she get?
- 11.12** In which of the following combinations of solutions will there be a chemical reaction? Which have ions in common? In which are the ions all different and unreactive?
- | |
|---|
| (a) $\text{HCl}(\text{aq}) + \text{K}_2\text{CO}_3(\text{aq})$ |
| (b) $\text{NaCl}(\text{aq}) + \text{LiNO}_3(\text{aq})$ |
| (c) $\text{LiCl}(\text{aq}) + \text{KNO}_3(\text{aq})$ |
| (d) $\text{Na}_2\text{SO}_4(\text{aq}) + \text{KBr}(\text{aq})$ |
| (e) $\text{CuCl}_2(\text{aq}) + \text{KCl}(\text{aq})$ |
| (f) $\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq})$ |

Problems**11.1 Definition and Uses of Molarity**

- 11.13** Calculate the molarity of a solution containing (a) 0.123 mol of solute in 0.7000 L of solution. (b) 123 mmol of solute in 700.0 mL of solution.
- 11.14** Calculate the molarity of a solution containing 1.17 mol of solute in 943 mL of solution.
- 11.15** Calculate the molarity of a solution containing 79.4 mmol of solute in 122.5 mL of solution.
- 11.16** Calculate the molarity of a solution containing 0.5050 mol of solute in 400.0 mL of solution.
- 11.17** Calculate the molarity of 29.7 mL of a solution that contains 6.11 g of methyl alcohol, CH_3OH .
- 11.18** Calculate the volume of 0.881 M solution that contains 0.175 mol of solute.
- 11.19** Calculate the number of milliliters of 1.38 M NaCl solution that contains 122 mg of NaCl.
- 11.20** Calculate the number of grams of NaNO_3 in 0.0112 L of 3.09 M NaNO_3 solution.
- 11.21** Calculate the molarity of 886 mL of a solution that contains 149 g of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$.
- 11.22** Calculate the number of moles of solute in 0.8122 L of 2.163 M solution.
- 11.23** Calculate the number of millimoles of solute in 41.0 mL of 2.611 M solution.
- 11.24** Calculate the number of grams of AlCl_3 in 1255 mL of 0.909 M AlCl_3 solution.
- 11.25** What is the final concentration if 225 mL of 0.500 M solution is diluted (a) with 1.100 L of solvent or (b) to 1.100 L with solvent?
- 11.26** Calculate the volume of 3.171 M solution that contains 25.5 mmol of solute.
- 11.27** Calculate the number of milliliters of 3.83 M NaCl solution that contains 14.7 g of NaCl.
- 11.28** Calculate the molarity of a solution prepared by diluting 20.8 mL of 2.11 M solution to 50.0 mL.
- 11.29** Calculate the volume of solution prepared by diluting 69.7 mL of 2.13 M solution to 1.51 M.
- 11.30** Calculate the volume of 2.50 M solution required to make 6.00 L of 0.450 M solution by dilution with water.
- 11.31** Calculate the molarity of a solution prepared by diluting 75.00 mL of 2.132 M solution to 125.0 mL.
- 11.32** Calculate the volume of solution prepared by diluting 6.929 mL of 3.555 M solution to 0.8229 M.
- 11.33** Calculate the volume of 3.00 M solution required to make 75.00 mL of 1.600 M solution by dilution with water.

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11.34 Calculate the concentration of each ion in each of the following solutions:

- (a) 0.344 M $\text{Al}_2(\text{SO}_4)_3$
- (b) 1.61 M $(\text{NH}_4)_3\text{PO}_4$
- (c) 0.0808 M $\text{Ba}(\text{OH})_2$
- (d) 3.75 M KBr
- (e) 3.09 M NaClO_3

11.35 In which one(s) of the following combinations of solutions is a reaction expected?

- (a) $\text{KC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HCl}(\text{aq})$
- (b) $\text{CaF}_2(\text{aq}) + \text{HNO}_3(\text{aq})$

11.36 Calculate the concentration of each ion in each of the following solutions:

- (a) 2.50 M HNO_3
- (b) 3.00 M $\text{Co}(\text{ClO}_3)_3$
- (c) 2.10 M CuSO_4
- (d) 0.136 M $\text{Ca}_3(\text{PO}_4)_2$
- (e) 3.11 M $(\text{NH}_4)_2\text{SO}_3$

11.37 Calculate the concentration of each ion in 0.715 M $\text{Al}_2(\text{SO}_4)_3$ solution.

11.38 Calculate the concentration of each ion in 0.128 M (a) $\text{Hg}(\text{NO}_3)_2$ solution, and (b) $\text{Hg}_2(\text{NO}_3)_2$ solution.

11.39 Calculate the concentration of each ion in solution after 12.3 mL of 0.816 M BaCl_2 is mixed with 14.3 mL of 0.806 M AlCl_3 and the resulting solution is diluted to 50.0 mL.

11.40 Calculate the *total* concentration of all the ions in each of the following solutions:

- (a) 3.25 M NaCl
- (b) 1.75 M $\text{Ca}(\text{ClO}_3)_2$
- (c) 12.1 g of $(\text{NH}_4)_2\text{SO}_3$ in 615 mL of solution

11.41 If 0.217 mol of Li_2SO_4 and 0.217 mol of K_2SO_4 are dissolved in enough water to make 650.0 mL of solution, what is the concentration of each ion in the solution?

11.42 Calculate the concentration of each ion in solution after 35.3 mL of 2.17 M MgCl_2 is mixed with 21.4 mL of 0.500 M AlBr_3 and the resulting solution is diluted to 100.0 mL.

11.43 If 0.500 mol of $\text{Al}_2(\text{SO}_4)_3$ and 0.500 mol of Na_2SO_3 are dissolved in enough water to make 250.0 mL of solution, what is the concentration of each ion in the solution?

11.44 Assuming that the final volume is the sum of the initial volumes, calculate the concentration of each ion in solution after

- (a) 30.00 mL of 4.000 M NaOH is added to 60.00 mL of 1.250 M HCl.
- (b) 30.00 mL of 4.000 M NaCl is added to 60.00 mL of 1.250 M HCl.

11.45 Calculate the concentration of each type of ion in solution after 30.0 mL of 3.35 M NaCl and 70.0 mL of 1.35 M Na_2SO_4 are mixed. Assume that the final volume is 100.0 mL.

CHAPTER 11 ■ Molarity

11.46 What is the concentration of each type of ion in solution after 23.69 mL of 3.611 M NaOH is added to 29.10 mL of 0.8921 M H_2SO_4 ? Assume that the final volume is the sum of the original volumes.

11.47 Calculate the concentration of each type of ion in solution after 50.0 mL of 4.00 M NaCl and 50.0 mL of 2.50 M NaBr are mixed. Assume that the final volume is 100.0 mL.

11.48 What is the concentration of each type of ion in solution after 42.00 mL of 3.000 M NaOH is added to 50.00 mL of 2.535 M HClO_3 ? Assume that the final volume is the sum of the original volumes.

11.49 Find the concentration of each type of ion in solution after 25.0 mL of 0.919 M CoCl_2 is diluted to 100.0 mL.

11.50 Find the concentration of each type of ion in solution after 10.0 mL of 0.650 M Na_3PO_4 is diluted to 50.0 mL.

11.3 Titration

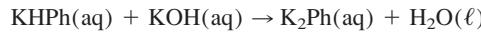
11.51 Calculate the concentration of an H_2SO_4 solution if 25.00 mL is completely neutralized by 21.73 mL of 4.000 M NaOH solution.

11.52 Calculate the concentration of a phosphoric acid solution if 25.00 mL is completely neutralized by 31.17 mL of 4.000 M sodium hydroxide solution.

11.53 Calculate the concentration of an H_3PO_4 solution if 25.00 mL is converted to Na_2HPO_4 by 39.13 mL of 2.000 M NaOH solution.

11.54 Calculate the concentration of a sulfuric acid solution if 25.00 mL is converted to sodium sulfate by 17.42 mL of 3.150 M sodium hydroxide solution.

11.55 When 2.818 g of potassium hydrogen phthalate (symbolized here as KHPh; molar mass = 204.2 g/mol) is titrated with KOH solution, it takes 31.74 mL of the base to achieve the end point. Calculate the concentration of the KOH solution.



11.56 How many millimoles of AgNO_3 will react with 21.29 mL of 2.500 M CaCl_2 ?

11.57 How many millimoles of H_2SO_4 will react completely with 12.88 mL of 1.500 M NaOH?

11.58 How many millimoles of CaO(s) can be “dissolved” with 25.00 mL of 4.000 M HCl?

11.59 How many millimoles of $\text{Ca}(\text{OH})_2(\text{s})$ will react with 29.17 mL of 4.000 M HClO_3 ?

11.60 How many millimoles of AgNO_3 will react with 17.13 mL of 0.203 M AlCl_3 ?

11.61 An antacid tablet contains 31.3 g of NaHCO_3 . What volume of 2.84 M stomach acid (HCl) can this tablet neutralize?

11.62 An antacid tablet contains NaHCO_3 . What mass of this compound is required to neutralize 178 mL of 2.91 M stomach acid (HCl)?

■ General Problems

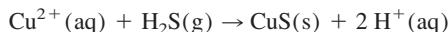
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General Problems

- 11.63** Calculate the concentration of each type of ion in solution after 37.22 mL of 1.000 M HCl is added to 19.29 mL of 4.107 M NaOH. Use a net ionic equation in solving this problem. Assume that the final volume is equal to the sum of the volumes of the two original solutions.

- 11.64** Calculate the number of milligrams of Na_2CO_3 in 725 mL of 715 mM solution.

- 11.65** Calculate the concentration of H^+ ion produced when H_2S is bubbled into 0.300 M Cu^{2+} solution, causing precipitation of all the copper(II) ion as CuS. Assume no change in the volume of the solution.



- 11.66** Calculate the concentration of acetic acid produced by reaction in 1.00 L of solution of

- (a) 2.0 mol $\text{KC}_2\text{H}_3\text{O}_2(\text{aq}) + 1.0 \text{ mol HCl}(\text{aq})$
 (b) 3.0 mol $\text{KC}_2\text{H}_3\text{O}_2(\text{aq}) + 2.0 \text{ mol HCl}(\text{aq})$

- 11.67** Calculate the concentration of each ion in solution after 47.33 mL of 1.807 M NaOH is mixed with 39.19 mL of 0.5093 M H_2SO_4 and then diluted to 100.0 mL.

- 11.68** Calculate the concentration of formaldehyde (CH_2O) in a solution prepared by mixing 125 mL of 6.13 M CH_2O and 175 mL of 4.34 M CH_2O and diluting the mixture to 500.0 mL with water.

- 11.69** Calculate the concentration of CH_2O in a solution prepared by mixing 1.25 L of 3.00 M CH_2O and 719 mL of 1.75 M CH_2O and diluting the mixture to 2.50 L with water.

- 11.70** If 5.033 g of potassium hydrogen phthalate, an acid salt having one ionizable hydrogen atom and a molar mass of 204.2 g/mol, is used to neutralize 39.17 mL of NaOH solution, calculate the concentration of the base.

- 11.71** Calculate the concentration of each ion in solution after 30.8 mL of 4.65 M NaOH is mixed with 21.9 mL of 0.750 M H_3PO_4 and then diluted to 100.0 mL.

- 11.72** Calculate the sodium ion concentration after 20.0 mL of 3.00 M NaOH is mixed with 30.0 mL of 1.00 M HCl and diluted to 100.0 mL.

- 11.73** Calculate the final sugar concentration after 2.25 L of 3.00 M sugar solution is diluted to 5.00 L with (a) water and (b) 1.00 M NaCl solution.

- 11.74** Vinegar contains several acids. Calculate the total concentration of acids in a 20.0-mL sample of vinegar if it takes 37.88 mL of 0.2000 M NaOH to neutralize the acids. Assume that each acid contains only one ionizable hydrogen atom per formula unit.

- 11.75** Calculate the concentration of each of the ions in solution with concentrations greater than 0.500 M after

- (a) 1.25 M HCl is mixed with an equal volume of 1.25 M NaCl.
 (b) 1.25 M $\text{HC}_2\text{H}_3\text{O}_2$ is mixed with an equal volume of 1.25 M $\text{NaC}_2\text{H}_3\text{O}_2$.

- 11.76** The label has fallen off a bottle of a solid organic acid. If 26.2 mL of 2.00 M NaOH is needed to completely neutralize 2.36 g of the acid, determine if the acid is oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), benzoic acid ($\text{HC}_7\text{H}_5\text{O}_2$), or bromobenzoic acid ($\text{HC}_7\text{H}_4\text{O}_2\text{Br}$).

- 11.77** Calculate the acetic acid concentration and the acetate ion concentration (a) after 0.150 mol of acetic acid and 0.100 mol of sodium acetate are dissolved in enough water to make 1.00 L of solution and (b) after 0.250 mol of acetic acid and 0.100 mol of sodium hydroxide are dissolved in enough water to make 1.00 L of solution.

- 11.78** Calculate the hydrogen ion concentration and the chloride ion concentration (a) after 0.150 mol of hydrochloric acid and 0.100 mol of sodium chloride are dissolved in enough water to make 1.00 L of solution, (b) after 0.250 mol of hydrochloric acid and 0.100 mol of sodium hydroxide are dissolved in enough water to make 1.00 L of solution and (c) compare your results to those of Problem 11.77.

- 11.79** Calculate the concentration of each ion in solution after 94.3 mL of 2.14 M MgCl_2 is mixed with 82.8 mL of 0.700 M AlCl_3 and then diluted to 500.0 mL.

- 11.80** When lithium nitride is treated with water, it reacts with the water to form hydroxide ions and ammonia. What concentration of hydroxide ions is present if 0.110 mol of solid Li_3N is treated with water and then diluted to 100.0 mL?

- 11.81** Calculate the percentage of CaCO_3 in a 5.000-g sample of limestone if 24.24 mL of 2.500 M HCl is required to react completely with the CaCO_3 . Assume that the rest of the limestone sample is inert.

- 11.82** In a certain experiment, 10.00 mL of 1.500 M H_3PO_4 was titrated to a certain end point with 27.61 mL of 1.630 M NaOH. Write the equation for the chemical reaction that occurred.

- 11.83** After a 10.0-g sample containing Na_2CO_3 and inert substances was treated with 32.74 mL of 5.000 M HCl, it took 4.20 mL of 1.000 M NaOH to neutralize the excess HCl. Calculate the percent of Na_2CO_3 in the sample.

- 11.84** After a 10.00-g sample containing Na_2CO_3 and inert substances was treated with 41.04 mL of 3.000 M HCl, it took 4.22 mL of 1.000 M NaOH to neutralize the excess HCl. Calculate the percent of Na_2CO_3 in the sample.

- 11.85** When an alkali metal oxide is treated with water, it reacts with the water to form hydroxide ions. What concentration of hydroxide ions is present if 0.250 mol of solid Li_2O is treated with water and the final volume is 500.0 mL?

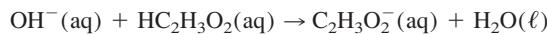
- 11.86** In a certain experiment, 25.00 mL of 2.500 M H_3PO_4 was titrated to a certain end point with 39.66 mL of 3.152 M NaOH. Write the equation for the chemical reaction that occurred.

- 11.87** What volume of 3.152 M NaOH would be required to completely neutralize the H_3PO_4 in the previous problem.

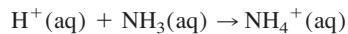
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- 11.88 (a) Calculate the concentration of each type of ion in 58.99 mL of a solution in which 9.404 mmol of Na_2SO_4 and 29.11 mmol of NaOH had been placed.
(b) Calculate the concentration of each type of ion in solution after 47.92 mL of 1.000 M NaOH is added to 11.07 mL of 0.8495 M H_2SO_4 . Assume that the volume of the final solution is the sum of the volumes of the two original solutions.
(c) Explain how parts (a) and (b) are related.

- 11.89 Calculate the concentrations of acetate ion and acetic acid in solution after 10.0 mL of 1.50 M $\text{HC}_2\text{H}_3\text{O}_2$ and 10.0 mL of 0.850 M NaOH are mixed. Assume that the final volume is 20.0 mL and that the excess acetic acid yields no acetate ions to the final solution (because it is a *weak* acid).



- 11.90 Calculate the concentrations of ammonium ion and ammonia in solution after 30.0 mL of 1.35 M NH_3 and 30.0 mL of 0.750 M HCl are mixed. Assume that the final volume is 60.0 mL and that the excess ammonia yields no ammonium ions to the final solution (because it is a *weak* base).

**CHAPTER 11 ■ Molarity**

- 11.91 (a) Calculate the concentration of each type of ion in 111.23 mL of a solution containing 49.68 mmol of NaCl plus 28.43 mmol of NaOH.

- (b) Calculate the concentration of each type of ion in solution after 78.11 mL of 1.000 M NaOH is added to 33.12 mL of 1.500 M HCl. Assume that the volume of the final solution is the sum of the volumes of the two original solutions.
(c) Explain how parts (a) and (b) are related.

- 11.92 Calculate the concentration of each ion in solution after 27.3 mL of 3.08 M NaCl is mixed with 19.1 mL of 0.877 M CaCl_2 and then diluted to 100.0 mL.

- 11.93 Calculate the molar mass of an unknown acid, HA, if a 12.11-g sample of the acid takes 38.38 mL of 5.000 M NaOH to neutralize it.

- 11.94 Calculate the molar mass of an unknown acid, H_2A , if a 12.11-g sample of the acid takes 38.38 mL of 5.000 M NaOH to neutralize it.



Hot air balloon

12

Gases

- 12.1 Gas Pressure
- 12.2 Boyle's Law
- 12.3 Charles' Law
- 12.4 The Combined Gas Law
- 12.5 The Ideal Gas Law
- 12.6 Dalton's Law of Partial Pressures
- 12.7 Molar Masses and Molecular Formulas
- 12.8 Gases in Chemical Reactions
- 12.9 Volume Ratios in Chemical Reactions
- 12.10 Kinetic Molecular Theory of Gases

Review Clues

- | | |
|----------------------|---------------------------------|
| Section 12.1 | Section 2.5 |
| Section 12.2 | Elementary algebra |
| Section 12.3 | Section 2.6, Elementary algebra |
| Section 12.4 | Elementary algebra |
| Section 12.5 | Section 7.3 |
| Section 12.7 | Sections 7.3, 7.5 |
| Section 12.8 | Sections 10.1, 10.3 |
| Section 12.9 | Sections 10.1, 10.3 |
| Section 12.10 | Section 2.6 |

Objectives

- 12.1** To measure gas pressures and convert them from one unit to another
- 12.2** To calculate the volume or the pressure of a given sample of gas at a given temperature
- 12.3** To calculate the volume or the temperature of a given sample of gas at a constant pressure
- 12.4** To calculate the volume, pressure, or temperature of a given sample of gas from other such data
- 12.5** To calculate the number of moles in a sample of gas, its pressure, its volume, or its temperature from the other three
- 12.6** To calculate the properties of each gas in a mixture of gases
- 12.7** To calculate molar masses from mass data along with pressure, volume, temperature data, and to use the molar masses thus calculated to enable calculation of molecular formulas from empirical formulas
- 12.8** To calculate the numbers of moles of gas involved in a chemical reaction using the properties of gases
- 12.9** To calculate the volume of any separate gas involved in a chemical reaction from the volume of any other gas in the reaction if their temperatures as well as their pressures are the same
- 12.10** To explain the behavior of gases using the kinetic molecular theory

This book covers gases before liquids and solids because gases are easiest to understand and, historically, were understood first. Experimental results show that every sample of matter that exists as a gas, regardless of its composition, follows the laws presented in this chapter.

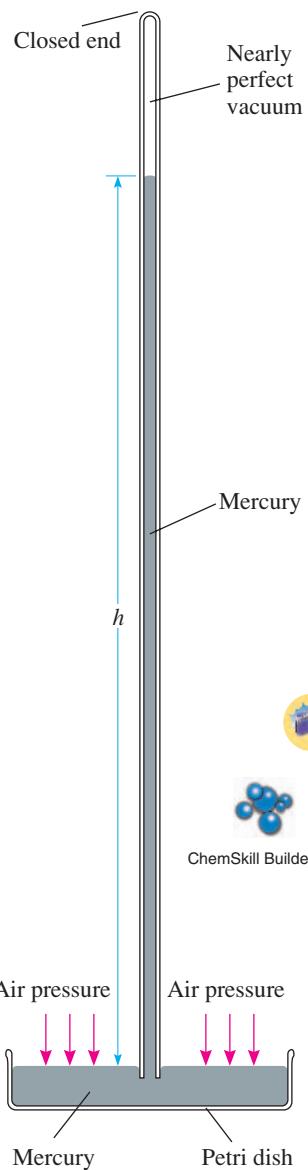
Section 12.1 introduces the concept of pressure and describes a simple way of measuring gas pressures, as well as the customary units used for pressure. Section 12.2 discusses Boyle's law, which describes the effect of the pressure of a gas on its volume. Section 12.3 examines the effect of temperature on volume and introduces a new temperature scale that makes the effect easy to understand. Section 12.4 covers the combined gas law, which describes the effect of changes in both temperature and pressure on the volume of a gas. The ideal gas law, introduced in Section 12.5, describes how to calculate the number of moles in a sample of gas from its temperature, volume, and pressure. Dalton's law, presented in Section 12.6, enables the calculation of the pressure of an individual gas—for example, water vapor—in a mixture of gases. The number of moles present in any gas can be used in related calculations—for example, to obtain the molar mass of the gas (Section 12.7). Section 12.8 extends the concept of the number of moles of a gas to the stoichiometry of reactions in which at least one gas is involved. Section 12.9 enables us to calculate the volume of any gas in a chemical reaction from the volume of any other separate gas (not in a mixture of gases) in the reaction if their temperatures as well as their pressures are the same. Section 12.10 presents the kinetic molecular theory of gases, the accepted explanation of why gases behave as they do, which is based on the behavior of their individual molecules.

12.1 Gas Pressure

Matter occurs in three **states**, or **phases**: solid, liquid, and gaseous. A **solid** has a definite shape and a definite volume. A **liquid** has a definite volume but assumes the shape of its container. A **gas** does not have a definite volume or shape; it expands to fill the entire volume of the container it occupies. The density of a gas is generally very much lower than the density of the same substance in the solid or liquid state. A gas (like a liquid) exerts a pressure in all directions at any point within the gas.

Pressure is defined as force per unit area. A **force** is a push or a pull. The difference between force and pressure is important, both theoretically and practically. We might not object if someone pushed on our shoulders with an open palm with a force of 10 lb. However, if someone pushed the point of a knife against a person's shoulder with a force of 10 lb, he surely would object. The same force exerted over the tiny area of the point of a knife would cause serious damage!

All gases exert pressure. At any point within the gas, the gas exerts an equal pressure in all directions. Gases at rest exert a pressure equal to the pressure exerted on them. An easy method of measuring gas pressure is to use a simple **barometer**, as shown in Figure 12.1. Fill a long tube with mercury, hold a finger over the open end, and invert the tube into a dish of mercury. When the

12.1 ■ Gas Pressure**317**

finger is removed, the mercury level falls. There are two forces on the mercury in the tube: the force of gravity pulling down and the force due to air pressure pushing up. When these two forces balance each other, the mercury in the tube stops falling. The greater the air pressure, the higher the mercury stands in the tube above the level of mercury in the dish. A simple unit of gas pressure is millimeters of mercury (abbreviated mm Hg). The vertical height of the mercury column, corresponding to h in Figure 12.1, is a measure of pressure. A unit equal to the pressure necessary to support 1 mm Hg is the **torr**, named for Evangelista Torricelli (1608–1647), an Italian physicist who discovered the principle of the barometer. At sea level at 0°C on a “normal” day, the atmosphere can hold the mercury at a height of 760 mm; its pressure is 760 torr. Another unit of gas pressure, the **atmosphere** (atm), or **standard atmosphere**, is therefore defined as 760 torr:

$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg}$$

Note the difference between *1 atmosphere pressure* and **atmospheric pressure**. The former is a constant. The latter varies widely from place to place and also varies over time at the same place. Atmospheric pressure is often referred to as **barometric pressure**.

The SI unit of pressure is the pascal (Pa), which is such a small unit that the kilopascal (kPa) is used for atmospheric pressures under ordinary conditions. Chemists do not often use either the pascal or kilopascal. Since some modern reference books present pressure data in these units, however, this conversion is presented here:

$$1.000 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 101.3 \text{ kPa}$$

Snapshot Review



- Pressure is defined as force per unit area.
- Fluids (gases and liquids) exert a pressure at any point within them in all directions.
- We can measure a gas pressure by the vertical height of mercury it can hold up.
- The most important units of pressure in this course are the atmosphere (atm) and the torr ($1 \text{ atm} = 760 \text{ torr}$)

- A. If we double the force exerted on a wall and also double the area of the wall, what happens to the pressure?
- B. Convert 782 torr to atmospheres.

Figure 12.1 Simple Barometer (not drawn to scale)

A simple barometer is made with a long tube closed at one end. Fill the tube completely with mercury. Hold a finger over the open end, invert the tube and put the open end under the surface of mercury in a Petri dish, and hold the tube vertically. The mercury in the tube falls to a height, h , determined by the pressure of the air on the surface of the mercury in the Petri dish. There is essentially no gas pressure in the tube above the mercury. *Caution:* Mercury is toxic; use rubber gloves when handling it.

12.2 Boyle's Law

Robert Boyle (1627–1691), an Irish physical scientist, discovered that the volume of a given sample of a gas at a constant temperature is *inversely proportional* to its pressure. This generalization, known as **Boyle's law**, applies approximately to any gas, no matter what its composition. (It does not apply to liquids or solids.)

Inverse proportionality occurs when one variable gets larger *by the same factor* as another gets smaller. For example, average speed and the time required to travel a certain distance are inversely proportional. If we double our speed, the time it takes us to complete the trip is halved. Similarly, if the pressure on a given sample of gas at a given temperature is doubled (increased by a factor of 2), its volume is halved (decreased by a factor of 2).

Boyle might have observed the following data on volume and pressure for a given sample of gas at a given temperature, under four different sets of conditions:

	Volume (L)	Pressure (atm)
1	4.00	1.00
2	2.00	2.00
3	1.00	4.00
4	0.500	8.00

Note that tabulating data is very helpful when two or more variables are being considered. The units are usually included in the column headings in such a table. The data in the table show that the product of the volume (V) and the pressure (P) is a constant. The table may be expanded to show this relationship:

	Volume (L)	Pressure (atm)	Volume \times Pressure (L·atm)
1	4.00	1.00	4.00
2	2.00	2.00	4.00
3	1.00	4.00	4.00
4	0.500	8.00	4.00

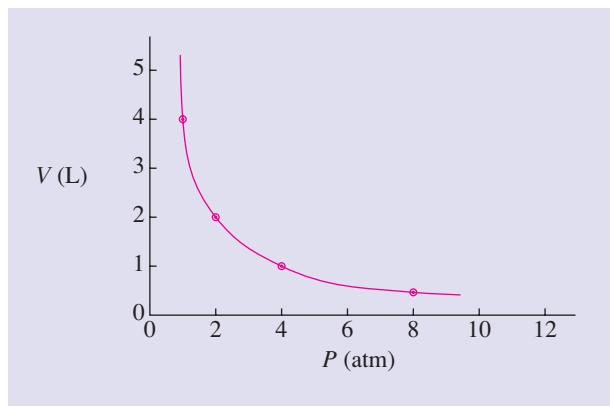
Inverse proportionality may be expressed as a mathematical relationship in any of the following ways:

$$V \propto \frac{1}{P} \quad V = \frac{k}{P} \quad P = \frac{k}{V} \quad PV = k$$

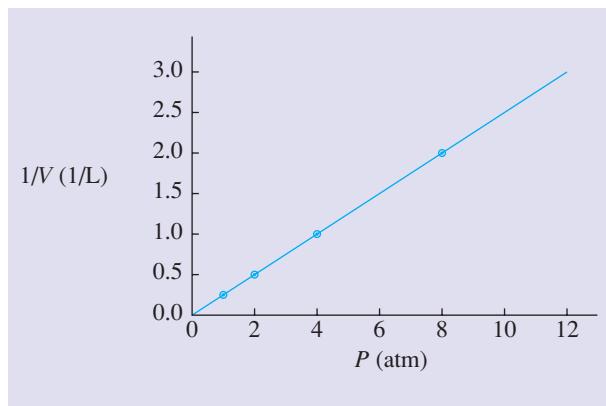
The proportionality sign (\propto) means that when V gets *bigger* the value $1/P$ gets *bigger* by the same factor. Therefore, P must get smaller so that $1/P$ will get bigger. The k that appears in the equations is a constant—a given value for a specific sample of gas at a given temperature.

Another way to represent inverse proportionality is by graphing the data. If we place the values of P on the horizontal axis and the values of V on the vertical axis, plot the preceding tabulated values for P and V , and smoothly connect the points, we get a curve that can tell us what the volume will be at any intermediate pressure (Figure 12.2a). We can also plot $1/V$ versus P and get a straight line through the origin (Figure 12.2b).

	V (L)	$1/V$ (1/L)	P (atm)
1	4.00	0.250	1.00
2	2.00	0.500	2.00
3	1.00	1.00	4.00
4	0.500	2.00	8.00

12.2 ■ Boyle's Law**319**

(a)



(b)

Figure 12.2 Graphs of Volume and Pressure Data

(a) Volume plotted against pressure results in a curved line. (b) When the reciprocal of volume is plotted against pressure, a straight line through the origin results. This indicates that $1/V$ is directly proportional to P and, therefore, that V is inversely proportional to P .

EXAMPLE 12.1

The following data were obtained in a laboratory experiment:

P (atm)	V (L)
0.700	0.707
1.102	0.450
1.524	0.325
1.902	0.261
2.420	0.205

- Plot these data, and determine what pressure is required to get a volume of 0.600 L.
- Determine the pressure required to get a volume of 0.150 L.
- Plot P versus $1/V$, and determine the two pressures again.

Solution

- The plot of the data is shown in Figure 12.3(a). With $V = 0.600$ L, the pressure is read as 0.82 atm.
- On Figure 12.3(a), the pressure is estimated to be 3.3 atm.
- The plot is shown in Figure 12.3(b). With $V = 0.600$ L, $1/V = 1.67/L$, and the pressure is read as 0.82 atm. With $V = 0.150$ L, $1/V = 6.67/L$, and the pressure is 3.26 atm. The linear plot of Figure 12.3(b) makes it easy to estimate data beyond the experimental points. Estimations beyond the experimental points are not as easy on the curve of Figure 12.3(a) because how much the curve bends is difficult to predict.

For a given sample of gas, $PV = k$. If we change that sample of gas from one pressure (P_1) to another (P_2) at constant temperature, the volume will change from V_1 to V_2 . Both products of P and V must equal the same constant, k :

$$P_1V_1 = k = P_2V_2$$

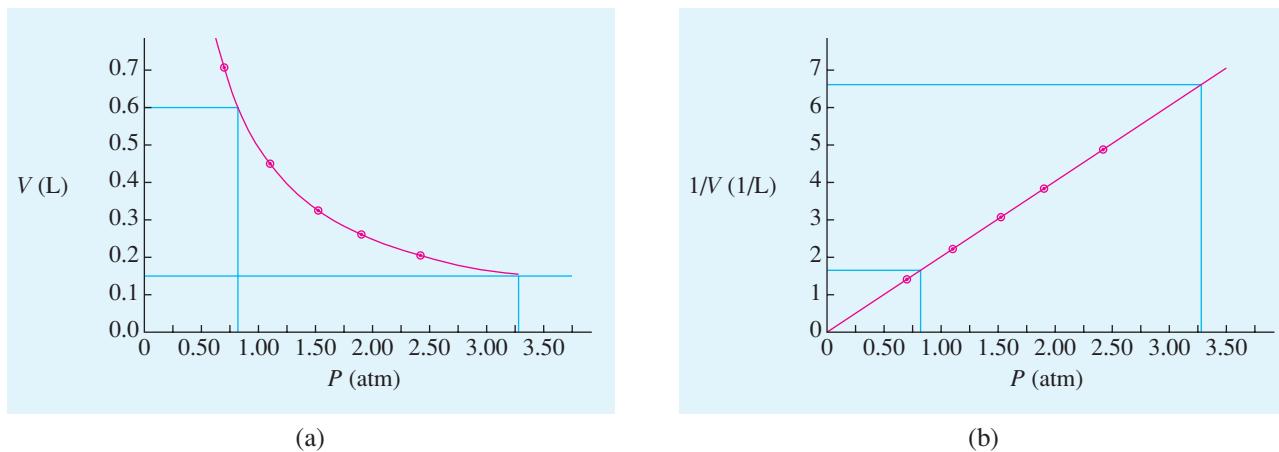


Figure 12.3 Pressure-Volume Plots for Example 12.1

- (a) Plot of V versus P .
(b) Plot of $1/V$ versus P .

Because both products are equal to the same constant, they must be equal to each other:

$$P_1V_1 = P_2V_2$$

We can use this expression to solve for any one of these variables when the other three are known.

EXAMPLE 12.2

A 3.50-L sample of gas has a pressure of 0.750 atm. Calculate the volume after its pressure is increased to 1.50 atm at constant temperature.

Solution

$$P_1V_1 = P_2V_2$$

In this type of problem, tabulating the given data is useful:

	Pressure	Volume
1	0.750 atm	3.50 L
2	1.50 atm	V_2

Substitution of the values into the equation yields

$$(0.750 \text{ atm})(3.50 \text{ L}) = (1.50 \text{ atm})V_2$$

$$V_2 = 1.75 \text{ L}$$

Note that multiplying the pressure by 2 causes the volume to be reduced to half.

Practice Problem 12.2 A sample of gas initially occupies 35.0 mL at 1.50 atm. Calculate the pressure required to reduce its volume to 20.5 mL at constant temperature.

Be careful with the units in gas law problems.

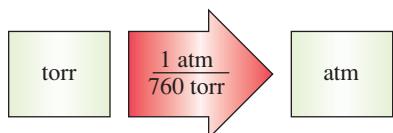
The units of pressure and volume must be the same on each side of the equation $P_1V_1 = P_2V_2$. If the units given in a problem are not the same, one or more of the units must be converted.

EXAMPLE 12.3

A 1.45-L sample of gas has a pressure of 0.950 atm. Calculate the volume after its pressure is increased to 787 torr at constant temperature.

Solution

Because the pressures are given in two different units, one of them must be changed.



	Pressure	Volume
1	0.950 atm	1.45 L
2	$787 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.036 \text{ atm}$	V_2

Now the problem can be solved as in Example 12.2:

$$P_1V_1 = P_2V_2$$

$$(0.950 \text{ atm})(1.45 \text{ L}) = (1.036 \text{ atm})V_2$$

$$V_2 = 1.33 \text{ L}$$

Alternatively, we could change the 0.950 atm to torr:

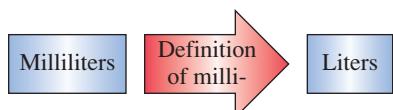
$$(722 \text{ torr})(1.45 \text{ L}) = (787 \text{ torr})V_2$$

$$V_2 = 1.33 \text{ L}$$

Practice Problem 12.3 Calculate the initial volume of a sample of gas at 1.20 atm if its volume is changed to 70.4 mL as its pressure is changed to 744 torr at constant temperature.

EXAMPLE 12.4

Calculate the pressure required to change a 3.38-L sample of gas initially at 1.15 atm to 925 mL, at constant temperature.

Solution

	Pressure	Volume
1	1.15 atm	3.38 L
2	P_2	$925 \text{ mL} = 0.925 \text{ L}$

$$(1.15 \text{ atm})(3.38 \text{ L}) = P_2(0.925 \text{ L})$$

$$P_2 = 4.20 \text{ atm}$$

The pressure must be raised to 4.20 atm.

Practice Problem 12.4 Calculate the initial pressure of a 485-mL sample of gas that has been changed at constant temperature to 1.16 L and 1.18 atm.

ChemSkill Builder
7.1, 7.2

Snapshot Review

Boyle's law applies to a given sample of gas at constant temperature.

- A. If the pressure on a sample of gas is increased fivefold and the temperature does not change, what happens to the volume?

12.3 Charles' Law

Section 12.2 discussed the effect of pressure on the volume of a gas at constant temperature. In 1787, 125 years after Boyle published the law that bears his name, J. A. C. Charles (1746–1823) discovered a law relating the volume of a given sample of gas to its **absolute temperature**. It took more than a century to discover this law because of the requirement that the temperature be absolute.

The volume of a sample of gas varies with the temperature, as shown in Table 12.1 and plotted in Figure 12.4(a) for a particular sample. Although the volume changes with the Celsius temperature, the relationship is *not* a **direct proportionality**. That is, when the Celsius temperature doubles, the volume does not double, all other factors being held constant. On the graph, the plotted points form a straight line, but the line does *not* pass through the origin. For a direct proportionality to exist, the straight line must pass through the origin. If the straight line corresponding to the points in Table 12.1 is extended until the volume reaches 0 L, the Celsius temperature is -273°C (Figure 12.4b). Charles defined a new temperature scale in which the lowest possible temperature is 0° absolute, corresponding to -273°C . This temperature is called **absolute zero**. Each unit on this scale is defined as being the same size as a degree on the Celsius scale. Thus, each temperature on the absolute scale is 273 units greater than the same temperature on the Celsius scale (Figure 12.5). The symbol T is used for absolute temperature, and t is used for Celsius temperature:

$$T = t + 273$$

William Thomson (1824–1907), known as Lord Kelvin, first suggested using gas thermometers for measuring temperature. The absolute temperature scale is named after him. The **Kelvin scale** has units called **kelvins**, symbolized K, which are the same size as Celsius degrees. The word *degree* and the symbol for degrees (°) are not used with the Kelvin scale. The Kelvin (absolute) scale must be used in all gas law problems involving temperature.

The Kelvin (absolute) scale must be used in all gas law problems involving temperature.

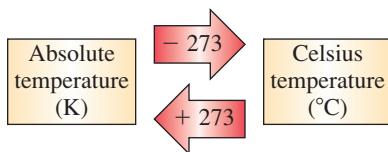
EXAMPLE 12.5

Calculate the equivalent temperature on the other scale (Kelvin or Celsius) for each of the following:

- (a) 0 K (b) 0°C (c) 37°C (d) -273°C (e) 273 K

Solution

- (a) $0 \text{ K} - 273 = -273^{\circ}\text{C}$ (b) $0 + 273 = 273 \text{ K}$
 (c) 310 K (d) 0 K (e) 0°C



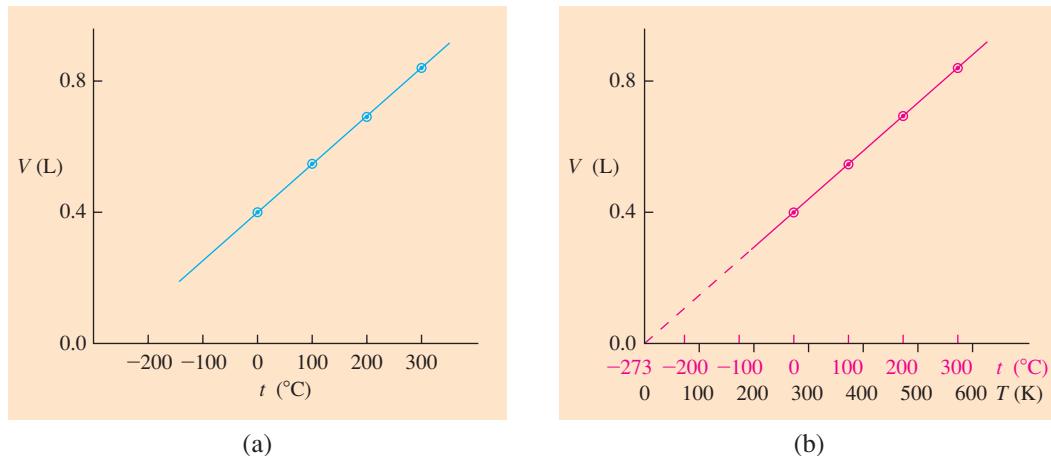
12.3 ■ Charles' Law**323**

Figure 12.4 Dependence of Volume on Temperature at Constant Pressure

(a) Plot of the data given in Table 12.1. (b) Extension of the line in part (a) to absolute zero, with the Kelvin scale added to the horizontal axis.

Practice Problem 12.5 What is normal human body temperature, 98.6°F, on the Kelvin scale? (See Section 2.6, if necessary.)

Charles' law states that the volume of a given sample of gas is directly proportional to its *absolute* temperature. In Table 12.2, the data of Table 12.1 are expanded to include the corresponding absolute temperatures. Note that dividing the volume by the corresponding absolute temperature for each experiment in Table 12.2 yields the same ratio for all the experiments. That means that the volume and the absolute temperature are directly proportional, which can be stated as an equation:

$$\frac{V}{T} = k \quad \text{or} \quad V = kT$$

Figure 12.5 Comparison of Temperature Scales (Schematic)

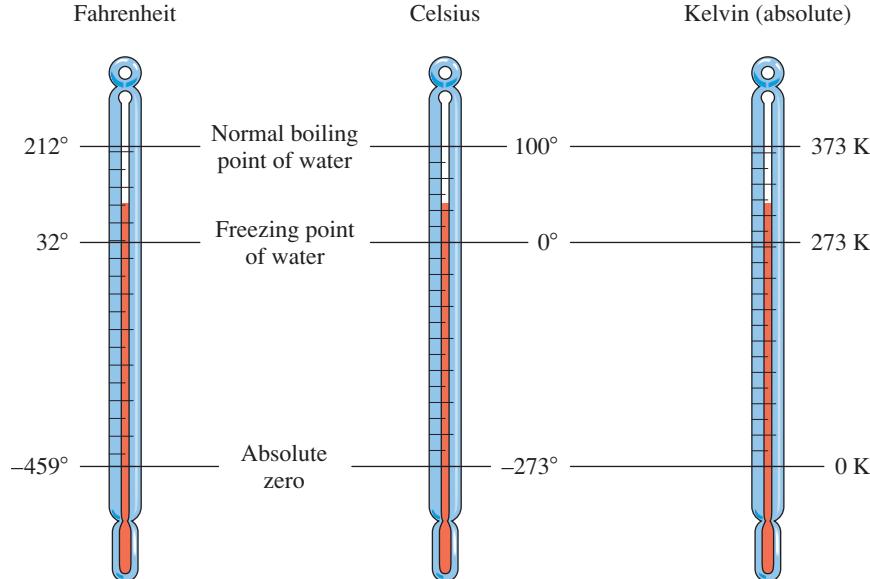


Table 12.2 Temperature and Volume Data for a Particular Sample of Gas at a Given Pressure

	Temperature (°C)	Volume (L)	Temperature (K)	V/T (L/K)
1	0	0.400	273	0.00147
2	100	0.548	373	0.00147
3	200	0.692	473	0.00146
4	300	0.840	573	0.00147

The equation may also be written in terms of two sets of conditions of a given sample of gas at constant pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Absolute temperatures must be used in all gas law problems involving temperature.

EXAMPLE 12.6

Show that the data in Table 12.2 prove (a) that the Celsius temperature is *not* directly proportional to volume and (b) that the Kelvin temperature is directly proportional to volume.

Solution

- One obvious example: As the temperature 0°C is doubled (to 0°C), the volume does not change. The volume is *not* directly proportional to Celsius temperature.
- As the absolute temperature 273 K is increased to 373 K or 473 K, the volume increases to $373/273 = 1.37$ or $473/273 = 1.73$ times the original volume. The ratio of V to T is constant (see Table 12.2). The volume is directly proportional to *absolute* temperature.

Practice Problem 12.6 Qualitatively, what is the effect on the volume of a sample of gas at constant pressure of doubling the Celsius temperature from -1°C to -2°C ?

As with the Boyle's law equation ($P_1V_1 = P_2V_2$), we can solve problems using the Charles' law equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

12.4 ■ The Combined Gas Law**325**

In most Charles' law problems, the values of three of these four variables are given, and the value for the remaining one is to be calculated. The units of temperature on both sides of this equation *must* be kelvins, however; they cannot merely be the same, as with the units of volume.

EXAMPLE 12.7

Calculate the Celsius temperature to which a 678-mL sample of gas at 0°C must be heated at constant pressure for the volume to change to 0.896 L.

Solution

The data are tabulated, with 678 mL converted to 0.678 L:

	Temperature (°C)	Volume (L)	Temperature (K)
1	0	0.678	0 + 273 = 273 K
2	t_2	0.896	T_2
	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	or, inverting <i>both sides</i> ,	$\frac{T_1}{V_1} = \frac{T_2}{V_2}$

$$\frac{273 \text{ K}}{0.678} = \frac{T_2}{0.896 \text{ L}}$$

$$T_2 = 361 \text{ K} \quad t_2 = 361 \text{ K} - 273 = 88^\circ\text{C}$$

Practice Problem 12.7 Calculate the original temperature of a 0.456-mL gas sample if it is expanded at constant pressure to 1.75 L at 55°C.

**Snapshot Review**

ChemSkill Builder
7.1, 7.2

- Charles' law applies to a given sample of gas at constant pressure.
 - The Kelvin temperature scale must be used with all gas laws that include a temperature.
- A. If the absolute temperature of a sample of gas doubles and the pressure does not change, what happens to the volume?
- B. Convert 325 K to degrees Celsius.

12.4 The Combined Gas Law

Boyle's and Charles' laws may be merged into one law, called the **combined gas law**, expressed in equation form as follows:

$$\frac{PV}{T} = k \quad \text{or} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Most combined gas law problems involve solving for one of the variables in the second of these equations when the other five variables are given. Neither temperature nor pressure has to be held constant, but the law applies only to a given sample of gas, and the temperatures must be in kelvins.

EXAMPLE 12.8

Calculate the volume of a sample of gas originally occupying 908 mL at 717 torr and 20°C after its temperature and pressure are changed to 72°C and 1.07 atm.

Solution

Again, tabulating the data is a good idea. The volume can be stated in milliliters in both states. The pressure can be stated in atmospheres in both. The temperature must be in kelvins in both states; it cannot merely be in the same unit in both states.

	Pressure	Volume	Temperature
1	$717 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.9434 \text{ atm}$	908 mL	$20 + 273 = 293 \text{ K}$
2	1.07 atm	V_2	$72 + 273 = 345 \text{ K}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
$$\frac{(0.9434 \text{ atm})(908 \text{ mL})}{(293 \text{ K})} = \frac{(1.07 \text{ atm})V_2}{(345 \text{ K})}$$
$$V_2 = 943 \text{ mL}$$

Practice Problem 12.8 Calculate the original volume of a sample of gas that is at 717 torr and 20°C before its volume, temperature, and pressure are changed to 908 mL, 72°C, and 1.07 atm.

A temperature of 0°C and a pressure of 1.00 atm constitute a set of conditions for a gas often called **standard temperature and pressure** (abbreviated STP).

EXAMPLE 12.9

A 17.3-mL sample of gas originally at standard temperature and pressure is changed to 10.9 mL at 678 torr. Calculate its final temperature in degrees Celsius.

Solution

	Pressure	Volume	Temperature
1	1.00 atm	17.3 mL	$0 + 273 = 273 \text{ K}$
2	$678 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.8921 \text{ atm}$	10.9 mL	T_2

12.5 ■ The Ideal Gas Law**327**

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{(1.00 \text{ atm})(17.3 \text{ mL})}{(273 \text{ K})} = \frac{(0.8921 \text{ atm})(10.9 \text{ mL})}{T_2}$$

$$(0.06337)T_2 = 9.724 \text{ K}$$

$$T_2 = 153 \text{ K}$$

The problem requires the answer in Celsius:

$$153 \text{ K} - 273 = -120^\circ\text{C}$$

Practice Problem 12.9 Calculate the volume at standard temperature and pressure of a sample of gas that has a volume of 49.7 mL at 52°C and 811 torr.



Snapshot Review



ChemSkill Builder
7.1, 7.2

- If both temperature and pressure of a given sample of gas change, the combined gas law can be used to calculate the volume.

- A. Calculate the new volume after a 2.00-L sample of gas at 1.50 atm and 127°C is changed to 27°C at 3.50 atm.

12.5 The Ideal Gas Law

The gas laws presented in the preceding sections apply to a given sample of gas. The combined gas law, written in the form

$$\frac{PV}{T} = k$$

may be rewritten as

$$\frac{PV}{T} = nR$$

where n represents the number of moles of gas molecules in the sample and R is another constant, valid for *any* sample of *any* gas. For the purpose of the gas laws, an atom of a monatomic gas, such as neon, is considered a molecule.

EXAMPLE 12.10

Consider a given sample of gas with pressure P and volume V at temperature T (Figure 12.6). A second sample of the same gas under the same conditions would have the same value of k , the constant in the combined gas law. What combined gas law constant would apply to the two samples of gas together?

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CHAPTER 12 ■ Gases

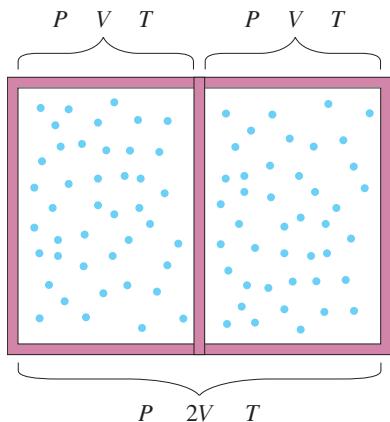
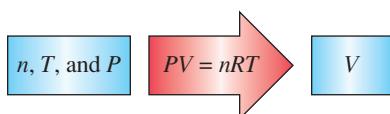


Figure 12.6 Combination of Two Identical Samples of Gas

Two samples of a gas that have the same volume, temperature, and pressure will have equal numbers of moles present. If the wall between the two samples were removed, the combined sample would have the same temperature and pressure as the original samples, but would have twice the volume and twice the number of moles. The volume of a gas under conditions of constant temperature and pressure is directly proportional to the number of moles present.



Solution

Because the volume would be doubled if the gas samples were combined at the same temperature and pressure, the constant would also have to be doubled: It would equal $2k$. The more gas there is, the bigger the constant. Thus, separating the quantity of gas from the part of the constant that is not dependent on quantity is appropriate, which is what the ideal gas law does. The new constant is called R instead of k . The quantity of gas is given as n , the number of moles of gas.

The ideal gas law works approximately for all samples of any gas. The law works exactly only for a hypothetical “ideal” gas, from which it gets its name. The constant R has the value of $0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$, no matter what gas or what size sample is under consideration. The value of R can be stated in other units, but the ideal gas law equation is easiest to use when pressure is in atmospheres and volume in liters. As usual, temperature must be expressed in kelvins. The equation expressing the **ideal gas law**, given as $PV/T = nR$ previously, is usually rearranged to the form

$$PV = nRT$$

Note that R is the same for any sample of any gas, no matter what its size or composition.

EXAMPLE 12.11

Calculate the volume of 1.63 mol of carbon dioxide gas at 295 K and 1.14 atm.

Solution

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(1.63 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(295 \text{ K})}{1.14 \text{ atm}} = 34.6 \text{ L}$$

Practice Problem 12.11 Calculate the volume of 0.898 mol of methane gas, CH_4 , at 292 K and 1.06 atm.

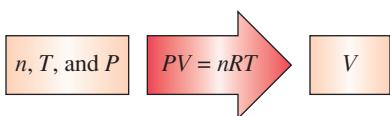
EXAMPLE 12.12

Calculate the volume of 42.6 g of oxygen gas at 35°C and 792 torr.

Solution

Because the value of R given previously has units of liters, atmospheres, moles, and kelvins, the data given here are converted to these units:

$$792 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.042 \text{ atm} \quad 35^\circ\text{C} + 273 = 308 \text{ K}$$

12.5 ■ The Ideal Gas Law**329**

$$42.6 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 1.331 \text{ mol O}_2$$

$$V = \frac{nRT}{P} = \frac{(1.331 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(308 \text{ K})}{1.042 \text{ atm}} = 32.3 \text{ L}$$

Practice Problem 12.12 Calculate the volume of 7.11 g of nitrogen gas at 16°C and 799 torr.

Students sometimes wonder “How do I decide when to use the combined gas law and when to use the ideal gas law?” The answer depends on the problem, naturally. If moles are involved, the combined gas law cannot be used.

EXAMPLE 12.13

Decide which gas law should be used to solve each of the following:

- Calculate the final volume of a sample of gas that has an initial volume of 7.10 L at STP if the temperature and pressure are changed to 33°C and 696 torr.
- Calculate the volume of 0.977 mol of gas at 33°C and 792 torr.

Solution

- The combined gas law can be used.
- This problem involves moles and must be solved with the ideal gas law.

EXAMPLE 12.14

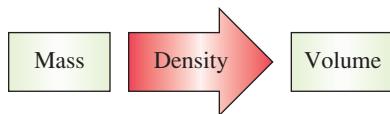
Calculate the volume of 12.7 g of water at 25°C and 1.00 atm.

Solution

Under these conditions, water is not a gas, and the ideal gas law cannot be used. The density of liquid water is 1.00 g/mL (Section 2.5), and thus the volume is 12.7 mL.

$$12.7 \text{ g} \left(\frac{1 \text{ mL}}{1.00 \text{ g}} \right) = 12.7 \text{ mL}$$

Not only the laws, but also when to use each one, must be learned.

**EXAMPLE 12.15**

Calculate the pressure of 0.0789 mol of chlorine gas that occupies 891 mL at –15°C.

Solution

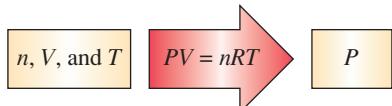
The quantities given are converted to the units generally used with the ideal gas law equation. Note that the nature of the gas is immaterial as long as the number of moles is known.

$$891 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.891 \text{ L} \quad -15 + 273 = 258 \text{ K}$$

The pressure is then calculated from the ideal gas law equation:

$$P = \frac{nRT}{V} = \frac{(0.0789 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(258 \text{ K})}{0.891 \text{ L}} = 1.88 \text{ atm}$$

Practice Problem 12.15 Calculate the pressure of 0.0855 mol of neon gas that occupies 66.1 mL at 25°C.

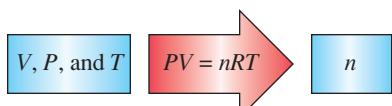
**EXAMPLE 12.16**

Calculate the number of moles of oxygen gas in a 2.60-L container at 19°C and 755 torr.

Solution

$$19^\circ\text{C} + 273 = 292 \text{ K} \quad 755 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.9934 \text{ atm}$$

$$n = \frac{PV}{RT} = \frac{(0.9934 \text{ atm})(2.60 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(292 \text{ K})} = 0.108 \text{ mol}$$

**Snapshot Review**

ChemSkill Builder 7.3

- The ideal gas law, $PV = nRT$, applies (at least approximately) to any sample of any gas.

A. Calculate the volume of 0.509 mol of O₂ at 289 K and 1.00 atm.

12.6 Dalton's Law of Partial Pressures

In a mixture of gases, all the components occupy the entire volume of the container, and all have the same temperature. The pressures of the individual gases, as well as the numbers of moles of the gases, may vary.

A mixture of gases follows the same laws as a gas composed of only one substance. **Dalton's law of partial pressures** enables us to consider the properties of each component of a gas mixture. The law states that the sum of the

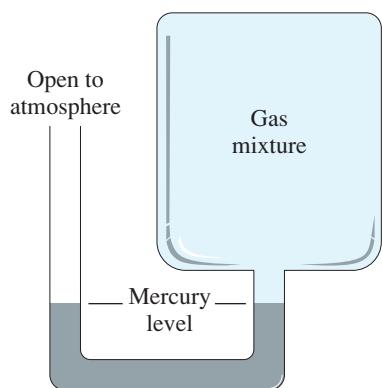
12.6 ■ Dalton's Law of Partial Pressures**331**

Figure 12.7 Situation in Which the Total Pressure of a Mixture of Gases Equals Barometric Pressure

Because the mercury levels are the same, the pressure of the gas mixture is equal to the pressure of the atmosphere—barometric pressure.

individual pressures of the components of a gaseous mixture is equal to the total pressure of the mixture:

$$P_{\text{total}} = P_1 + P_2 + \cdots + P_n \quad (\text{One pressure, } P_i, \text{ for each gas, } i)$$

The pressures of the individual components of a mixture are called **partial pressures**. If the mixture is contained in a way that its pressure is equal to that of the atmosphere (Figure 12.7), the total pressure is equal to the barometric pressure.

EXAMPLE 12.17

A mixture of oxygen and neon contains oxygen at a pressure of 726 torr and neon at a pressure of 44 torr. What is the pressure of the mixture?

Solution

$$P_{\text{total}} = P_{\text{Ne}} + P_{\text{O}_2} = 44 \text{ torr} + 726 \text{ torr} = 770 \text{ torr}$$

Practice Problem 12.17 A mixture of oxygen and neon has a barometric pressure of 1.031 atm. If the pressure of the oxygen is 0.922 atm, what is the pressure of the neon?

The ideal gas law applies to a mixture of gases as a whole and also to each of its components. That is,

$$P_{\text{total}}V = n_{\text{total}}RT \quad \text{and} \quad P_iV = n_iRT$$

where i stands for any component of the mixture.

EXAMPLE 12.18

Calculate the total number of moles in a 10.5-L sample of gas at 292 K, containing O₂ at 0.622 atm and N₂ at 0.517 atm. Also calculate the number of moles of O₂ present.

Solution

The total pressure of the gas mixture is

$$0.622 \text{ atm} + 0.517 \text{ atm} = 1.139 \text{ atm}$$

The total number of moles is

$$n_{\text{total}} = \frac{(1.139 \text{ atm})(10.5 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(292 \text{ K})} = 0.499 \text{ mol}$$

The number of moles of O₂ is

$$n_{\text{O}_2} = \frac{(0.622 \text{ atm})(10.5 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(292 \text{ K})} = 0.272 \text{ mol O}_2$$

We can calculate the number of moles of oxygen another way. Because the oxygen and the gas mixture are both at the same temperature and have the same volume, the numbers of moles are proportional to the pressures:

$$\frac{P_{O_2}V}{P_{\text{total}}V} = \frac{n_{O_2}RT}{n_{\text{total}}RT}$$

$$\frac{P_{O_2}}{P_{\text{total}}} = \frac{n_{O_2}}{n_{\text{total}}}$$

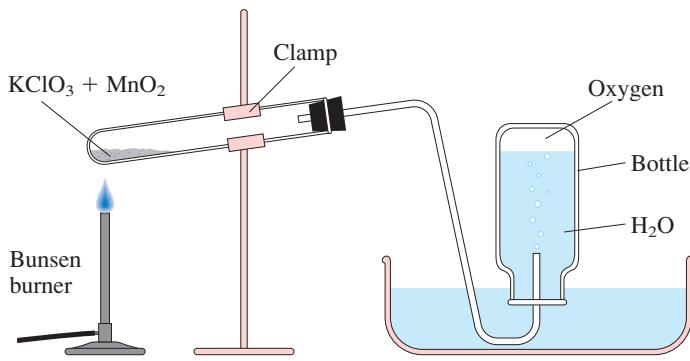
$$\frac{0.622 \text{ atm}}{1.139 \text{ atm}} = \frac{n_{O_2}}{0.499 \text{ mol}}$$

$$n_{O_2} = 0.273 \text{ mol O}_2$$

Gases that are only very slightly soluble in water are often collected over water (Figure 12.8). Gases in contact with liquid water will contain water vapor. The pressure of the water vapor in such a system does not vary as the pressure of an ordinary gas varies. For example, if we expand the gas, the pressure of the other components will drop (according to Boyle's law). The pressure of the water vapor drops initially, but, more liquid water will evaporate into the gas phase, and the pressure of the water vapor will climb back to its original value (as long as there is liquid water left and once enough time has elapsed for the evaporation process to have taken place). If the gas mixture is compressed instead, the pressure of the water vapor does not increase; instead some of the water vapor condenses into the liquid phase. At a given temperature, the pressure of water vapor in contact with liquid water is a constant, called the **vapor pressure** of water at that temperature. Vapor pressure is independent of the volume of the liquid and the volume of the gas mixture; it is also independent of the shape of the container and the surface area of the liquid. The *only* factor that determines the vapor pressure of pure water is *temperature*. The higher the temperature, the higher the vapor pressure of water is (Figure 12.9). The relationship is *not* a direct proportionality, however. Table 12.3 lists water vapor pressures at various temperatures. These values need not be memorized (except that at 100°C, which is easy to remember).

Figure 12.8 Collection of Oxygen over Water

A bottle filled with water is inverted in a pan of water. A test tube containing potassium chlorate and manganese(IV) oxide (the catalyst) is arranged so that the oxygen produced when the tube is heated displaces the water in the bottle. The mass lost from the test tube corresponds to the mass of oxygen produced. The oxygen in the bottle will have water vapor mixed with it.

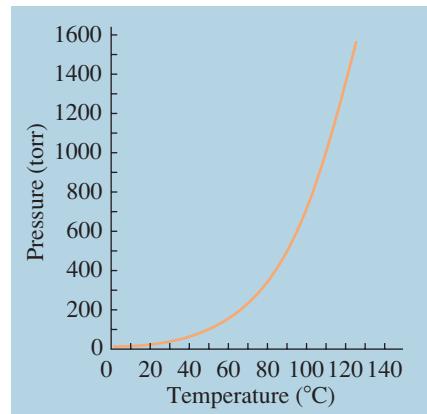


12.6 ■ Dalton's Law of Partial Pressures**333**

Figure 12.9 Variation of the Vapor Pressure of Water with Temperature

Table 12.3 Vapor Pressure of Water at Various Temperatures

Temperature (°C)	Pressure (torr)
-15	1.436
-10	2.149
-5	3.163
0	4.579
5	6.543
10	9.209
15	12.788
20	17.535
21	18.650
22	19.827
23	21.068
24	22.377
25	23.756
26	25.209
27	26.739
28	28.349
29	30.043
30	31.824
35	42.175
40	55.324
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
99	733.24
100	760.00
101	787.57
105	906.07
110	1074.56



The law of partial pressures applies to mixtures containing water vapor, as well as to other gas mixtures. Problems involving water vapor in contact with liquid water can be solved by taking the vapor pressure from a table such as Table 12.3.

EXAMPLE 12.19

Oxygen gas is collected over water in an apparatus such as that shown in Figure 12.8 at a barometric pressure of 759 torr at 23°C.

- What is the pressure of the water vapor?
- What is the pressure of the oxygen gas?

Solution

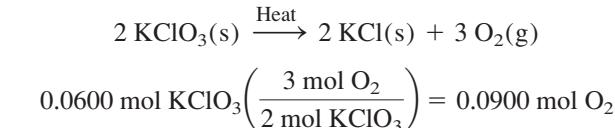
- The water vapor pressure at 23°C is 21.1 torr, taken from Table 12.3.
- The pressure of the oxygen gas is

$$P_{\text{O}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}} = 759 \text{ torr} - 21.1 \text{ torr} = 738 \text{ torr}$$

EXAMPLE 12.20

What volume of oxygen, collected over water, will be obtained at 23°C and 762 torr barometric pressure from the thermal decomposition of 0.0600 mol of KClO_3 ?

Solution



Since we have the number of moles of *oxygen*, we must use the partial pressure of oxygen, which is the barometric pressure minus the water vapor pressure (from Table 12.3):

$$\begin{aligned}P_{\text{O}_2} &= 762 \text{ torr} - 21.1 \text{ torr} = 741 \text{ torr} \\V &= \frac{nRT}{P} = \frac{(0.0900 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(296 \text{ K})}{(741 \text{ torr})(1 \text{ atm}/760 \text{ torr})} \\&= 2.24 \text{ L}\end{aligned}$$



ChemSkill Builder 7.4

Snapshot Review

- A *mixture* of gases behaves physically much like a gaseous sample of a pure substance.
 - The volume of each gas in a mixture is the same; the temperature of each gas in a mixture is the same; the ratio(s) of the partial pressures is (are) the same as the ratio(s) of numbers of moles.
 - The ideal gas law can be used for the entire mixture or any single component. If the entire mixture is used, the total pressure and the total number of moles are used.
- A. Calculate the mole ratio of gases A and B in a mixture if A has a partial pressure of 0.500 atm and B has a partial pressure of 0.750 atm.

12.7 Molar Masses and Molecular Formulas

The ideal gas law may be used to determine the molar mass of a gaseous substance. To determine a molar mass, we need the mass of a given sample and also the number of moles in that sample. The ideal gas law can be used to determine the number of moles.

EXAMPLE 12.21

Calculate the volume that 48.3 g of sulfur dioxide gas occupies at standard temperature and pressure.

Solution

The molar mass of SO_2 is used to calculate the number of moles of SO_2 present:

$$48.3 \text{ g } \text{SO}_2 \left(\frac{1 \text{ mol } \text{SO}_2}{64.1 \text{ g } \text{SO}_2} \right) = 0.7535 \text{ mol } \text{SO}_2$$

The ideal gas law then enables us to calculate the volume under the stated conditions:

$$V = \frac{nRT}{P} = \frac{(0.7535 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}} = 16.9 \text{ L}$$

12.7 ■ Molar Masses and Molecular Formulas**335**

Practice Problem 12.21 Calculate the volume that 48.3 g of CO₂ occupies at 0°C and 1.00 atm. Compare the answer with that of Example 12.21, and explain any difference.

EXAMPLE 12.22

A 92.8-g sample of a pure gaseous substance occupies 29.5 L at 27°C and 1.25 atm. Calculate the molar mass of the gas.

Solution

We recognize immediately that given the volume, temperature, and pressure of a gaseous substance, we can calculate the number of moles:

$$n = \frac{PV}{RT} = \frac{(1.25 \text{ atm})(29.5 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(300 \text{ K})} = 1.497 \text{ mol}$$

The molar mass is simply the mass divided by the number of moles:

$$\frac{92.8 \text{ g}}{1.497 \text{ mol}} = 62.0 \text{ g/mol}$$

Practice Problem 12.22 Calculate the molar mass of a gas if a 3.38-g sample occupies 2.76 L at 22°C and 793 torr.

With empirical formulas (Section 7.4) and molar masses, we can calculate molecular formulas (Section 7.5).

EXAMPLE 12.23

Calculate the molecular formula of a gaseous compound composed of 92.26% C and 7.74% H if 0.507 g of the compound occupies 478 mL at 23°C and 0.989 atm pressure.

Solution

Even if we cannot see how to solve this problem completely at first glance, we can tell immediately that the empirical formula can be calculated from the percent composition and that the number of moles can be calculated from its pressure-volume-temperature data.

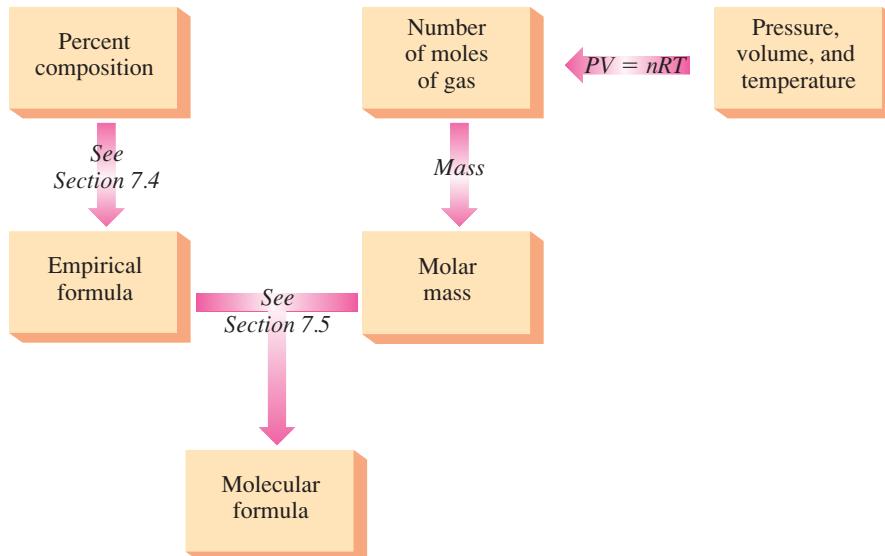
$$92.26 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.682 \text{ mol C}$$

$$7.74 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 7.68 \text{ mol H}$$

The mole ratio of hydrogen to carbon is 1 : 1, so the empirical formula is CH.

We can calculate the number of moles of gas present from the pressure, volume, and temperature data:

$$n = \frac{PV}{RT} = \frac{(0.989 \text{ atm})(0.478 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(296 \text{ K})} = 0.01945 \text{ mol}$$



The molar mass is the mass divided by the number of moles:

$$\frac{0.507 \text{ g}}{0.01945 \text{ mol}} = 78.1 \text{ g/mol}$$

The mass of a mole of empirical formula units is

$$12.0 \text{ g} + 1.0 \text{ g} = 13.0 \text{ g}$$

$$\frac{26.1 \text{ g}}{13.0 \text{ g}} = 6$$

so the molecular formula is twice the empirical formula, C_2H_2 .

Practice Problem 12.23 A 3.53-g sample of a gaseous hydrocarbon occupies 2.90 L at 24°C and 749 torr. The gas is composed of 79.89% C and the rest hydrogen. What is the molecular formula of the gas?

We can calculate the density of a gas using the ideal gas law plus molar mass data.

EXAMPLE 12.24

Determine the density of nitrogen at STP.

Solution

It is easy to calculate the number of moles of nitrogen gas per liter using the ideal gas law:

$$\begin{aligned}\frac{n}{V} &= \frac{P}{RT} = \frac{1.00 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(273 \text{ K})} \\ &= 0.04462 \text{ mol/L}\end{aligned}$$

12.8 ■ Gases in Chemical Reactions**337**

The density, the number of grams per liter, is obtained using the molar mass as a conversion factor:

$$\text{Density} = (0.04462 \text{ mol/L})(28.0 \text{ g/mol}) = 1.25 \text{ g/L}$$

Practice Problem 12.24 Determine the density of SO_3 at 25°C and 789 torr.

EXAMPLE 12.25

Calculate the pressure at 22°C at which oxygen has a density of 1.44 g/L.

Solution

We first change the density in grams per liter to moles per liter, then use that value in the ideal gas law:

$$(1.44 \text{ g O}_2/\text{L})[(1 \text{ mol O}_2)/(32.0 \text{ g O}_2)] = 0.0450 \text{ mol O}_2/\text{L}$$

$$P = \left(\frac{n}{V}\right)RT = (0.0450 \text{ mol/L})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(295 \text{ K}) \\ = 1.09 \text{ atm}$$

Practice Problem 12.25 Calculate the temperature at which oxygen has a density of 3.00 g/L at 1.50 atm.

**Snapshot Review**

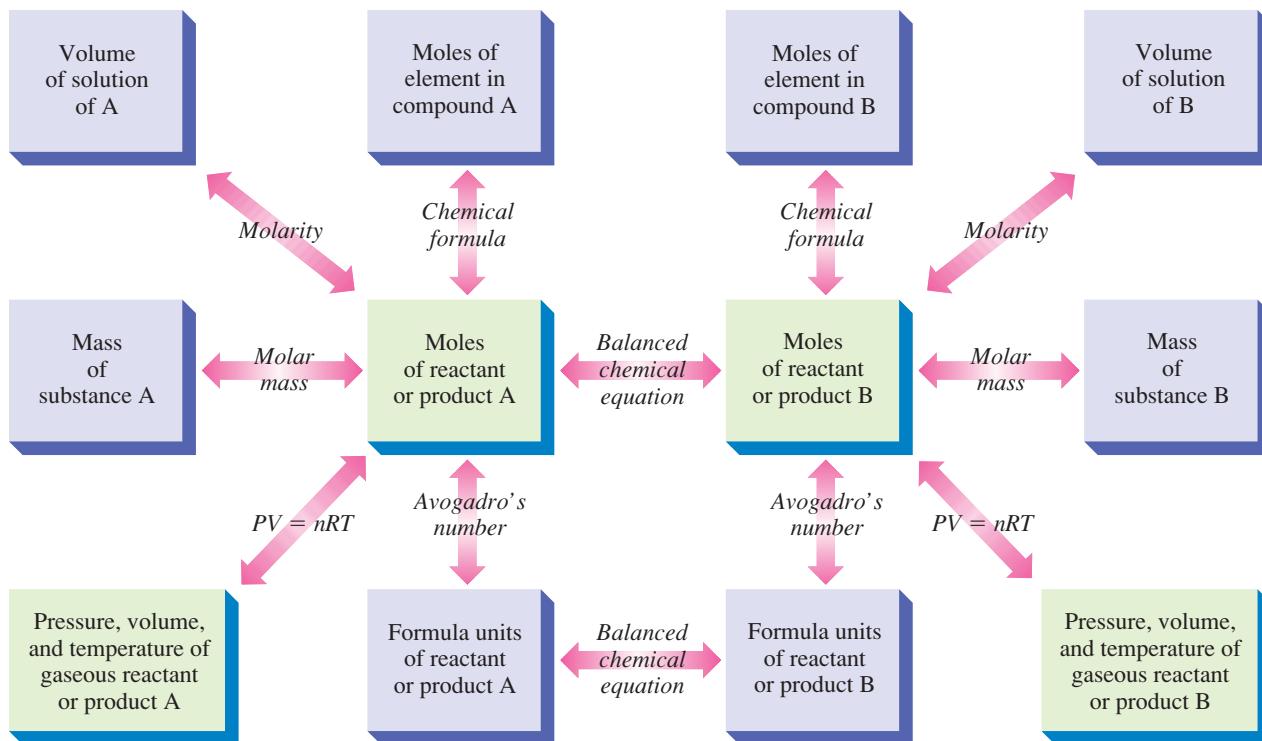
- The ideal gas law can be used to calculate the number of moles of gas in a sample of known mass. The number of grams divided by the number of moles in the sample yields the molar mass.
 - The density of a gas can be converted to moles per liter, and that value used in the ideal gas law equation.
- A. Calculate the molar mass (MM) of a gas if 2.24 g occupies 0.912 L at 287 K and 1.45 atm.
 B. Calculate the molar mass of a gas with density 2.75 g/L at STP.

12.8 Gases in Chemical Reactions

Gases that are involved in chemical reactions obey the same laws of stoichiometry that apply to substances in any other state, as described in Chapters 8 and 10. Therefore, the ideal gas law can be used to calculate the quantities of gaseous substances involved in a reaction and then those results used to find the quantities of other substances. Figure 12.10 presents the conversions allowed by the ideal gas law (with green backgrounds), in addition to those originally shown in earlier figures.

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CHAPTER 12 ■ Gases

**Figure 12.10** Mole

Conversions, Including Application of the Ideal Gas Law to Determine the Number of Moles of a Gaseous Reactant or Product

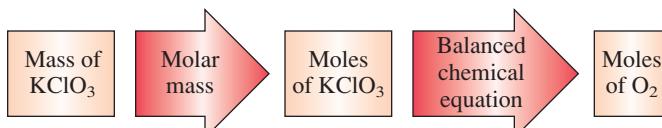
The green boxes represent the new additions to concepts already learned.

EXAMPLE 12.26

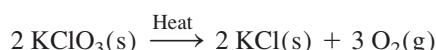
How many liters of oxygen gas at 21°C and 1.13 atm can be prepared by thermal decomposition of 0.950 g of KClO₃?

Solution

The number of moles of oxygen produced in a chemical reaction can be calculated as shown in Chapter 10. Thus, the problem involves moles (even though the word *moles* is not explicitly stated), and so the ideal gas law is used.



$$0.950 \text{ g KClO}_3 \left(\frac{1 \text{ mol KClO}_3}{122 \text{ g KClO}_3} \right) = 0.007787 \text{ mol KClO}_3$$

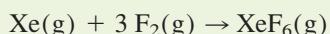


The number of moles of O₂ produced is

$$0.007787 \text{ mol KClO}_3 \left(\frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \right) = 0.01168 \text{ mol O}_2$$

12.8 ■ Gases in Chemical Reactions**339****ITEM OF INTEREST**

In 1962, Neil Bartlett produced a reaction of xenon, the first reported reaction of any noble gas. Later it was found that fluorine reacts directly with xenon to give one of three xenon fluorides, depending on temperature and pressure. Because all the products and the reactants are colorless, the easiest way to tell that a reaction is occurring is the drop in the total pressure of the system as the number of moles of gas decreases. For example,

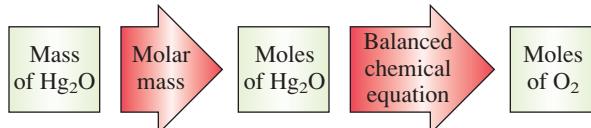
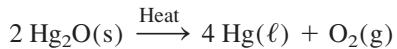


We can now use the ideal gas law equation:

$$V = \frac{nRT}{P} = \frac{(0.01168 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(294 \text{ K})}{1.13 \text{ atm}} = 0.249 \text{ L}$$

EXAMPLE 12.27

A chemist decomposes 1.06 g of Hg_2O in a sealed system. The oxygen produced has a pressure of 0.514 atm and a volume of 62.5 mL at 35°C. Calculate the value of R from these data.

Solution

$$1.06 \text{ g Hg}_2\text{O} \left(\frac{1 \text{ mol Hg}_2\text{O}}{417 \text{ g Hg}_2\text{O}} \right) \left(\frac{1 \text{ mol O}_2}{2 \text{ mol Hg}_2\text{O}} \right) = 0.001271 \text{ mol O}_2$$

$$R = \frac{PV}{nT} = \frac{(0.514 \text{ atm})(0.0625 \text{ L})}{(0.001271 \text{ mol})(308 \text{ K})} = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$$

Practice Problem 12.27 Calculate the volume of 1.00 mol of a gas at STP.

EXAMPLE 12.28

As N_2 and H_2 react to form NH_3 in a large cylinder at 500°C, what happens to (a) the total number of atoms? (b) the total number of molecules? (c) the total pressure?

Solution

- (a) The number of atoms stays the same, as is true for all reactions. That is the basis for the balanced chemical equation.
- (b) $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$
The total number of moles of gas decreases as this reaction proceeds, so the number of molecules also decreases.
- (c) The total pressure decreases as the total number of moles of gas decreases.

**Snapshot Review**

The number of moles of gas involved a chemical reaction, calculated from the ideal gas law, can be used with the balanced chemical equation to determine the number of moles of any other reactant or product in the reaction. Also, the number of moles of any gas, calculated from the balanced chemical equation, can be used with other data in the ideal gas law to calculate the volume, temperature, or pressure of the gas.

- A. How many liters of CO_2 at STP can be prepared by the complete thermal decomposition of 0.150 mol of $\text{Ca}(\text{HCO}_3)_2$. The products are CaO , CO_2 , and H_2O .

12.9 Volume Ratios in Chemical Reactions

Gay-Lussac's law is true only for separate gases and only when their temperatures as well as their pressures are all equal.

For the special case when more than one gas is involved in a chemical reaction and all the gases are separate and measured at the same temperature and pressure, the **volume ratio** of the gases is equal to the mole ratio given in the balanced equation. This statement is known as **Gay-Lussac's law of combining volumes**.

EXAMPLE 12.29

Ammonium carbonate decomposes when heated to yield carbon dioxide, ammonia, and water vapor. Calculate the ratio of the (separate) volume of ammonia to that of water vapor, each at 450°C and 1.00 atm.

Solution

The mole ratio of the gases, given in the balanced equation, is

$$2 \text{ mol NH}_3 : 1 \text{ mol CO}_2 : 1 \text{ mol H}_2\text{O}$$

12.9 ■ Volume Ratios in Chemical Reactions**341**

The ammonia and water vapor are separated and measured at the given temperature and pressure. The ratio of their volumes can be calculated as follows:

$$\frac{V_{\text{NH}_3}}{V_{\text{H}_2\text{O}}} = \frac{n_{\text{NH}_3}RT/P}{n_{\text{H}_2\text{O}}RT/P}$$

Because R is a constant and both T and P are the same for the two gases, this equation reduces to

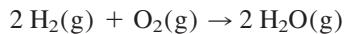
$$\frac{V_{\text{NH}_3}}{V_{\text{H}_2\text{O}}} = \frac{n_{\text{NH}_3}}{n_{\text{H}_2\text{O}}}$$

The right side of this equation is the ratio of the numbers of moles—the ratio given by the balanced chemical equation. The left side of the equation is the ratio of the volumes, so the ratio given by the balanced chemical equation is equal to the volume ratio *under these conditions*. The ratio is 2 : 1.

EXAMPLE 12.30

If 2.00 L of H₂ and 1.00 L of O₂, both at standard temperature and pressure, are allowed to react, will the water vapor they form at 250°C and 1.00 atm occupy 2.00 L?

Solution

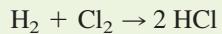


The volumes of H₂ and O₂ that react are in the ratio given in the balanced equation *because the two gases have the same temperature and pressure*. The volume of water vapor formed is *not* in that ratio, however, because its temperature is different. Its volume will be much greater than 2 L.

Practice Problem 12.30 If ammonium chloride is heated sufficiently to yield 4.29 L of hydrogen chloride gas and a separate sample of ammonia at the same temperature and pressure, what volume of ammonia gas is expected? What, if anything, can we tell about the volume of the ammonium chloride that decomposed?

ITEM OF INTEREST

The law of combining volumes contributed to the understanding that the elemental gases H₂, N₂, O₂, F₂, and Cl₂ are diatomic. For example, consider the reaction of H₂ and Cl₂. We write the reaction today as



In 1800, chemists did not know that the elementary gases were diatomic, and they wondered how *two* molecules of HCl were formed from *one* “molecule” of H and *one* of Cl. The law of combining volumes led Amedeo Avogadro (1776–1856) to postulate in 1811 a hypothesis that equal volumes of gases under like conditions of temperature and pressure contain equal numbers of *molecules*. The fact that molecules of hydrogen and chlorine had to be diatomic stemmed from this generalization.



Snapshot Review

- Two or more gases (not all substances in the reaction have to be gases) in a chemical reaction have a volume ratio equal to their mole ratio as long as the gases are separated and their volumes are measured at the same temperature and the same pressure.
- A. For the reaction $3 A(g) + B(s) \rightarrow 2 Z(g) + Q(g)$, how many liters of Z and how many liters of Q can be expected from 4.50 L of A, assuming that all the gases are measured at STP.

12.10 Kinetic Molecular Theory of Gases

When a wide variety of observations is grouped together in one generalization, that generalization is called a scientific law. The law of gravity is an example; it generalizes millions of observations that, when dropped, any object more dense than air near the surface of the Earth falls downward (toward the Earth). When an explanation for a law is proposed, that explanation is called a hypothesis. When a hypothesis is accepted as true by the scientific community in general, the hypothesis becomes a theory. For example, Einstein's theory of relativity is an explanation of the law of gravity (Section 1.6).

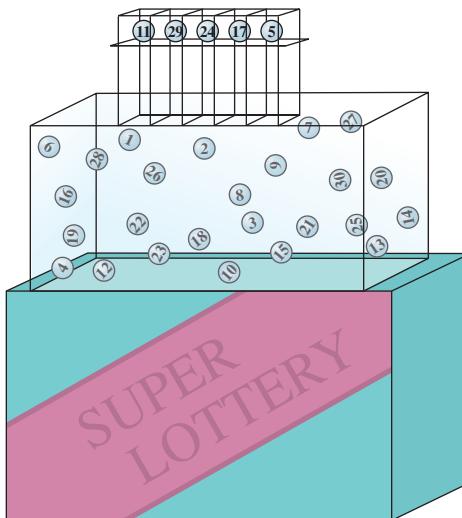
Several gas laws have been introduced in this chapter, but no explanation as to *why* those laws apply to all gases has been proposed. This section introduces the **kinetic molecular theory** of gases, which explains the gas laws and when extended, also explains some properties of liquids and solids. Five postulates explain why gases behave as they do:

1. Gases are composed of small molecules that are in constant, *random motion*.
2. The volume of the molecules is insignificant compared with the volume occupied by the gas.
3. Forces between the molecules are negligible, except when the molecules collide with one another.
4. Molecular collisions are *perfectly elastic*; that is, no energy is lost when the molecules collide.
5. The **average kinetic energy** of the gas molecules is directly proportional to the absolute temperature of the gas.

The **random motion** referred to in postulate 1 means that the molecules travel in straight lines in any arbitrary direction until they hit other molecules or the walls of the container (Figure 12.11). A **perfectly elastic collision**, referred to in postulate 4, means that the molecules bounce off one another without any loss of total energy. No friction or energy loss of any kind occurs. (Bowling balls returning to the top of the alley often hit other bowling balls in almost perfectly elastic collisions.) The average kinetic energy of the molecules referred to in postulate 5 does not mean that all the molecules travel with the same velocity at any one time or that one molecule travels with a constant velocity for any appreciable time. The average kinetic energy is the average of the **kinetic energies** of the individual molecules at any instant.

12.10 ■ Kinetic Molecular Theory of Gases**343****Figure 12.11** Lottery
Machine

The molecules of a gas are somewhat like the balls in a lottery machine. The balls travel in (relatively) straight paths until they hit the wall or another ball. The collisions do not produce much heat, so the total kinetic energy of the balls does not decrease much. Although the balls “fill” the machine, their total volume is much less than that of the machine, and there are no forces of attraction between the balls.

**EXAMPLE 12.31**

Calculate the volume occupied by 1.00 mol of H₂O at 100°C and 1.00 atm pressure when it is (a) in the vapor state and (b) in the liquid state (density = 0.958 g/mL).

Solution

(a) The ideal gas law (Section 12.5) yields the volume:

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(373 \text{ K})}{1.00 \text{ atm}} = 30.6 \text{ L}$$

(b) The volume of liquid water is its mass divided by its density (Section 2.5):

$$1.00 \text{ mol} \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) \left(\frac{1 \text{ mL H}_2\text{O}}{0.958 \text{ g H}_2\text{O}} \right) = 18.8 \text{ mL}$$

The same mole of H₂O occupies only 0.0188 L in the liquid state, but after it has been evaporated into the gas state, it occupies 30.6 L. As shown by the modern technique of electron diffraction, the molecules themselves do not expand. Because they do not expand, they cannot occupy more than 0.0188 L of the 30.6 L of the gas. The volume occupied by the molecules is negligible (less than one-tenth of 1% of the total volume). Thus, most of the volume of the gas is composed of empty space!

The kinetic molecular theory also explains why only an ideal gas obeys the gas laws exactly. Since the volume of the molecules themselves is negligible but not zero, the higher the pressure the smaller the volume of the gas will be, and the less negligible the volume of the molecules themselves becomes. Also, the lower the temperature, the lower the average kinetic energy of the molecules, and the more important the slight intermolecular forces become. Thus gases behave more ideally the higher the temperature and the lower the pressure.

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CHAPTER 12 ■ Gases



Snapshot Review



ChemSkill Builder 7.5

- The kinetic molecular theory explains the behavior of samples of gas based on the behavior of the molecules of the gas.
- The kinetic energy of any particle in motion is given by $KE = \frac{1}{2}mv^2$.

- A. Which postulate of the kinetic molecular theory explains why gases expand to fill their containers?

Key Terms

Key terms are defined in the Glossary.

absolute temperature (12.3)
absolute zero (12.3)
atmosphere (12.1)
atmospheric pressure (12.1)
average kinetic energy (12.10)
barometer (12.1)
barometric pressure (12.1)
Boyle's law (12.2)
Charles' law (12.3)
combined gas law (12.4)
Dalton's law of partial pressures (12.6)
direct proportionality (12.3)

force (12.1)
gas (12.1)
Gay-Lussac's law of combining volumes (12.9)
ideal gas law (12.5)
inverse proportionality (12.2)
kelvin (12.3)
Kelvin scale (12.3)
kinetic energy (12.10)
kinetic molecular theory (12.10)
liquid (12.1)
partial pressure (12.6)

perfectly elastic collision (12.10)
phase (12.1)
pressure (12.1)
random motion (12.10)
solid (12.1)
standard atmosphere (12.1)
standard temperature and pressure (12.4)
state (12.1)
torr (12.1)
vapor pressure (12.6)
volume ratio (12.9)

Symbols/Abbreviations

atm (atmosphere) (12.1)

P (pressure) (12.2)

t (Celsius temperature) (12.3)

K (kelvin) (12.3)

Pa (pascal) (12.1)

T (absolute temperature) (12.3)

mm Hg (millimeters of mercury) (12.1)

R (ideal gas law constant) (12.5)

V (volume) (12.2)

n (moles of gas) (12.5)

STP (standard temperature and pressure) (12.4)

Summary

The physical properties of gases do not depend on the composition of the gas. Pressure is defined as force per unit area. The pressure of a gas may be measured with a simple barometer, and one of the usual units used for pressure is related to that apparatus. A torr is the pressure required to hold one millimeter of mercury vertically in the barometer, and a standard atmosphere is the pressure required to hold 760 mm Hg vertically in the barometer (Section 12.1).

Boyle's law states that the volume of a given sample of gas at constant temperature is inversely proportional to its pressure. The law is often expressed in equation form as

$$P_1V_1 = P_2V_2 \quad (\text{At constant temperature})$$

If three of these quantities are known, the fourth may be calculated. In all gas law calculations, be sure to use the proper units for quantities (Section 12.2).

Charles' law states that the volume of a given sample of gas at constant pressure is directly proportional to its *absolute* temperature. The Kelvin scale is used with all gas laws in which temperature is involved. A Kelvin (absolute) temperature is equal to the corresponding Celsius temperature plus 273. In equation form, Charles' law may be written as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{At constant pressure})$$

■ Items for Special Attention

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If three of these quantities are known, the fourth can be calculated (Section 12.3).

Boyle's and Charles' laws may be combined into one law related to a given sample of gas. This combined gas law may be expressed as:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

If five of these quantities are given, the sixth may be calculated. Again, temperatures must be expressed in kelvins, and the units of pressure and of volume must be the same on both sides of the equation. Standard temperature and pressure, abbreviated STP, refers to 0°C and 1.00 atm (Section 12.4).

The ideal gas law relates (at least approximately) the pressure, volume, number of moles, and temperature of any sample of any gas under any conditions: $PV = nRT$. The value of the constant R usually used is 0.0821 L·atm/mol·K. If any three of the four variables are given, the fourth may be calculated. The ideal gas law is often useful for finding the number of moles of a gas. Because R is given in atmospheres and liters, these same units should be used for the pressure and volume, respectively. As always, the temperature must be in kelvins (Section 12.5).

Dalton's law of partial pressures states that in a mixture of gases, the total pressure is equal to the sum of the pressures of the individual gases—the partial pressures. The partial pressures are directly proportional to the numbers of moles of the individual gases. The ideal gas law can be used for the mixture of gases as a whole or for any component in the mixture. Water vapor in a gas mixture, like any other gas in the mixture, obeys Dalton's law. However, the gaseous water will condense if the pressure

of the water vapor is above a certain value, and if the mixture of gases is in contact with liquid water, the liquid water will evaporate when the pressure of the water vapor is below that value. The vapor pressure of water in contact with liquid water is thus a constant at any given temperature and depends only on temperature (Section 12.6).

The molar mass of a gas may be calculated if the mass of a sample and the number of moles of the sample are both known. The ideal gas law may be used to determine the number of moles, from which the molar mass may be calculated. As introduced in Section 7.4, the molar mass, along with the empirical formula, may then be used to determine the molecular formula (Section 12.7).

The ideal gas law can be used to calculate the number of moles of any gas involved in a chemical reaction, and that information can be used as numbers of moles were used in Section 10.3. The ideal gas law is just another way to determine the number of moles of gaseous reactant(s) or products(s) (Section 12.8).

Gay-Lussac's law of combining volumes relates the volumes of gases involved in a reaction, all measured separately at the same temperature and pressure. The volume ratio under these conditions is equal to the mole ratio and, therefore, to the ratio of coefficients in the balanced chemical equation (Section 12.9).

The kinetic molecular theory explains the behavior of gases in terms of characteristics of their molecules. It postulates that gases are made up of molecules that are in constant, random motion and whose sizes are insignificant relative to the total volume of the gas. Forces of attraction between the molecules are negligible, and when the molecules collide, the collisions are perfectly elastic. The average kinetic energy of the gas molecules is directly proportional to the absolute temperature (Section 12.10).

Items for Special Attention

- Absolute (Kelvin) temperature must be used with all the gas laws in which temperature is a factor.
- The units must be the same on each side of the equation in all gas law calculations.
- In solving problems using Boyle's law, Charles' law, or the combined gas law, it does not make any difference which set of conditions is defined as the initial set and which is defined as the final set (see Problem 12.24).
- Note that the value of R in the units usually used with the ideal gas law equation has a zero to the right of the decimal point: 0.0821 L·atm/mol·K.
- All the gas laws are approximations for real gases. Only a hypothetical "ideal" gas follows any of the laws exactly.

- The volume ratios that correspond to mole ratios involve volumes of separate gas samples at the same temperature and pressure. In gas mixtures, the partial pressure ratios are equal to the mole ratios.
- In problems involving chemical reactions, be sure to use the ideal gas law only for substances that are gases.
- The gas laws deal with matter in the gaseous state. They have nothing to do with gasoline, a liquid.
- Molecules of a gas in a container are somewhat like the balls in a lottery machine. They are in motion and hit all the walls, and their total volume is much smaller than the volume of their container.

Answers to Snapshot Reviews

12.1 A. The pressure stays the same.

$$\text{B. } 782 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.03 \text{ atm}$$

12.2 A. The volume is reduced to one-fifth.

12.3 A. The volume doubles.

$$\text{B. } 325 \text{ K} - 273 = 52^\circ\text{C}$$

$$\text{12.4 A. } \frac{\frac{P_1 V_1}{T_1}}{(1.50 \text{ atm})(2.00 \text{ L})} = \frac{\frac{P_2 V_2}{T_2}}{400 \text{ K}}$$

$$\frac{1.50 \text{ atm}}{400 \text{ K}} = \frac{3.50 \text{ atm}}{300 \text{ K}}$$

$$V_2 = 0.643 \text{ L}$$

$$\text{12.5 A. } PV = nRT$$

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

$$= \frac{(0.509 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(289 \text{ K})}{1.00 \text{ atm}}$$

$$= 12.1 \text{ L}$$

$$\text{12.6 A. The ratio is } (0.500 \text{ atm A})/(0.750 \text{ atm B})$$

$$= (0.667 \text{ mol A})/(1.00 \text{ mol B}).$$

$$\text{12.7 A. } n = \frac{PV}{RT} = \frac{(1.45 \text{ atm})(0.912 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(287 \text{ K})}$$

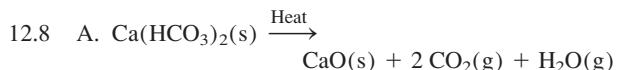
$$= 0.05612 \text{ mol}$$

$$\text{MM} = \frac{(2.24 \text{ g})}{(0.05612 \text{ mol})} = 39.9 \text{ g/mol}$$

B. Per liter there is 2.75 g and a number of moles calculated by

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}$$

$$= 0.04462 \text{ mol}$$

The molar mass is
(2.75 g)/(0.04462 mol) = 61.6 g/mol

$$0.150 \text{ mol Ca}(\text{HCO}_3)_2 \left(\frac{2 \text{ mol CO}_2}{1 \text{ mol Ca}(\text{HCO}_3)_2} \right)$$

$$= 0.300 \text{ mol CO}_2$$

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

$$= \frac{(0.300 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}}$$

$$= 6.72 \text{ L}$$

12.9 A. 3.00 L of Z and 1.50 L of Q

12.10 A. Postulate 1: the molecules travel in straight lines until they hit other molecules or a wall.

Self-Tutorial Problems

12.1 Solve each of the following equations for the unknown. (The integers are regarded as exact numbers, not measurements.)

$$(a) \frac{1}{x} = \frac{(20)(6)}{(24)}$$

$$(b) \frac{1}{V} = \frac{(20)(6)}{(24)}$$

$$(c) \frac{x(3)}{(4)} = \frac{(9)(12)}{(10)}$$

$$(d) \frac{(6)(3)}{(8)} = \frac{(9)(2)}{x}$$

$$(e) \frac{(9)(7)}{x} = \frac{(2)(12)}{(6)}$$

$$(f) \frac{(6.19)(12.1)}{x} = \frac{(3.82)(8.05)}{(2.07)}$$

$$(g) \frac{(4.48)(6.92)}{x} = \frac{(1.17)(13.8)}{(3.34)}$$

$$(h) \frac{(14.7)(0.977)}{(21.6)} = \frac{x(12.3)}{(3.19)}$$

12.2 What are the two criteria for (a) Boyle's law? (b) Charles' law? (c) What is the criterion for the combined gas law?

12.3 To which of the following substances, all at 25°C and 1.00 atm, do the gas laws apply?

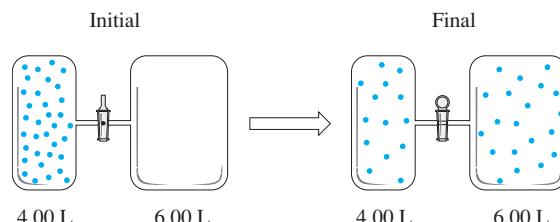
N₂ C₃H₆(g) I₂ Cl₂ CO₂ Al

12.4 To which of the following substances, all at 25°C and 1.00 atm, do the gas laws apply?

HCl(g) HCl(aq) H₂O NH₃ C₆₀(s)

12.5 If the Celsius temperature of a sample of gas is "doubled" from -10°C to -20°C at constant pressure, will its volume go up or down? Is Celsius temperature directly proportional to volume?

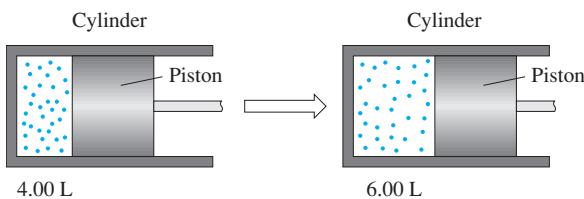
12.6 (a) What is the final volume of gas if the 4.00 L of gas is allowed to expand into the 6.00-L evacuated space, as shown in the accompanying figure?



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- (b) What is the final volume of the 4.00 L of gas in the cylinder if the piston is withdrawn, as shown in the accompanying figure?



- 12.7 Show that the combined gas law equation simplifies to
 (a) the Boyle's law equation if the temperature is constant and (b) the Charles' law equation if the pressure is constant.
- 12.8 Initially, a 4.00-L sample of gas is at 1.00 atm and 262 K. What is its final pressure if its final volume is 4000 mL and its final temperature is -11°C ?

Problems

12.1 Gas Pressure

- 12.14 Change:
 (a) 0.985 atm to torr (b) 1.75 atm to mm Hg
 (c) 698 torr to atm (d) 909 torr to mm Hg
 (e) 355 mm Hg to torr (f) 472 mm Hg to atm
- 12.15 (a) What is the volume of a mercury column 1.00 cm^2 in cross-sectional area and 76.0 cm high?
 (b) What is the mass of this mercury? ($d = 13.6\text{ g/cm}^3$).
 (c) If the column in part (a) were 3.00 cm^2 in cross-sectional area, what would its mass be?
 (d) Why does the column with smaller mass stand as high as the one with greater mass under the same atmospheric pressure?
- 12.16 Calculate the pressure in torr corresponding to
 (a) 93.44 kPa
 (b) $1.00 \times 10^2\text{ Pa}$
 (c) $3.13 \times 10^5\text{ Pa}$
- 12.17 Calculate the pressure in atmospheres corresponding to
 (a) 1.000 kPa
 (b) 213.4 kPa
 (c) $3.09 \times 10^3\text{ Pa}$
 (d) $1.013 \times 10^5\text{ Pa}$
- 12.18 What will happen if the gas in a cylinder has a higher pressure than the pressure of the piston on the gas? (The apparatus is shown in the figure for Problem 12.6[b].)

- 12.9 Compare the distance between molecules in a liquid and in a gas.
- 12.10 According to the kinetic molecular theory, what happens to gas molecules as a gas expands?
- 12.11 How many significant digits are in the Kelvin scale temperature corresponding to 5°C ?
- 12.12 Starting with 3.00 L of a gas, what will be the final volume in each case?
 (a) The volume is increased 4.00 L.
 (b) The volume is increased to 4.00 L.
 (c) The volume is increased by 4.00 L.
- 12.13 On which temperature scale are there no negative temperatures?

12.2 Boyle's Law

- 12.19 Calculate the final pressure of a sample of gas that is changed at constant temperature to 14.3 L from 7.55 L at 828 torr.
- 12.20 Calculate the final pressure of a sample of gas that is changed at constant temperature to 0.980 L from 2.112 L at 1.12 atm.
- 12.21 A sample of gas is compressed at constant temperature from 6.44 L at 1.75 atm to 548 mL .
 (a) Change the number of milliliters to liters.
 (b) Calculate the final pressure of the sample.
- 12.22 A sample of gas is expanded at constant temperature from 898 mL at 1.09 atm to 1.63 L . Calculate the final pressure of the sample.
- 12.23 Calculate the final pressure required to increase the volume of a 3.00-L sample of gas initially at 1.00 atm
 (a) by 5.00 L and (b) to 5.00 L .
- 12.24 (a) Calculate the final pressure of a sample of gas that is expanded to 3.79 L at constant temperature from 992 mL at 1.13 atm .
 (b) Calculate the initial pressure of a sample of gas compressed at constant temperature to 992 mL at 1.13 atm from 3.79 L .
- 12.25 (a) Calculate the final pressure of a sample of gas that is expanded to 1.16 L at constant temperature from 457 mL at 812 torr .
 (b) Calculate the initial pressure of a sample of gas compressed at constant temperature to 457 mL at 812 torr from 1.16 L .

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- 12.26** (a) Using Figure 12.2(a), estimate the volume that the sample of gas would occupy at 3.00 atm and the given temperature.
 (b) Is the same estimation for a pressure of 11.0 atm as easy? Explain.
- 12.27** Calculate the pressure required to change a 689-mL sample of gas at 712 torr and 25°C to 1.31 L at 25°C.
- 12.28** Calculate the pressure required to change a 2.26-L sample of gas at 1.61 atm and 30°C to 671 mL at 30°C.
- 12.29** Complete each line in the following table for a given sample of gas, assuming constant temperature:

	<i>V</i> ₁	<i>P</i> ₁	<i>V</i> ₂	<i>P</i> ₂
(a)	3.38 L	1.07 atm	_____	2.11 atm
(b)	_____	372 torr	909 mL	492 torr
(c)	3.18 L	_____	702 mL	2.46 atm
(d)	3.19 mL	811 torr	_____	1.35 atm

- 12.30** Using Figure 12.2(b), estimate the values of $1/V$ and V at 11.0 atm.
- 12.31** Calculate the final volume of a 4.68-L sample of gas that has its pressure tripled.

12.3 Charles' Law

- 12.32** Calculate the final volume at 302 K of a 5.41-L sample of gas originally at 353 K if the pressure does not change.
- 12.33** Calculate the initial volume at 301 K of a sample of gas that is changed to 52.5 mL by cooling to 285 K at constant pressure.
- 12.34** A sample of gas is heated at constant pressure from 7°C to 21°C.
 (a) Will the volume triple?
 (b) If not, by what ratio will the volume increase?
- 12.35** A sample of gas is cooled at constant pressure from 50°C to 10°C.
 (a) Will the volume decrease to one fifth its original volume?
 (b) If not, by what ratio will the volume decrease?
- 12.36** Calculate the final volume at 402 K of a sample of gas originally 122 mL at 55°C if the pressure does not change.
- 12.37** Calculate the final volume at 319°C of a sample of gas originally 51.3 mL at 171°C if the pressure does not change.
- 12.38** Calculate the final volume at 33°C of a sample of gas that is originally 6.00 L at -33°C, assuming that the pressure does not change.
- 12.39** Calculate the initial volume at 0°C of a sample of gas that is changed to 731 mL by cooling to -14°C at constant pressure.

CHAPTER 12 ■ Gases

- 12.40** Plot the following data, and extrapolate to zero volume to estimate the value of absolute zero on the Celsius scale:

<i>V</i> (L)	1.20	1.40	1.60	1.80	2.00
<i>t</i> (°C)	25	75	125	175	225

- 12.41** Will sample A or sample B be increased more (at constant pressure) by the indicated changes in temperature?
 A. 10°C to 20°C
 B. 100°C to 200°C

- 12.42** Complete each line in the following table for a given sample of gas, assuming constant pressure:

	<i>V</i> ₁	<i>T</i> ₁	<i>V</i> ₂	<i>T</i> ₂
(a)	_____	312 K	1.55 L	393 K
(b)	104 mL	_____	141 mL	27°C
(c)	1.72 L	77°C	972 mL	_____
(d)	0.171 m ³	22°C	_____	88°C

12.4 The Combined Gas Law

- 12.43** Calculate the final volume of a sample of gas initially occupying 6.40 L at STP after its pressure is increased to 1.17 atm and its temperature is increased 37°C.

- 12.44** Calculate the final pressure of a gas that is expanded from 769 mL at 24°C and 1.15 atm to 2.00 L at 33°C.

- 12.45** Calculate the missing values in the following table:

	<i>V</i> ₁	<i>P</i> ₁	<i>T</i> ₁	<i>V</i> ₂	<i>P</i> ₂	<i>T</i> ₂
(a)	2.03 L	3.50 atm	_____	3.11 L	1.72 atm	259 K
(b)	1.33 L	_____	317 K	794 mL	903 torr	291 K
(c)	16.5 L	0.999 atm	282 K	12.9 L	_____	24°C
(d)	6.00 L	2.00 atm	_____	975 mL	4.50 atm	422°C
(e)	829 mL	1.57 atm	30°C	_____	982 torr	289 K
(f)	602 mL	717 torr	47°C	_____	3.00 atm	47°C
(g)	6.12 L	1.33 atm	382 K	4.48 L	665 torr	_____
(h)	2.13 L	797 torr	31°C	9.11 L	_____	351 K

- 12.46** Complete the following table:

	<i>V</i> ₁	<i>P</i> ₁	<i>T</i> ₁	<i>V</i> ₂	<i>P</i> ₂	<i>T</i> ₂
(a)	213 mL	_____	273 K	0.822 L	2.04 atm	321 K
(b)	627 mL	4.89 atm	_____	0.552 L	4.89 atm	49°C
(c)	1.71 L	6.86 atm	22°C	3.11 L	2.19 atm	_____
(d)	13.1 L	_____	298 K	10.0 L	1.99 atm	27°C
(e)	6.55 mL	2.27 atm	330 K	14.8 mL	2.11 atm	_____
(f)	1.13 L	_____	303 K	909 mL	891 torr	281 K
(g)	_____	0.995 atm	299 K	173 mL	2.03 atm	332 K
(h)	1.07 L	616 torr	72°C	_____	1.25 atm	72°C

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12.5 The Ideal Gas Law

- 12.47 Solve the problems in Example 12.13.
- 12.48 Solve the problem in Example 12.13(a), using the ideal gas law.
- 12.49 (a) Determine the temperature of a gas if 1.50 mol occupies 14.0 L at 1.25 atm.
 (b) Is the gas more likely to be H₂ or H₂O? Explain.
- 12.50 Determine the volume of 0.800 mol of SO₂(g) at 55°C and 0.950 atm.
- 12.51 Determine the pressure of 0.515 mol of NH₃ gas in a volume of 8.05 L at 307 K.
- 12.52 Determine the number of moles of O₂ in a volume of 14.3 mL at 292 K and 606 torr.
- 12.53 Calculate the value of *R* in (a) L·torr/mol·K and (b) mL·atm/mol·K.
- 12.54 Determine the number of moles of gas in a volume of 152 mL at 419 K and 382 torr.
- 12.55 Determine the volume of 0.413 mol of F₂ at 31°C and 787 torr.
- 12.56 Determine the temperature of a gas if 0.813 mol occupies 10.1 L at 798 torr.
- 12.57 Determine the number of moles of gas in a volume of 14.0 L at 333 K and 1.73×10^{-3} torr.
- 12.58 Determine the pressure of 0.300 mol of CO gas in a volume of 14.7 L at 303 K.
- 12.59 Determine the number of moles of gas in a volume of 1.90×10^{-3} mL at 273 K and 1.00 atm.

12.6 Dalton's Law of Partial Pressures

- 12.60 A gaseous mixture contains 2.00 mol of He, 2.00 mol of Ne, and 2.00 mol of Ar. The total pressure of the mixture is 6.69 atm. What is the partial pressure of each gas?
- 12.61 A gaseous mixture contains 0.170 mol of H₂, 0.230 mol of N₂, and 0.200 mol of Ne. The total pressure of the mixture is 1.45 atm. What is the partial pressure of each gas?
- 12.62 A gaseous mixture contains 1.50 mol of O₂, 2.50 mol of He, and 0.500 mol of N₂. The partial pressure of the oxygen is 0.300 atm. What are the partial pressures of the nitrogen and the helium?
- 12.63 A mixture of gases exists in which the numbers of moles of all the components are the same. What can be said about the partial pressures of the components?
- 12.64 A gaseous mixture contains 0.550 mol of H₂, 0.350 mol of N₂, and 0.950 mol of Ne. The partial pressure of the nitrogen is 0.517 atm. (a) What are the partial pressures of the hydrogen and the neon? (b) If the temperature is 325 K, what is the volume of the nitrogen? (c) What is the volume of the mixture?

12.65 Oxygen gas is standing over water at a total pressure of 782 torr. The partial pressure of the oxygen is found to be 752 torr. Determine the temperature of the system.

12.66 Oxygen gas is standing over water at a total pressure of 781 torr at 35°C. Determine the partial pressure of the oxygen.

12.67 What volume of O₂ can be collected over water at 25°C and 1.14 atm barometric pressure from thermal decomposition of 0.200 g of KClO₃?

12.68 What mass of KClO₃ must be decomposed to produce 207 mL of O₂, collected over water, at 25°C and a barometric pressure of 771 torr?

12.69 What volume of O₂ can be collected over water at 20°C and 1.000 atm barometric pressure from thermal decomposition of 0.104 g of KClO₃?

12.70 What mass of KClO₃ must be decomposed to produce 1.00 L of O₂, collected over water, at 15°C and a barometric pressure of 769 torr?

12.71 What volume will 0.500 g of hydrogen occupy when collected over water at 25°C and 0.877 atm barometric pressure?

12.72 What volume will 0.500 g of O₂ occupy when collected over water at 20°C and 1.63 atm barometric pressure?

12.7 Molar Masses and Molecular Formulas

12.73 Determine the pressure of (a) 0.901 g of N₂ in a 12.4-L vessel at 25°C and (b) 0.901 g of Cl₂ in a 12.4-L vessel at 25°C. (c) Explain the difference.

12.74 What is the volume of 6.04 g of CO₂ at 1.00 atm and 27°C?

12.75 Determine the molar mass of a gaseous substance if 11.4 g occupies 5.52 L at 1.10 atm and 12°C.

12.76 Calculate the molar mass of a gas if 15.0 g occupies 11.8 L at 314 K and 1.06 atm.

12.77 Calculate the density of argon at 25°C and 1.11 atm.

12.78 Calculate the molar mass of a gas with density 6.53 g/L at STP.

12.79 A 1.60-g sample of a gaseous hydrocarbon occupies 1.55 L at 25°C and 682 torr. The gas is composed of 85.63% C and 14.37% H. What is the molecular formula of the gas?

12.80 Calculate the molecular formula of a gaseous hydrocarbon of which 24.0 g occupies 19.9 L at 791 torr and 21°C. The hydrocarbon consists of 85.6% carbon and 14.4% hydrogen.

12.8 Gases in Chemical Reactions

12.81 Explain why it is so important to write the correct formula for an elemental gas that exists as diatomic molecules.

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- 12.82 What mass of H₂ is required to react with O₂ to produce 912 mL of H₂O(g) at 112°C and 0.989 atm?
- 12.83 What volume of ammonia at 456 K and 1.00 atm can be produced by the reaction of 1.00 metric ton (1.00 × 10⁶ g) of hydrogen gas with nitrogen gas?
- 12.84 How many moles of aluminum metal are required to produce 4.04 L of hydrogen gas at 1.11 atm and 27°C by reaction with HCl?
- 12.85 Calculate the volume of CO₂ (measured after cooling to 25°C at 1.00 atm) that will be liberated by heating 22.9 g of Mg(HCO₃)₂. MgCO₃ is another product.
- 12.86 What mass of O₂ is required to react with H₂ to produce 4.19 L of H₂O(g) at 172°C and 0.801 atm?
- 12.87 How many moles of mercury(II) oxide must be thermally decomposed to produce 2.26 L of oxygen gas at 1.00 atm and 23°C?
- 12.88 What volume of hydrogen at 282 K and 1.00 atm can be produced by the reaction of 6.59 g of aluminum with hydrochloric acid?
- 12.89 Determine the number of moles of aqueous sodium hydroxide required to react with 16.7 L of carbon dioxide gas at 298 K and 1.00 atm to form sodium carbonate.
- 12.90 Calculate the volume of CO₂ (measured after cooling to 25°C at 1.00 atm) that will be liberated by heating 14.2 g of NaHCO₃. Na₂CO₃ is also a product.
- 12.91 What volume of ammonia at 555 K and 1.77 atm can be produced by the reaction of 1.50 kg of hydrogen gas with nitrogen gas?
- 12.92 How many moles of mercury(I) oxide must be thermally decomposed to produce 1.03 L of oxygen gas at 1.00 atm and 25°C?

12.9 Volume Ratios in Chemical Reactions

- 12.93 When 5.00 mol of O₂ reacts with 4.00 mol of NH₃, 4.00 mol of NO and 6.00 mol of H₂O are formed.
- Write a balanced chemical equation for the reaction.
 - Calculate the volumes of 5.00 mol of O₂, 4.00 mol of NH₃, and 4.00 mol of NO at STP.
 - Compare the ratio of the volumes of the gases to the coefficients in the balanced equation. What can be

stated about the volumes of gases involved in a reaction when they are *at the same temperature and pressure*?

- 12.94 Repeat Problem 12.93 at 25°C and 1.50 atm pressure. Are the results the same, that is, are the volume ratios the same as the mole ratios in the balanced chemical equation?
- 12.95 Repeat Problem 12.93 with any other given temperature and pressure. Are the results the same, that is, are the volume ratios the same as the mole ratios in the balanced chemical equation?
- 12.96 What ratio of volumes (all at 25°C and 1.00 atm) would be involved in the reaction represented by the following equation?
$$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$$
- 12.97 What ratio of volumes (all at 327°C and 1.00 atm) would be involved in the reaction represented by the following equation?
$$2 \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g})$$
- 12.98 Using the ideal gas law, show that equal volumes of two gases under like conditions of temperature and pressure have equal numbers of moles of gas and thus equal numbers of molecules.

12.10 Kinetic Molecular Theory of Gases

- 12.99 Calculate the percentage of the 30.6 L occupied by the molecules of the 1.00 mol of water vapor at 1.00 atm and 100°C, as calculated in Example 12.31. Assume that the molecules of liquid water actually occupy all the 18.8-mL volume.
- 12.100 Imagine a sheet of paper suspended by one edge and hanging vertically. What would happen if a rapid succession of peas was shot from a peashooter at the paper? Compare the impact of the peas to the impact of molecules of a gas bombarding a wall.
- 12.101 Use the kinetic molecular theory to explain why the number of moles of gas enclosed in a certain container at a certain temperature is directly proportional to the gas pressure.
- 12.102 Use the kinetic molecular theory to explain why Dalton's law of partial pressure works.

General Problems

- 12.103 A 5.43-g sample of which elemental diatomic gas occupies 4.38 L at 25°C and 0.950 atm?
- 12.104 A 3.74-g sample of which noble gas occupies 1.00 L at STP?

- 12.105 (a) Using Boyle's law and Charles' law, show that the *pressure* of a gas is directly proportional to its *absolute temperature at constant volume*.
- (b) Repeat part (a), using the combined gas law instead.

■ General Problems

- 12.106 A 6.50-L steel vessel that holds a sample of oxygen gas at 25°C and 1.00 atm develops a leak, and 3.00 g of oxygen escapes before the leak is repaired.
- Calculate the initial number of moles of oxygen present.
 - Calculate the number of moles that escape.
 - Calculate the pressure of oxygen in the vessel, still at 25°C, after the leak is repaired.
- 12.107 Calculate the final volume of a sample of gas initially occupying 355 mL after its pressure is increased 25% and its absolute temperature is decreased 10.0%.
- 12.108 What, if anything, happens to the total pressure in the system as each of the following reactions occurs in a constant-volume reaction vessel at constant temperature?
- $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$
 - $\text{Br}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$
 - $2 \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g})$
- 12.109 What are the volume and the pressure for neon, argon, and the mixture in the following experiments?
- Samples of 0.0110 mol of Ne and 0.0200 mol of Ar are placed in identical 1.00-L containers at 25°C.
 - Samples of 0.0110 mol of Ne and 0.0200 mol of Ar are placed in a single 1.00-L container at 25°C.
- 12.110 Calculate the pressure ratio of He to N₂ at which helium would have the same density as nitrogen if their temperatures were the same.
- 12.111 Calculate the percentage by mass of oxygen in a mixture of oxygen and nitrogen that has a density of 1.41 g/L at STP.
- 12.112 Convert the temperatures of Table 12.1 to Fahrenheit, plot those versus the volumes, and determine the value of absolute zero on the Fahrenheit scale.
- 12.113 Determine the formula of a gaseous substance if 1.40 g occupies 14.9 L at 1.08 atm and 9°C.

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- 12.114 A 4.92-g sample of which hydrogen halide occupies 3.00 L at 25°C and 836 torr?
- 12.115 A 210-mL sample of pure oxygen gas at 1.00 atm and 25°C was subjected to an electric discharge. The pressure dropped to 0.975 atm, but the temperature and volume did not change. Explain what happened. Include a statement of how much change occurred.
- 12.116 A 2.71-g sample of a substance occupies 6.87 L at 2.59 atm and 320 K. Determine the identity of the substance.
- 12.117 Calculate the volume of a 75.0-mL sample of gas after its pressure is halved and its absolute temperature is increased 25.0%.
- 12.118 A gaseous mixture contains 2.75 L of helium, some argon at 1.10 atm, and some neon at 25°C. Calculate the number of moles present of one of the gases.
- 12.119 Which parts of Problems 12.45 and 12.46 can be solved with Boyle's law or with Charles' law?
- 12.120 A 0.756-g sample of a substance occupies 4.32 L at 1.00 atm and 280 K. Determine the identity of the substance.
- 12.121 A 10.0-L steel vessel that holds a sample of oxygen gas at 25°C and 741 torr develops a leak, and 5.75 g of oxygen escapes before the leak is repaired. After the leak is repaired, what is the pressure of oxygen in the vessel, if the temperature is still 25°C?
- 12.122 Which one(s) of the following samples of gas most nearly contains 1.00 mol of gas?

	P (atm)	V (L)	T (K)
A	1.00	8.21	100
B	1.00	82.1	1000
C	82.1	1.00	1000
D	8.21	1.00	100

13

Atomic and Molecular Properties

- 13.1 Atomic and Ionic Sizes
- 13.2 Ionization Energy and Electron Affinity
- 13.3 Electronegativity and Bond Polarity
- 13.4 Molecular Shape
- 13.5 Polar and Nonpolar Molecules
- 13.6 Intermolecular Forces



Needles of ice crystals

Review Clues

- Section 13.1** Chapters 4 and 5, Sections 1.5, 3.3, 3.5, 4.7
- Section 13.2** Section 12.10
- Section 13.3** Sections 5.1, 5.4, 5.5
- Section 13.4** Sections 5.4, 5.5
- Section 13.6** Section 5.1

Objectives

- 13.1** To predict how changes in the numbers of protons, electrons, or both affect the size of the resulting atom or ion, and to deduce the relative sizes of atoms from their positions in the periodic table
- 13.2** To deduce the relative ionization energies of different elements from their positions in the periodic table, and to distinguish (1) a combination of ionization energy and electron affinity of two elements from (2) the energy of reaction of the elements in their standard states
- 13.3** To use electronegativity differences to predict the bond types between atoms of the elements
- 13.4** To deduce the shape of a molecule or a polyatomic ion from its electron dot diagram
- 13.5** To deduce the polarity of a molecule from the orientations of its polar bonds
- 13.6** To show how the three intermolecular forces affect the properties of substances

This chapter examines many aspects of atomic and molecular properties. These properties affect the properties of the substances that the atoms and molecules constitute. We begin with the sizes of atoms and ions, especially the periodic variation of sizes (Section 13.1). We then discuss the effects the sizes have on the energies associated with the gain or loss of an electron by an atom—ionization energy and electron affinity, respectively (Section 13.2). From that more theoretical discussion of gaseous atoms and ions, we progress to electronegativity, a more practical, semiquantitative measure of the electron-attracting ability of atoms in molecules or ionic substances (Section 13.3). The atoms' varying abilities to attract electrons in molecules lead to polar and nonpolar covalent bonds (Section 13.3). Section 13.4 discusses molecular shapes. Depending on the molecular shapes, polar bonds can lead to dipolar or nondipolar molecules (Section 13.5). Intermolecular forces, the small forces between molecules that result from molecular polarity and other causes, are discussed in Section 13.6.

These discussions will enable us to consider the nature of the solid and liquid states in Chapter 14.

13.1 Atomic and Ionic Sizes

Before we discuss the sizes of atoms and ions, let us review briefly some basic scientific principles:

1. Oppositely charged particles attract each other.
2. Like charged particles repel each other.
3. The greater the charge(s), the greater the attraction or repulsion.
4. The closer the two charged bodies, the stronger the force of attraction or repulsion.
5. Electrons are negative and lie outside the nucleus, whereas protons are positive and lie within the nucleus.

The greater the number of electrons in an atom or its ions, all other factors being equal, the larger the **atomic** or **ionic size**. The more electrons, the greater the electronic repulsion. With the same nuclear charge but greater electronic repulsion, the electrons occupy a larger volume of space.

EXAMPLE 13.1

Compare the relative sizes of Co, Co^{2+} , and Co^{3+} .

Solution

In each case, the nucleus has 27 protons and, therefore, 27 positive charges. This quantity of positive charge can attract the 24 electrons in Co^{3+} better than the 25 electrons in Co^{2+} or the 27 electrons in Co. Hence, Co is the largest, and Co^{3+} is the smallest.

Practice Problem 13.1 Compare the relative sizes of Cl and Cl^- .

Understanding the size relationships is equally straightforward if the number of electrons is constant in several species and the number of protons changes. The greater the positive charge in the nucleus, the greater is the attraction for the set of electrons and, therefore, the smaller is the atom or ion.

EXAMPLE 13.2

Compare the sizes of Cl^- , Ar, and Ca^{2+} .

Solution

Each of these atoms or ions has 18 electrons. The greater positive charge in the Ca^{2+} nucleus (20 protons) has a greater pull on the electrons than do the smaller charges in Ar (18 protons) and Cl^- (17 protons). Thus, Ca^{2+} is the *smallest* and Cl^- is the *largest* of these three.

Practice Problem 13.2 Compare the sizes of O^{2-} , Ne, and Na^+ .



ENRICHMENT

When we investigate the effects of changes on some property, we like to make only one change at a time so that we know that any effect is caused by that change. If we were to make more than one change, we would not know which of the changes caused the final effect. This procedure is known as doing a **controlled experiment**. When we change the number of protons

in a series of atoms and ions, we first hold the number of electrons constant. We then know that the change in size is due to the effect of the protons. After we know that effect (and the effect of changing the number of electrons only), we can change both and figure out what is happening.

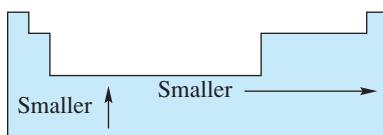


Figure 13.1 General Periodic Trends in Atomic Size

Predicting size variations of neutral atoms of neighboring elements in the periodic table, in which both the number of protons and the number of electrons change, is more difficult. It turns out that increasing the number of protons, which tends to make the atom or ion smaller, is more important than increasing the number of electrons, which tends to make the atom or ion larger, *except when the last electron starts a new shell of electrons*. That is, as we compare neighboring elements in a given period of the periodic table, the atoms get somewhat smaller as we go to the right. Starting a new shell of electrons (at each alkali metal) causes a *very large increase* in size, so that in going down a group, the atoms get larger. Figure 13.1 indicates the periodic variation in size of the neutral atoms, and Figure 13.2 shows a representation of the actual sizes of atoms and ions.

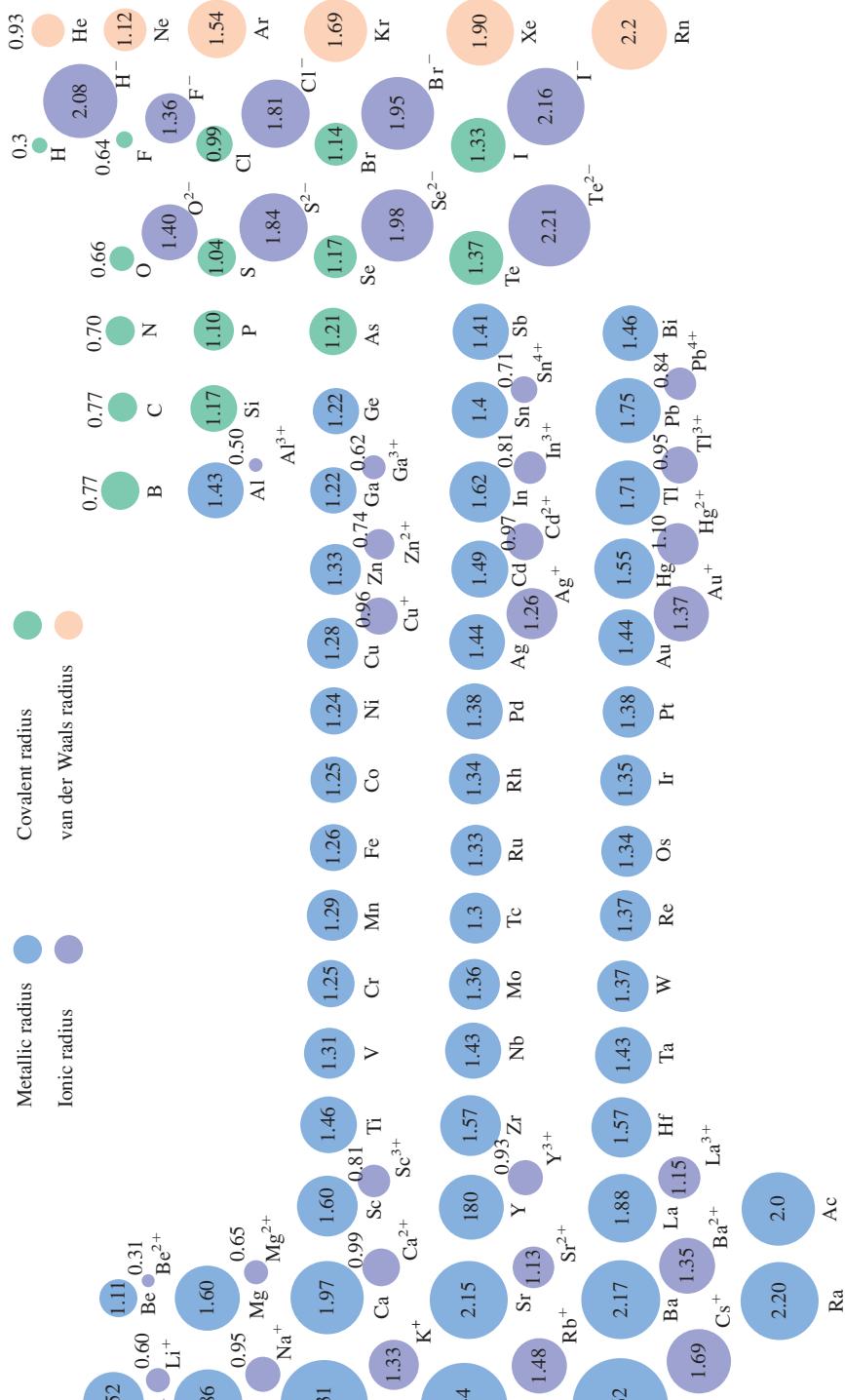


Figure 13.2 Periodic Table Showing the Relative Sizes of Atoms and Ions
(Atomic and Ionic Radii in Ångström units; 1 Å = 10^{-10} m = 0.1 nm)

The data include metallic radii, ionic radii, covalent radii, and van der Waals radii. Although the various types of radii cannot be directly compared, the figure does illustrate the periodic trends in sizes.

EXAMPLE 13.3

Which atom in each of the following parts is largest?

- (a) Be Mg Ca (b) Na Mg Al (c) F Cl Br I

Solution

- (a) Ca (The atoms get larger as we go down the group.)
(b) Na (The atoms get smaller as we go to the right.)
(c) I (The atoms get larger as we go down every group, not only the alkaline earth metal group.)

Practice Problem 13.3 Which atom in each of the following parts is largest?

- (a) S Se Te (b) Mg Si Cl

**Snapshot Review**

ChemSkill Builder 11.1

- The more protons in an atom or ion, all other factors being the same, the smaller is the size of the species.
- The more electrons in an atom or ion, all other factors being the same, the greater is the size of the species.
- When both the number of electrons and the number of protons vary, the size varies periodically.

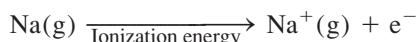
- A. Explain why a larger number of protons produces a smaller species, all other factors being equal.

13.2 Ionization Energy and Electron Affinity

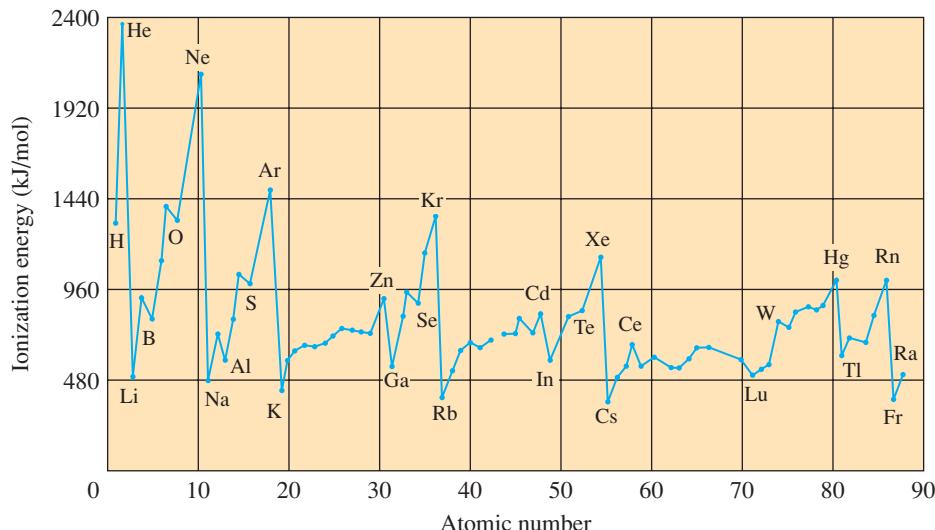
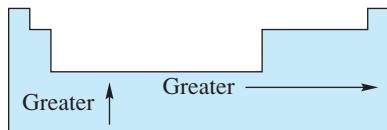
Both ionization energy and electron affinity are measures of energies involving gaseous atoms and gaseous ions and are not the same as the energies involved when ionic solids or solutions are formed. The latter energies involve ionization energy and electron affinity, but also include many other types of energy terms.

Ionization Energy

The **ionization energy** of an element is defined as the energy *required* to remove an electron from a *gaseous* atom to produce a *gaseous* cation. For example,



Gaseous atoms and ions are specified because they are far from any other chemical species (Section 12.10), and thus few extraneous interactions interfere with the nucleus-electron attraction. Note that this is *not* the energy for the more familiar reaction of solid sodium to produce sodium ions in a lattice or in solution.

13.2 ■ Ionization Energy and Electron Affinity**357****Figure 13.3** First Ionization Energy as a Function of Atomic Number

The ionization energy of the elements varies periodically. In general, as an atom gets larger (and the outermost electron gets farther away from the nucleus), less energy is needed to remove an electron. Figure 13.3 shows ionization energies, and the periodic variation of ionization energies is represented in Figure 13.4.

Figure 13.4 Relative Periodic Trends in Ionization Energy**EXAMPLE 13.4**

Which atom in each of the following parts has the largest ionization energy?

- (a) K Ga Se (b) O S Se (c) In As Cl

Solution

- (a) Se (The ionization energy gets larger as we go to the right in the periodic table.)
 (b) O (The ionization energy gets smaller as we go down the group.)
 (c) Cl (The ionization energy gets larger as we go to the right and as we go up.)

Practice Problem 13.4 Which atom in each of the following parts has the largest ionization energy?

- (a) Be C N (b) Mg Ca Sr (c) Sn Se F

Note that although the general trend is for ionization energies to increase toward the right, some small exceptions exist (see Figure 13.3). Many of these stem from the extra stability of a half-filled subshell of electrons.

The **second ionization energy** of an atom is the energy required to remove the second electron from the monopositive gaseous ion; the **third ionization**

Table 13.1 Successive Ionization Energies for Some Main Group Elements (kilojoules per mole)

	First	Second	Third
Na	495.8	4562	6912
Mg	737.7	1451	7733
Al	577.6	1817	2745

energy is the energy required to remove the third electron from the dipositive ion; and so on. For every element, the second ionization energy is higher than the first because it is harder to remove an electron (a negative particle) from a positively charged body than from the corresponding neutral one. The ionization energy increases dramatically as the octet of electrons is disrupted (Table 13.1). The term *ionization energy* always means *first* ionization energy unless otherwise specified.

EXAMPLE 13.5

Predict which of the first three ionizations of potassium has the greatest *increase* in ionization energy from the preceding ionization.

Solution

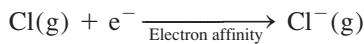
The second ionization energy of potassium is much greater than the first because the octet of electrons in the third shell is broken in ionizing that electron. (The actual values for the first three ionization energies are 418 kJ/mol, 3050 kJ/mol, and 4400 kJ/mol, respectively.)

Practice Problem 13.5 Predict which of the first four ionizations of calcium has the greatest *increase* in ionization energy from the preceding ionization.

Electron Affinity

Positive electron affinity values signify that energy is *liberated*, in contrast to ionization energy values and values of other variables to be introduced in Chapter 14.

Electron affinity is defined as the energy *liberated* when an electron is added to a *gaseous atom* to form a *gaseous anion*. For example,



Note that this energy is *not* the energy for the more familiar reaction of gaseous chlorine *molecules* to form chloride ions in a solid lattice or in solution.

Table 13.2 presents the electron affinities of a number of elements. The electron affinities of some elements are negative, meaning that energy is *required* to add an electron to the gaseous atoms. Periodic variation of electron affinity is more difficult to rationalize than is the variation of ionization energy, but note that the halogens have the greatest electron affinities of all the elements.

EXAMPLE 13.6

Determine from Table 13.2 which periodic groups of elements generally require energy when an electron is added to their atoms.

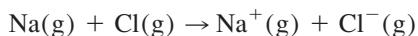
Solution

The alkaline earth metals and noble gases are the only groups of elements with negative (first) electron affinities.

13.3 ■ Electronegativity and Bond Polarity**359****Table 13.2** Electron Affinities of Some Elements (kilojoules per mole)

H	72.6	K	48.2	Te	189.8
He	-21	Ca	-156	I	294.8
Li	59.7	Cr	64	Xe	-40
Be	-240	Ni	111	Cs	45.5
B	23	Cu	122.9	Ba	-52
C	122.3	Ga	36	Ta	80
N	0.0	Ge	116	W	50
O	141.1	As	77	Re	14
F	321.5	Se	194.5	Pt	204.9
Ne	-29	Br	323.9	Au	222.4
Na	52.8	Kr	-39	Tl	50
Mg	-230	Rb	46.8	Pb	101
Al	44	Sr	-168	Bi	101
Si	119	Mo	96	Po	173
P	74	Ag	125.5	At	270
S	200.0	In	34	Rn	-40
Cl	348	Sn	120	Fr	43.9
Ar	-35	Sb	101		

If we combine the ionization energy of sodium with the electron affinity of chlorine, we deduce that an overall energy input is required for the reaction



because 496 kJ is *required* to remove the electrons from a mole of gaseous sodium atoms and only 348 kJ is *produced* when these electrons are added to a mole of gaseous chlorine atoms. This conclusion emphasizes that we are talking about *gaseous* atoms and ions. (When the energy to form a solid lattice of NaCl from the ions, and other factors, are taken into account [Chapter 14], the process of combining metallic sodium and gaseous chlorine molecules produces energy.)

**Snapshot Review**

ChemSkill Builder 11.2

- Ionization energy and electron affinity both refer to the energetics of reaction of atoms and ions *in the gas phase*.
- Ionization energy increases toward the right and toward the top of the periodic table.

- A. Arrange each of the following sets in order of increasing ionization energy: (a) Sr Mg Ca, (b) As F S, and (c) Sb S Se

13.3 Electronegativity and Bond Polarity

Electronegativity (Section 5.1) is a semiquantitative measure of the electron-attracting ability of an atom. The larger the electronegativity, the greater is the pull on the electrons. In general, electronegativity increases to the right and

Table 13.3 Approximate Electronegativity Differences for Various Bond Types

Electronegativity Difference	Bond Type
1.5 or more	Ionic bond
0.3 to 1.0	Polar covalent bond
0.0 to 0.2	Nonpolar covalent bond

to the top of the periodic table, just as ionization energy does, but the lighter noble gases do not have defined electronegativity values because they form no bonds. Electronegativity values for the main group elements are shown in Figure 5.4 (p. 129).

Electronegativity is useful in predicting the nature of the bond expected to form between two atoms (Table 13.3). If the electronegativity values are very different, an ionic bond is expected. If the electronegativity values are the same, a covalent bond will form with an equally shared pair of electrons. Such a bond is said to be **nonpolar**. For example, the bond in Cl_2 is nonpolar:



When electrons are shared between atoms of different elements, the electronegativities (the attractions of the atoms for the electrons) are generally not equal. Therefore, the electrons are not shared equally. (Because they are still shared, however, the bond is covalent.) The bond is said to be a **polar bond**. This unequal sharing of electrons may cause one end of the molecule to be *slightly* positive and the other end *slightly* negative. For example, in HCl, the bonding electrons are drawn *somewhat* more toward the chlorine atom than toward the hydrogen atom, yielding



The charges on the atoms in a polar covalent bond are not full charges.

These are not full ionic charges; there is about one sixth of a single positive charge on the hydrogen atom in HCl and the same amount of negative charge on the chlorine atom. The *partial* nature of these charges is denoted by the lowercase Greek delta (δ). (Other polar bonds have partial charges of different magnitudes.) Polar bonds caused by unequal sharing of electrons can lead to polar molecules (see Section 13.5).

EXAMPLE 13.7

What type of bond would be formed between each of the following pairs of atoms?

- (a) S and O (b) Cl and Cl (c) K and F

Solution

- (a) The electronegativity difference is $3.5 - 2.5 = 1.0$, so the bond should be polar covalent.
(b) The electronegativity difference is $3.0 - 3.0 = 0$, so the bond is nonpolar covalent.
(c) The electronegativity difference is $4.0 - 0.8 = 3.2$, so the bond is ionic.

Practice Problem 13.7 What type of bond would be formed between each of the following pairs of atoms?

- (a) P and Cl (b) Al and F



Snapshot Review



ChemSkill Builder 12.1

- The greater the electronegativity of an atom, the stronger is its attraction for electrons.
- Covalent bonds between atoms of different electronegativity are polar.

- A. The electrons in each of the following bonds are closer to which atom, if either?
- (a) O—F (b) N—I (c) C—Br

13.4 Molecular Shape

We discuss the shapes of molecules next, before we examine the effect of polar bonds on the properties of molecules as a whole. Both the bond polarity and the shape can have a distinct effect on the molecule's properties.

Molecular shape is defined by the location of the atoms.

Molecular shape is defined by the locations of a molecule's *atoms*, not from the location of its electrons, because, experimentally, the scientist can determine the location of the atoms by X-ray diffraction and other studies. We can predict the shapes of molecules from their formulas by using a few simple rules. The ability to make such predictions enables us to understand better the properties of the substances.

To predict the shape of a molecule from its formula, we first draw an electron dot diagram of the molecule (Sections 5.3 and 5.5). We assume that the **electron groups** around the **central atom** are as far apart as possible while remaining attached to the central atom. The electron groups are ordinarily the electrons in the single, double, or triple bonds, or in the lone pairs on the central atom, which is the atom to which the other atoms are attached. Then we bond the other atoms, using some or all of the electron groups, and finally describe the molecule by the locations of the *atoms*.

As a first example of the process, we consider the molecule BeH₂, experimentally known to be a **linear molecule** with two identical bonds. The electron dot diagram has only four electrons around the beryllium, two from the outermost shell of that atom and one each from the two hydrogen atoms:



We place the electron pairs as far apart as possible (180°) while still being attached to the Be atom. Then we add the two hydrogen atoms to form the molecule:



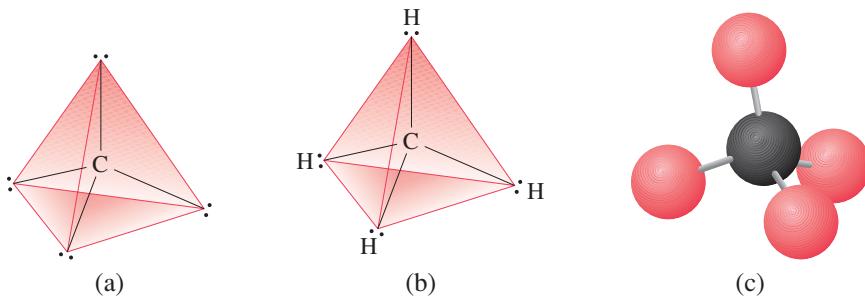
We have deduced that the molecule is linear because all three atoms lie on a straight line.

Next, we consider BF₃. The B atom has three outermost electrons to contribute. The three fluorine atoms each contribute their 1 unpaired electron, which makes a total of 6 electrons available. These are distributed in three pairs symmetrically about the B atom:

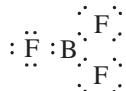


Figure 13.5 Tetrahedral Orientation of Electron Pairs and Hydrogen Atoms

(a) Tetrahedral orientation of the electron pairs around the carbon atom. (b) A tetrahedral molecule is produced when the four hydrogen nuclei are attached. (c) The molecule is usually shown as a ball-and-stick model, in which each stick represents an electron pair.



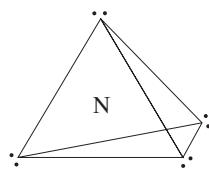
We add the three fluorine atoms and again get a symmetrical molecule:



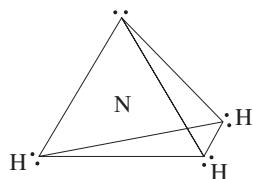
In this case, we call the molecular shape **trigonal planar** because the triangle of fluorine atoms and the boron atom all lie in the same plane.

Our next example is CH_4 , methane. The 4 outermost carbon electrons plus the 4 electrons from the hydrogen atoms total 8. These are distributed in four pairs as far apart as possible. In this case, the distribution is toward the corners of a tetrahedron (Figure 13.5a). Note that the electrons are not limited to a single plane. The addition of the hydrogen atoms produces a **tetrahedral molecule** (Figure 13.5b and c).

Ammonia, NH_3 , is our next case. The 5 outermost electrons in the nitrogen atom, plus the 3 electrons from the three hydrogen atoms, again make 8. Once more, these are distributed toward the corners of a tetrahedron:



This time, however, only three hydrogen atoms are to be attached. Although the *electrons* are located toward the corners of a tetrahedron, the molecular shape is called **trigonal pyramidal**, not tetrahedral, because the *atoms* lie at the corners of a triangular pyramid:



Molecular geometry is defined by the locations of the atoms.

EXAMPLE 13.8

Deduce the electronic arrangement and the molecular shape of the water molecule.

13.4 ■ Molecular Shape**363****Solution**

The 8 valence electrons, 6 from oxygen and 2 from hydrogen, are oriented toward the corners of a tetrahedron. Adding hydrogen atoms to any 2 of those electron pairs results in a nonlinear molecule. The shape of water is described as **nonlinear, angular, or bent**.

Practice Problem 13.8 Determine the shapes of (a) PCl_3 , (b) SF_2 , and (c) HI .

The electrons in each multiple bond are considered to be one group of electrons.

In summary, the four electron pairs tetrahedrally oriented around a central atom give rise to different *molecular* geometries because of the different numbers of atoms that are attached (Figure 13.6).

Compounds with multiple bonds are only slightly different. The electrons in each multiple bond are considered to be one group of electrons.

EXAMPLE 13.9

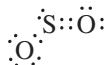
Determine the shape of the sulfur dioxide molecule.

Solution

The 6 valence electrons of sulfur and the 6 from each oxygen atom make 18 total. The electron dot diagram for SO_2 is



The double bond is considered one electron group, the single bond is another, and the lone pair is a third. The three groups arrange themselves as far apart as possible: 120° . The addition of the oxygen atoms results in an angular molecule:



Practice Problem 13.9 Determine the geometry of the SOF_2 molecule, in which the S atom is the central atom.

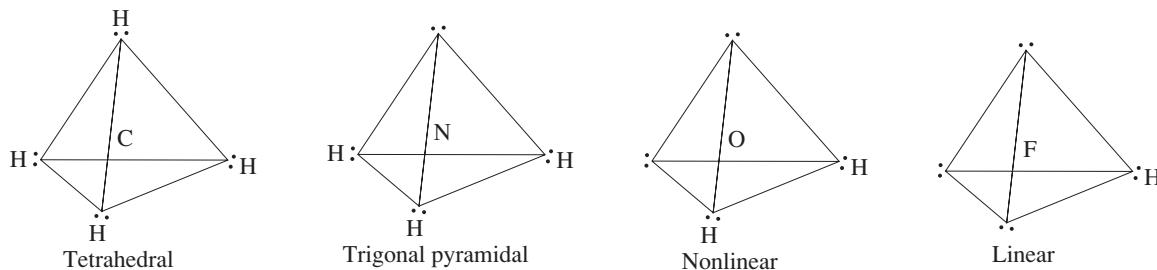


Figure 13.6 Tetrahedral Orientation of Electron Pairs Leads to Different Molecular Geometries

Table 13.4 Orientations of Electron Groups and Shapes of Molecules

Example	Number of Groups of Electrons	Number of Attached Atoms	Orientation of Electron Groups	Shape of Molecule
BeH ₂	2	2	Linear	Linear
BF ₃	3	3	Trigonal planar	Trigonal planar
CH ₄	4	4	Tetrahedral	Tetrahedral
NH ₃	4	3	Tetrahedral	Trigonal pyramidal
H ₂ O	4	2	Tetrahedral	Nonlinear
CO ₂	2	2	Linear	Linear
CH ₂ O	3	3	Trigonal planar	Trigonal planar

Table 13.4 presents several typical molecules with the orientations of their electron groups and their molecular shapes.



ENRICHMENT

If a molecule has two or more central atoms, the geometry around each is deduced separately. The orientation of one central atom to another is rather arbitrary if the central atoms are connected by single bonds.

EXAMPLE 13.10

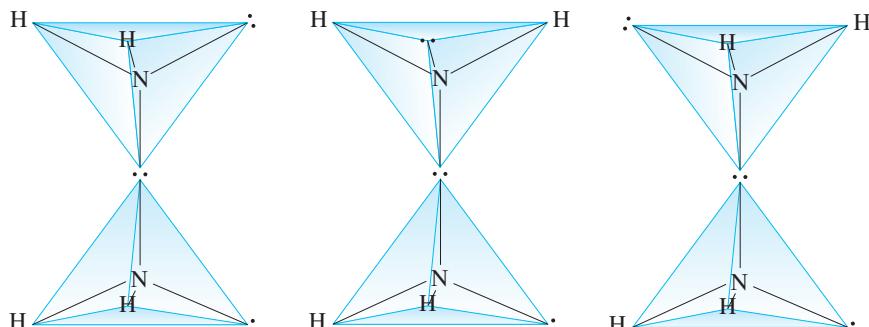
Deduce the geometry of NH₂NH₂.

Solution

The orientation about each nitrogen atom is trigonal pyramidal, as deduced previously for ammonia. The hydrogen atoms on one nitrogen atom can be oriented at any angle with respect to those on the other, as shown in Figure 13.7.

Practice Problem 13.10 Deduce the geometry of hydrogen peroxide, HOOH. Draw the molecule in several orientations.

Figure 13.7 Examples of Various Possible Orientations of One NH₂ Group with Respect to the Other



13.5 ■ Polar and Nonpolar Molecules**365*****Snapshot Review***ChemSkill Builder 12.3,
12.5

- The shape of a molecule is defined by the locations of its *atoms*, not its electron groups.

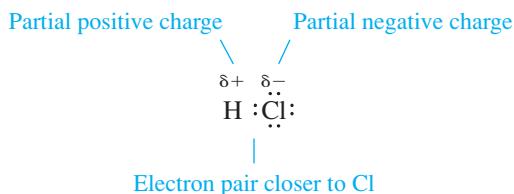
- A. Describe the shape of each of the following molecules, all of which have essentially the same arrangement of electron pairs: (a) CF₄, (b) PF₃, and (c) SF₂.

13.5 Polar and Nonpolar Molecules

A molecule with its center of positive charge in a location different from its center of negative charge is said to be a **polar molecule** or to have a **dipole** or a **dipole moment**. One effect of such asymmetry of charge is intermolecular attraction (Section 13.6). Where do these dipoles come from? Do all molecules with polar bonds (Section 13.3) have dipoles?

Care must be exercised in deciding whether molecules have dipoles. Every molecule with only one polar bond will be a polar molecule. In some molecules with more than one identical polar bond, the effect of one bond will exactly offset the effect of the other(s), and the molecule as a whole will have no dipole.

In diatomic molecules, if the (only) bond is polar, the molecule as a whole has an asymmetrical electronic distribution. For example, HCl has an unequally shared electron pair:

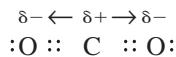


The charges in polar covalent bonds are *partial*. If there were a full charge on each atom, the bond would be ionic.

If the electrons are shared equally, the bond is nonpolar. For example, F₂ has a nonpolar bond.

In these cases of diatomic molecules, such as HCl and F₂, the molecules as a whole can be described as *dipolar* and *nondipolar*, respectively. For simplicity, many chemists refer to them as polar or nonpolar. When using these expressions, be careful to remember the difference between polar *bonds* and polar *molecules*.

When there are two or more bonds—that is, more than two atoms in the molecule—polar bonds might cancel out each other's effects, resulting in a **nonpolar molecule**. For example, in carbon dioxide, two polar bonds connect the carbon and oxygen atoms. However, these bonds lie exactly opposite each other (along a straight line), and the effect of one polar bond is canceled by the effect of the other, so the CO₂ molecule has no dipole; it is a nonpolar molecule.



Although each oxygen atom attracts the electrons more than the carbon atom does (so two polar bonds result), the effect is somewhat like a tug-of-war between

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CHAPTER 13 ■ Atomic and Molecular Properties

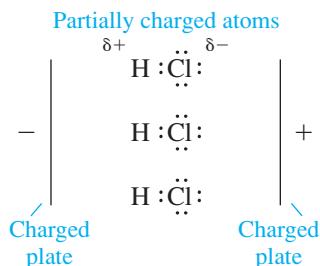


Figure 13.8 Alignment of Dipolar Molecules in an Electric Field

equally strong opponents. The electrons in the one bond are pulled toward one oxygen atom exactly as much as the electrons in the other bond are pulled toward the other oxygen atom. The molecule as a whole has no net dipole.

Another way to look at the situation in CO₂ is that the center of the partial positive charge is on the carbon atom, and the center of the partial negative charges is halfway between the oxygen atoms. But the carbon atom is at the position halfway between the oxygen atoms, so the centers of positive and negative charge are at the same place, and there is no dipole. If the two bonds were not identical or if they were at an angle other than 180° (other than in a straight line), a net dipole would result from two such polar bonds.

EXAMPLE 13.11

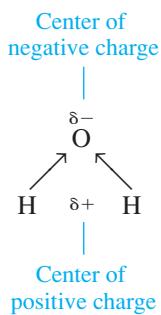
In water molecules, the H—O—H bond angle is 105° . Does the water molecule have a dipole?

Solution

Because the two polar bonds do not exactly cancel each other, a polar molecule results.

Practice Problem 13.11 State the bond type (polar or nonpolar) and the molecular polarity (dipole or no dipole) for each of the following substances:

- (a) Cl_2 (b) NF_3 (c) BrF (d) BCl_3 (e) BeH_2



Polar molecules align themselves in an external electric field. For example, HCl molecules have partial negative charges on the chlorine atoms and partial positive charges on the hydrogen atoms. In a field between two charged plates, HCl molecules tend to align themselves as shown in Figure 13.8.



Snapshot Review



ChemSkill Builder 13.4

- Be sure to distinguish between polar bonds and polar molecules.

A. Which one of the following compounds has polar bonds but not polar molecules?

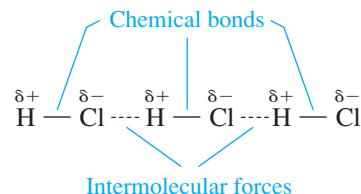
(a) PCl_3 (b) Cl_2O (c) CCl_4

13.6 Intermolecular Forces

In addition to the chemical bonds that hold atoms or ions together, three **intermolecular forces** tend to hold molecules to one another. Note that the atoms *within* molecules are held to one another by chemical bonds and that intermolecular forces are the forces *between* molecules. In general, intermolecular forces are much weaker than chemical bonds.

13.6 ■ Intermolecular Forces**367**

The following three molecules of hydrogen chloride illustrate the difference between chemical bonds and intermolecular forces:



Within each molecule, the hydrogen atom is held to the chlorine atom by a covalent bond; the HCl molecules are attracted to one another by much weaker intermolecular forces.

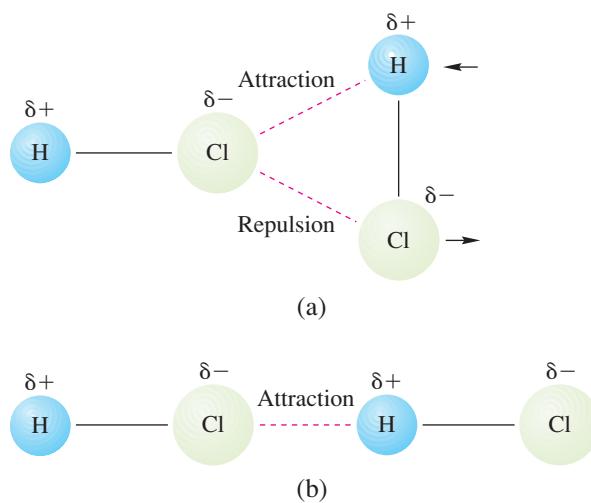
The three intermolecular forces are dipolar attractions, van der Waals forces (also called London forces), and hydrogen bonding. The effects of dipoles (Section 13.5) are considered first, followed by discussions of van der Waals forces and hydrogen bonding.

Dipolar Attractions

As discussed in Section 13.5, when molecules are polar, partial positive and negative charges exist at different positions in molecules of the substance, and adjacent molecules tend to orient themselves so that the somewhat positively charged portion of one molecule is near the somewhat negatively charged portion of the next molecule (Figure 13.9). These portions of adjacent molecules will then exert an attractive force on one another. That is, the attractions of positive charges to negative charges first tend to orient the molecules so that oppositely charged portions are adjacent to each other; the nearness of the oppositely charged portions of the molecules causes a net force of attraction between them. These attractions are an example of intermolecular forces known as dipolar attractions.

Figure 13.9 Orientation of Dipoles

The molecule on the right side in (a) is rotated to the more favorable orientation in (b).



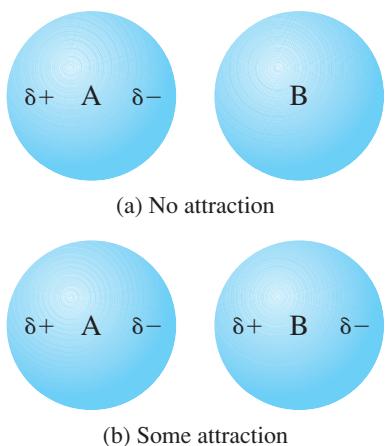


Figure 13.10 Origin of van der Waals Forces

van der Waals Forces

A molecule with no permanent dipole may have an unsymmetrical distribution of electrons for an instant (Figure 13.10a). In that instant, the unsymmetrical charge distribution will tend to induce a similar charge dissymmetry in an adjacent molecule, creating an intermolecular force (Figure 13.10b). Such a force is called a **van der Waals force**, after Johannes D. van der Waals (1837–1923), a Dutch physicist who worked on intermolecular forces. (Many chemists refer to van der Waals forces as *London forces* or *dispersion forces*.) Because the attraction between a particular pair of molecules may last for only an instant, this type of intermolecular force is weaker than dipolar attractions (all other factors being equal). The more electrons in the molecules of a substance, the greater is the van der Waals force. The greater the intermolecular force, the higher is the melting point, the boiling point, or the sublimation point of the substance, and the more energy is required to melt, vaporize, or sublime the substance. **Sublimation** is the process of changing directly from the solid to the gas state.

EXAMPLE 13.12

Which of the following molecules is expected to have the larger van der Waals forces?



Solution

The larger molecule, C_8H_{18} , has more electrons and therefore should have greater van der Waals forces.

Practice Problem 13.12 Which of the following substances would be expected to exhibit the least van der Waals forces? F_2 Cl_2 O_2 H_2 N_2

EXAMPLE 13.13

Which of the following substances will boil at the highest temperature at 1 atm pressure? Cl_2 F_2 O_2 N_2 H_2

Solution

The only intermolecular forces that occur in these substances are the van der Waals forces. The more electrons present, the greater is the van der Waals force; the greater the van der Waals force, the higher is the normal boiling point. Thus, Cl_2 is expected to have the highest boiling temperature.

Hydrogen Bonding

Hydrogen bonding is the intermolecular force of attraction between a hydrogen atom in one molecule and a small, highly electronegative atom with an

13.6 ■ Intermolecular Forces**369**

Figure 13.11 Hydrogen Bonding in Hydrogen Fluoride
Each hydrogen atom is bonded to a fluorine atom and forms a hydrogen bond with an adjacent fluorine atom.

unshared pair of electrons in another molecule. The most electronegative atoms have a great affinity for electrons (Section 5.1). Fluorine, oxygen, nitrogen, and chlorine are the most electronegative elements, but a chlorine atom is too large to be very effective in hydrogen bonding. A bonded hydrogen atom has its bonding electrons oriented away from an adjacent molecule. That “outer” side of the hydrogen atom is rather positive and can attract an unshared pair of electrons, as shown in two molecules of hydrogen fluoride:



The electrons bonding the hydrogen atom on the right are located to its right, which leaves the left side of that atom rather positive. It is attracted almost equally by the unshared electron pair of the fluorine atom to its left and the electron pair it shares with the fluorine atom to its right.

In fact, hydrogen atoms in liquid hydrogen fluoride migrate rather freely from one fluorine atom to another. They are attracted first by one, then by the other. As an overall result, these attractions tend to keep the fluorine atoms close together, resulting in a rather substantial intermolecular force. Consider the model of hydrogen fluoride in Figure 13.11. If the ends of the illustration are covered, it is hard to tell which pair of electrons each hydrogen atom is sharing covalently with a fluorine atom and which is involved in the hydrogen bonding.

In summary, for hydrogen bonding to occur, the requirements are

1. A hydrogen atom
2. A nitrogen, oxygen, or fluorine atom
3. An unshared (lone) pair of electrons on the nitrogen, oxygen, or fluorine atom

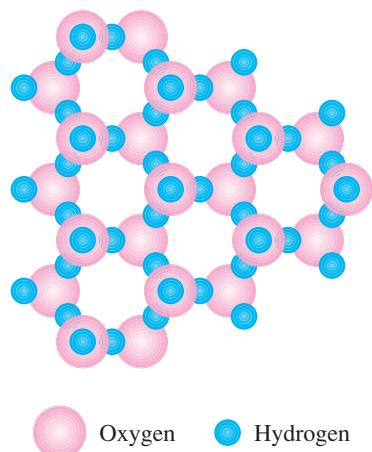


Figure 13.12 Hydrogen Bonding in Ice

EXAMPLE 13.14

Which of the following form hydrogen bonds?

- (a) HF (b) C₂H₄ (c) HBr (d) NH₄⁺ (e) H₂

Solution

- (a) HF will form hydrogen bonds because it has (1) hydrogen atoms; (2) a small, highly electronegative atom; and (3) at least one free pair of electrons on that atom.

**ENRICHMENT**

Hydrogen bonding is responsible for the low density of ice compared with liquid water (Figure 13.12). This difference is absolutely necessary for life as we know it. Because ice is less dense than water, it floats on top of water and acts as a blanket to protect

the aquatic life below from the extremes of cold that occur above the ice. If it is pure, the water at the bottom never gets below 0°C (32°F) unless it freezes. Hydrogen bonding is also responsible for the helical structure of certain proteins in plants and animals (Figure 13.13).

- (b) C_2H_4 will not form hydrogen bonds because the carbon atoms have no lone pairs to bond with hydrogen atoms from other molecules.
- (c) HBr will not form hydrogen bonds because the bromine atom is too large and not electronegative enough.
- (d) NH_4^+ by itself cannot form hydrogen bonds because it has no lone pairs.

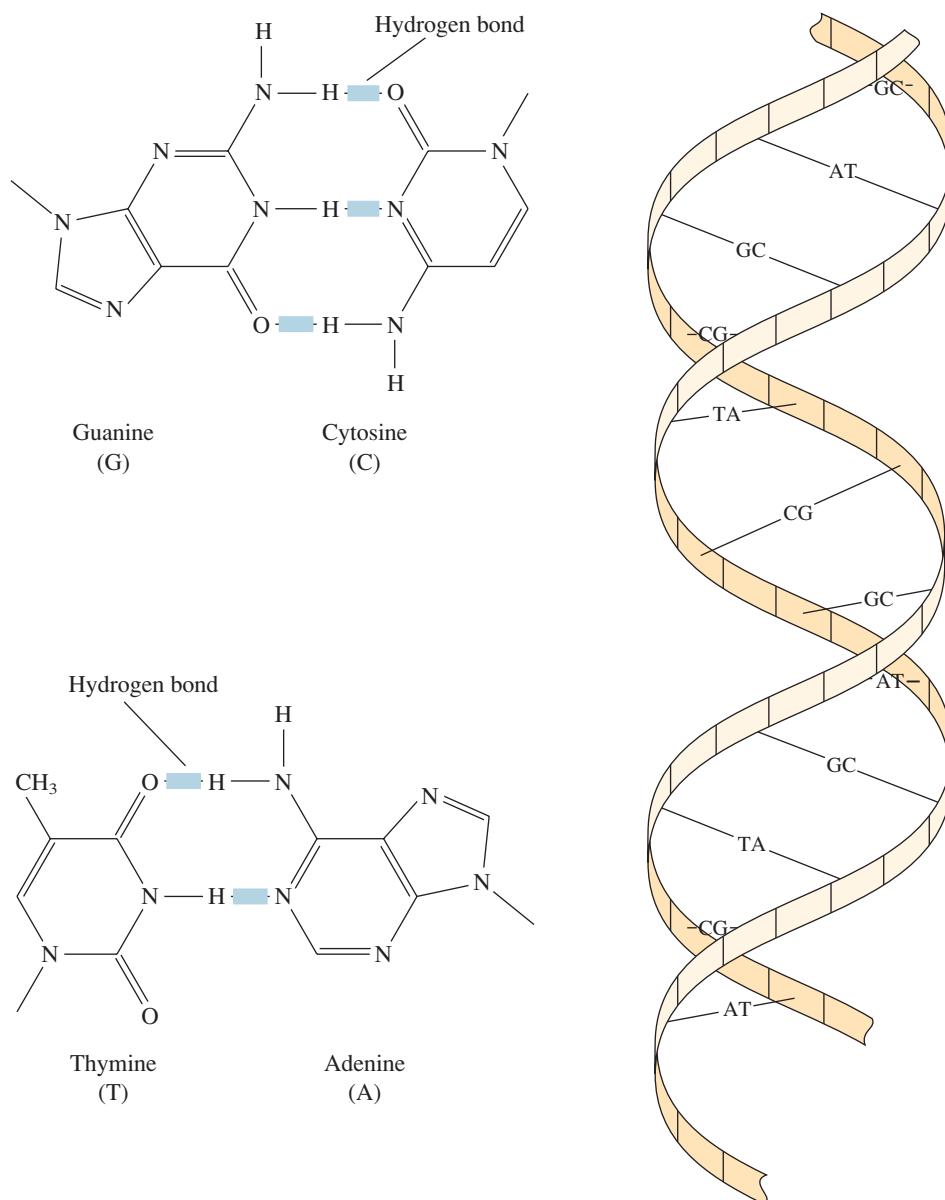


Figure 13.13 Hydrogen Bonding in the DNA Double Helix

The hydrogen bonding is indicated by the blue shading in the structural formulas. The base groups detailed on the left are represented by their initials in the double helix on the right. Other than those occupied by a nitrogen atom, each corner of each hexagon or pentagon is occupied by a carbon atom.

■ Summary**371****Table 13.5 Forces of Attraction**

Chemical bonds
Covalent
Ionic
Metallic
Intermolecular forces
van der Waals forces
Dipolar attractions
Hydrogen bonding



ChemSkill Builder 14.4

- (e) The covalent bond in _____ is a chemical bond, not the intermolecular force called hydrogen bonding.

Practice Problem 13.14 Which of the following substances are expected to form hydrogen bonds?

- (a) H₂O (b) CH₃OH (c) NH₃

All the forces of attraction discussed so far are outlined in Table 13.5.

Snapshot Review

- Intermolecular forces must be distinguished from chemical bonds. Intermolecular forces are the forces *between* molecules; chemical bonds are the bonds *within* molecules (and polyatomic ions) and between ions.

- A. Classify each of the following as an intermolecular force or a chemical bond: (a) bond in H₂ and (b) hydrogen bond.

Key Terms

Key terms are defined in the Glossary.

angular molecule (13.4)
atomic size (13.1)
bent molecule (13.4)
central atom (13.4)
controlled experiment (13.1)
dipole (13.5)
dipole moment (13.5)
electron affinity (13.2)
electronegativity (13.3)
electron group (13.4)

hydrogen bonding (13.6)
intermolecular force (13.6)
ionic size (13.1)
ionization energy (13.2)
linear molecule (13.4)
molecular shape (13.4)
nonlinear molecule (13.4)
nonpolar bond (13.3)
nonpolar molecule (13.5)
polar bond (13.3)

polar molecule (13.5)
second ionization energy (13.2)
sublimation (13.6)
tetrahedral molecule (13.4)
third ionization energy (13.2)
trigonal planar molecule (13.4)
trigonal pyramidal molecule (13.4)
van der Waals force (13.6)

Symbols/Abbreviations

δ (delta) (13.3)

Summary

The properties of atoms and molecules affect the properties of the substances they constitute. Ionic size is an important property, affecting the ability of the atom to gain or lose an electron. The size of an atom or ion increases as electrons are added, decreases with greater numbers of protons, and varies periodically if both electrons and protons are varied (Section 13.1).

The ionization energy of an atom is the energy required to remove an electron from it; the electron affinity is the energy liberated when an electron is added

to the atom. Both of these quantities refer to gaseous atoms producing gaseous ions. For some atoms, the electron affinity is negative—that is, energy is required to add an electron to the atom (Section 13.2).

Electronegativity is a semiquantitative measure of the electron-attracting power of a bonded atom. The greater the electronegativity, the more the atom attracts electrons. Covalent bonding between atoms of different electronegativity yields polar bonds; that between atoms of the same electronegativity yields nonpolar bonds (Section 13.3).

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We can deduce the shapes of many molecules from their electron dot diagrams and the fact that the electron groups on the central atom tend to get as far apart as possible while remaining attached to that atom. We then attach the outer atoms and describe the molecular shape by the positions of the atoms. The electron groups and their attached atoms are not necessarily limited to a planar arrangement (Section 13.4).

A molecule with more than one polar bond in which all the effects of the polar bonds do not cancel out has a dipole moment—an electrical dissymmetry that causes an intermolecular attraction between this molecule and other similar ones. This attraction is called a dipolar attraction, and it lowers the ability of the substance to exist in the gas phase. However, if the polar bonds in a molecule are oriented so that their effects are canceled out, as in carbon dioxide, then a molecule with no dipole results (Section 13.5).

CHAPTER 13 ■ Atomic and Molecular Properties

Intermolecular attractions include dipolar attractions, as well as van der Waals forces and hydrogen bonding. van der Waals forces are similar to dipolar attractions but result from instantaneous dissymmetry of charge, which may disappear the next instant. The more electrons in the molecule, the greater is the van der Waals force. However, van der Waals forces tend to be lower in magnitude than dipolar attractions.

Hydrogen bonding is an intermolecular force between a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom and an unshared pair of electrons on another such atom in an adjacent molecule (or sometimes even in the same molecule). The hydrogen atom may be bonded to one small electronegative atom and attracted to another at one instant and then bonded to the second and attracted to the first at the next instant (Section 13.6).

Items for Special Attention

- Be sure to distinguish between atomic size and ionic size.
- Ionization energy and electronegativity vary in the same ways in the periodic table, but opposite to the way atomic size varies.
- If a bond is either polar or nonpolar, it is covalent.
- Adding a new shell of electrons considerably increases the size of the atom; breaking into a complete octet to ionize an electron requires a huge quantity of energy.
- The term *ionization energy* means “first ionization energy” unless otherwise specified.
- Any molecule with one or more lone pairs on the central atom will have a different shape of the electron groups from the shape of the molecule (defined by the locations of the atoms).

- Molecular geometry is actually determined experimentally. We can deduce the geometry of many molecules from their electron dot diagrams, with correct results in a great majority of cases.
- Remember the difference between polar bonds and polar molecules. A molecule can have polar bonds without being a polar molecule.
- Hydrogen bonding is the intermolecular force between molecules that have hydrogen atoms attached to very small, highly electronegative atoms with unshared pairs of electrons (nitrogen, oxygen, or fluorine atoms). It has nothing to do with the chemical bond between the two hydrogen atoms in H_2 molecules.

Answers to Snapshot Reviews

- 13.1 A. Opposite charges attract, and the more protons there are, the greater will be the attraction for the electrons.
13.2 A. (a) $\text{Sr} < \text{Ca} < \text{Mg}$ (b) $\text{As} < \text{S} < \text{F}$
 (c) $\text{Sb} < \text{Se} < \text{S}$
13.3 A. (a) F (b) N (c) Br

- 13.4 A. (a) Tetrahedral (b) Trigonal pyramidal
 (c) Angular
13.5 A. (a) CCl_4 (It has a symmetrical structure.)
13.6 A. (a) Chemical bond (b) Intermolecular force

Self-Tutorial Problems

- 13.1 (a) In which periodic group does each atom have a new shell of electrons?
(b) In which periodic group does the size of each element increase markedly from the preceding atom in the periodic table?

- 13.2 Make a table of the number of protons, the number of electrons, and the relative sizes for each of the following parts:
(a) F and F^- (b) Ne and O^{2-}
(c) Na and Na^+ (d) Ar and Cl^-

■ Problems**373**

- 13.3** In each part determine which of the following is larger.
 (a) N Li (b) N^{3-} Li^+
- 13.4** Would a polyatomic anion (like SO_4^{2-}) be expected to be larger or the same size as the ion of the central atom (for example, S^{2-})?
- 13.5** (a) Which alkali metal atom is smallest?
 (b) Which one has the smallest radius?
 (c) Which one has the smallest volume?
 (d) What difference is there, if any, among these questions?
- 13.6** (a) Does any gaseous atom lose an electron spontaneously to form a gaseous ion?
 (b) Is any ionization energy negative?

Problems**13.1 Atomic and Ionic Sizes**

- 13.11** Select the largest atom or ion in each of the following parts:
 (a) Na^+ Na (b) Rb^+ Na^+ K^+
 (c) Br^- Cl^- F^- (d) S S^{2-}
 (e) Sr^{2+} Kr Br^- (f) O S^{2-}

- 13.12** Which one in each of the following groups is largest?
 (a) Co Co^{2+}
 (b) Fe Fe^{2+} Fe^{3+}
 (c) S^{2-} SO_4^{2-}

- 13.13** Which one in each of the following groups is largest?
 (a) O^{2-} F^- Ne Na^+ Mg^{2+}
 (b) Na^+ Al^{3+} F^-

- 13.14** Which second-period anion is smallest?
13.15 Which of the following is largest?
 Ac Cm Lr

- 13.16** Referring to the periodic table only, identify the element, excluding hydrogen, that has (a) the largest atoms and (b) the smallest atoms.

- 13.17** Select the largest atom in each of the following parts:
 (a) F Cl Br I (b) P N O
 (c) K Fe Zn (d) K Li Na
 (e) Cs Si F (f) Ge Si N

- 13.18** Select the largest ion of the following:
 Cl^- ClO^- ClO_3^- IO_3^-

13.2 Ionization Energy and Electron Affinity

- 13.19** (a) Referring to the periodic table only, tell which element has the highest ionization energy.
 (b) Which element has the lowest?

- 13.7** State the difference between a polar bond and a polar molecule.
- 13.8** (a) Give an example of a nonpolar molecule with polar bonds.
 (b) Is there any polar molecule with all nonpolar bonds?
- 13.9** Describe the orientation of the electron groups and the geometry of each molecule in (a) CCl_4 (b) NCl_3 (c) Cl_2O
- 13.10** What is the difference between the bonding in the hydrogen molecule and hydrogen bonding?

- 13.20** What periodic group of elements, on average, has (a) the highest ionization energies? (b) the lowest?
- 13.21** (a) Is hydrogen an alkali metal, as reflected by ionization energy?
 (b) Is hydrogen an alkali metal, as reflected by size?
- 13.22** (a) What periodic group of elements has the lowest ionization energy?
 (b) What main group elements are next lowest?
- 13.23** Select the atom with the highest ionization energy in each of the following parts:
 (a) O S Se (b) Li K Rb
 (c) Ca Se Kr (d) Na O S
 (e) C O P (f) Cs Ga F
- 13.24** Atoms of elements of which periodic group(s) do not produce energy as they gain electrons?

13.3 Electronegativity and Bond Polarity

- 13.25** From the data of Figure 5.4, predict the bond type (ionic, polar covalent, nonpolar covalent) in each of the following:
 (a) PF_3 (b) SrF_2 (c) N_2
- 13.26** Predict the bond type (ionic, polar covalent, nonpolar covalent) in each of the following:
 (a) H_2O_2 (b) Mg_3N_2 (c) CO_2
- 13.27** From the data of Figure 5.4, predict the bond type(s) (ionic, polar covalent, nonpolar covalent) in each of the following:
 (a) Li_2O (b) CCl_2Br_2
- 13.28** Predict the bond type (ionic, polar covalent, nonpolar covalent) in each of the following:
 (a) IF_5 (b) $\text{H}-\text{C}\equiv\text{C}-\text{H}$

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13.29 Predict the bond types (ionic, polar covalent, nonpolar covalent) in each of the following:

- (a) $\text{Fe}(\text{ClO}_3)_2$ (b) $(\text{NH}_4)_2\text{SO}_3$

13.4 Molecular Shape

13.30 Determine the shape of (a) the BeF_2 molecule and (b) the OF_2 molecule.

13.31 Determine the shape of (a) NO_2^- and (b) NO_3^- .

13.32 Deduce the shape of each of the following:

- (a) CH_3F (b) CF_4
(c) CHF_3 (d) CH_4

13.33 Determine the shape of (a) the SO_4^{2-} ion, (b) the PO_4^{3-} ion, and (c) the NH_4^+ ion.

13.34 Determine the shapes of (a) NO_2 and (b) ClO_2 .

Hint: Unpaired electrons are “groups.”

13.35 (a) Determine the shape of the SO_2 molecule. (b) Does the fact that SO_2 has two resonance forms (Chapter 5) affect the answer to part (a)?

13.5 Polar and Nonpolar Molecules

13.36 What is the difference between a nonpolar bond and a nonpolar molecule?

13.37 Can a molecule have polar bonds and not a dipole?

13.38 Can a molecule have nonpolar bonds only and have a dipole?

13.39 Can a molecule have some nonpolar bonds and have a dipole?

13.40 Give an example of a nonpolar molecule with:

- (a) Two polar bonds
(b) Three polar bonds
(c) Four polar bonds

13.41 XeF_4 molecules each have four F atoms at the corners of a square with the Xe atom at the center. Are they polar molecules?

General Problems

13.50 (a) Predict the geometry of NO_2 (a nonoctet molecule with only seven electrons around the central nitrogen atom).

(b) Predict whether the O—N—O angle in NO_2^- , which has the extra electron on the nitrogen atom?

13.51 (a) Calculate the sum of the first *two* ionization energies of sodium and the first *three* ionization energies of aluminum (see Table 13.1).

CHAPTER 13 ■ Atomic and Molecular Properties

13.42 (a) Give an example of a nonpolar molecule with three polar bonds.

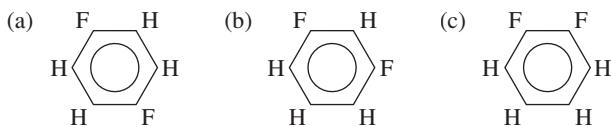
(b) Give an example of a polar molecule with three polar bonds.

13.43 (a) Are either CH_4 or CF_4 molecules expected to have dipoles?

(b) Are CH_2F_2 molecules?

(c) Explain.

13.44 Which one of the following rigid molecules has no dipole?



13.45 (a) Will carbon disulfide molecules be oriented in an external electric field (see Figure 13.8)?

(b) Will water molecules?

13.6 Intermolecular Forces

13.46 State whether each of the following substances has only van der Waals forces, dipole moments but no hydrogen bonding, or hydrogen bonding:

- (a) CH_3OH (b) Ne (c) F_2
(d) CH_2F_2 (e) BCl_3 (f) CBr_4

13.47 Explain how we can tell that the BCl_3 molecule, which is triangular and planar, has no dipole. (See part [d] of Practice Problem 13.11.)

13.48 In which of the diatomic elemental gases (H_2 , N_2 , O_2 , F_2 , Cl_2) are van der Waals forces (a) least and (b) greatest?

13.49 Using Figure 5.4, determine the formulas of two binary compounds of nonmetals that have only nonpolar bonds and thus only van der Waals forces and lack of total symmetry.

(b) Would Na^{2+} or Al^{3+} be easier to obtain in the gas state?

(c) Which is a familiar ion in the solid state?

13.52 When a *gaseous* atom and ion are specified in Section 13.2, how close are their nearest neighbors? (See Section 12.10.) Are there apt to be any significant attractions between such atoms or ions?

■ General Problems

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13.53 Why is the polarity of the covalent bonds in Na_2SO_3 of little interest, compared with that in a covalent molecule such as SO_3 ?

13.54 (a) The AX_3 molecule, where A is one element and X is another element with a significantly different electronegativity, has no dipole. What is its geometry?

(b) The ZX_3 molecule, where Z is one element and X is another element with a significantly different electronegativity, has a finite dipole. What is its probable geometry?

13.55 Determine the shape of (a) the SOCl_2 molecule and (b) the H_2SO_4 molecule.

13.56 Determine the shape of (a) the $\text{O}_2\text{N}-\text{NO}_2$ molecule and (b) the HOOH molecule.

13.57 Determine the bond angles around each nitrogen atom in (a) the $\text{HN}=\text{NH}$ molecule and (b) the NH_2-NH_2 molecule.

13.58 Consider the size of H^+ . Is it qualitatively any different from the size of every other cation? Would you expect such an ion to attract electrons well or poorly?

13.59 The force of attraction between oppositely charged ions varies inversely as the square of the distance between them:

$$f = \frac{k}{d^2}$$

Ions in a solid might be at a distance about 2.0×10^{-10} m apart. If a pair of ions is separated to twice the distance in the solid, what percentage of the force of attraction remains? If they are separated to the average distance between gas molecules (say 3×10^{-9} m), how much force is expected to remain?

13.60 If two ions are separated to a distance 10 times their normal separation, what happens to their normal force of attraction?

13.61 (a) Calculate the average volume occupied by one gas molecule at STP.

(b) Assuming that each molecule occupies a cube with that volume, calculate the length of each edge of the cube. That is the average distance between molecules in this sample of gas.

(c) Compare the attraction of two monatomic ions at this distance with that of the same two ions in a solid

lattice, about 2.00×10^{-10} m apart. (See Problem 13.59.)

13.62 Which anion in Figure 13.2, when compared with its parent atom, has had the greatest percentage increase in radius in acquiring the extra electron(s)?

13.63 Calculate the difference between the ionization energy of lithium and the electron affinity of bromine. Deduce whether the transfer of an electron from one to the other in the gas phase is spontaneous.

13.64 Without looking at Figure 5.4, deduce the bond type (ionic, polar covalent, nonpolar covalent) in each of the following:

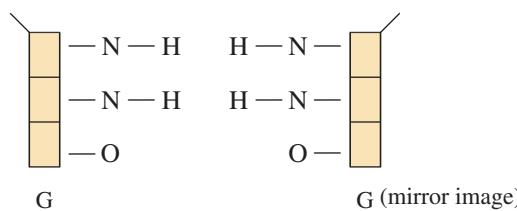
(a) SeCl_2 (b) CO_2 (c) AlBr_3

13.65 Calculate the difference between the sum of the first two ionization energies of magnesium and the sum of the first two electron affinities of oxygen. Deduce whether the transfer of two electrons from one to the other in the gas phase is spontaneous. (The second electron affinity of oxygen is -816 kJ/mol.)

13.66 Plot the normal boiling points of H_2S (-60.7°C), H_2Se (-42°C), and H_2Te (-2°C) versus the atomic number of the central atom. Extrapolate the line to atomic number 8, for H_2O . Predict the normal boiling point that water would have if it were not for its hydrogen bonding.

13.67 The hydrogen bonding in water seems to raise the boiling point from that expected if there were no hydrogen bonding $1\frac{1}{2}$ to 2 times more than the hydrogen bonding in HF or NH_3 . (See Problem 13.66.) Give a possible explanation.

13.68 Draw representations of the four bases of Figure 13.13, with the covalent bond (to the rest of the DNA) pointing up. Also draw their mirror images, as shown below for guanine (G). See if any combination other than G with C or A with T would be as effective in hydrogen bonding to hold the strands of DNA together.



14

Solids, Liquids, and Energies of Physical and Chemical Changes

- 14.1 Nature of the Solid and Liquid States
- 14.2 Changes of Phase
- 14.3 Measurement of Energy Changes
- 14.4 Enthalpy Changes in Chemical Reactions



Cubic crystals of pyrite, FeS_2

Review Clues

- Section 14.1** Chapter 13, Sections 5.2,
5.5, 12.10
- Section 14.3** Section 2.6, Appendix 1
- Section 14.4** Section 2.2

Objectives

- 14.1** To describe the characteristics of the solid and liquid states and to determine how the intermolecular forces influence solids and liquids
- 14.2** To describe the processes involved when a substance changes from one state to another
- 14.3** To calculate the heat required to change a substance from one temperature to another, or from one phase to another, or both
- 14.4** To calculate enthalpies of many reactions from known data for other reactions, and to recognize the difference between energy and enthalpy

14.1 ■ Nature of the Solid and Liquid States**377****Table 14.1** Properties of the Particles of Solids, Liquids, and Gases

	Solids	Liquids	Gases
<i>Strength of attractive forces</i>	Strong	Moderately strong	Negligible
<i>Components</i>	Molecules or bonded atoms or ions	Molecules	Molecules
<i>Distance between particles</i>	Touching	Touching	Far apart
<i>Permanence of position</i>	Permanent	Variable	Variable

Gases are characterized by having little or no forces of attraction between their molecules (Section 12.10). In contrast, the forces between the particles of which liquids and solids are composed are significant. These forces range from ionic or covalent bonds, which are strong, to much weaker intermolecular forces. Intermolecular forces were discussed in Section 13.6. Substances that are liquid or gaseous at room temperature are composed of molecules. In contrast, solids may be composed of (1) macromolecules (atoms covalently bonded together in large networks), (2) ions bonded together, (3) molecules, or (4) atoms bonded together by loosely held valence electrons. The particles that make up solids are held more or less stationary in their positions; the molecules that make up liquids and gases are much freer to move about. In gases, the distance between molecules is very large compared with the size of the molecules themselves; in liquids and solids, the particles are essentially touching one another. These characteristics are summarized in Table 14.1.

Section 14.1 examines the liquid and solid states. Section 14.2 discusses changes of phase and concepts related to systems with two phases in contact, such as vapor pressure. In Section 14.3, the measurement of quantities of heat added to or removed from a system is introduced, and the energies involved in phase changes are calculated. Section 14.4 deals with the enthalpies involved in chemical reactions.

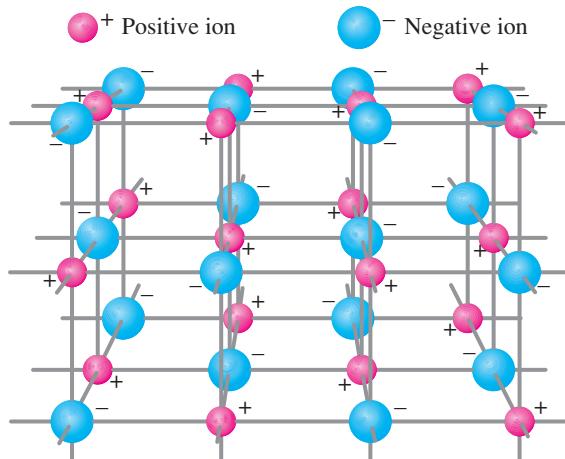
14.1 Nature of the Solid and Liquid States

The Solid State

Solids are classified as **crystalline solids** or **amorphous solids**. Crystalline solids, such as an ice cube or a sodium chloride crystal, have a definite melting point. Amorphous solids, such as a chocolate bar or glass, get softer and softer as the temperature is raised. The structures of crystalline solids feature regularly repeating arrangements of the constituent particles. The structure of amorphous solids is not regular, but something like that of liquids; sometimes, amorphous solids are called “supercooled liquids.”

Crystalline solids may be classified as (1) **ionic solids**, in which the repeating units are ions; (2) **network solids** (or macromolecular solids), in which covalently bonded atoms are the repeating units; (3) **molecular solids**, in which individual molecules are the repeating units; and (4) **metallic solids**, in which individual metal atoms are held together by their loosely held valence electrons.

Figure 14.1 Sodium Chloride Structure



The regularity of the units is characteristic of crystalline solids. The sodium chloride structure (also called the rock salt structure) is an example of an ionic lattice (Figure 14.1). Diamond, graphite (pencil “lead”), and silica (sand) are examples of network lattices (Figure 14.2). Molecular solids include such solids as ice and naphthalene (mothballs), $C_{10}H_8$. Most elemental metals are examples of metallic solids. Regardless of their specific classifications, all crystalline solids are characterized by regularly repeating arrangements of their component particles.

EXAMPLE 14.1

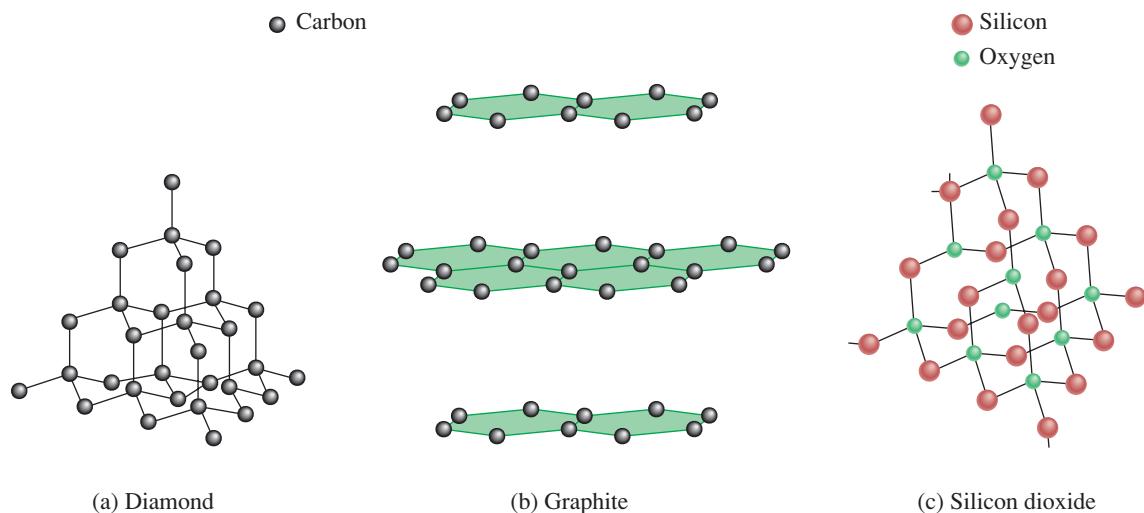
- What is the difference between a stack of concrete blocks and a concrete wall?
- The atoms in both network (macromolecular) and molecular solids are covalently bonded. What is the difference in their structures?

Solution

- The concrete in each block in a stack is held firmly to the rest of that block, but the blocks are not held tightly to one another. The concrete wall is held together tightly from one end to the other.
- In molecular solids, a few to hundreds of atoms (or even thousands of atoms in polymeric substances such as plastics) are bonded into each molecule, as for example in I_2 , P_4O_{10} , or $C_6H_{12}O_6$. These individual molecules are held to one another by intermolecular forces. In macromolecular solids, covalent bonds connect all the atoms—hundreds of thousands or even millions of them—in a network (see Figure 14.2).

Practice Problem 14.1 What type of solid is described by each of the following statements?

- Fourteen atoms are bonded in each molecule.
- About 500 million ions are bonded to one another.
- About 500,000 atoms are bonded to one another with covalent bonds.

14.1 ■ Nature of the Solid and Liquid States**379****Figure 14.2** Tiny Portions of Structures of Three Macromolecular Solids

The structures extend almost indefinitely in all directions, left and right, up and down, in and out.

ITEM OF INTEREST

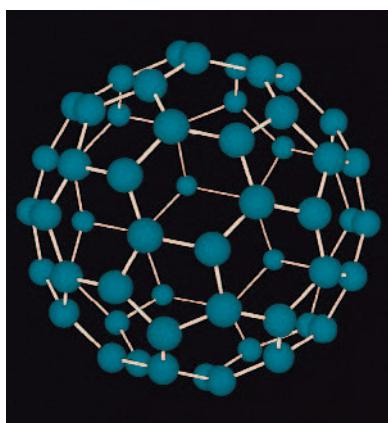
Twenty years ago Robert Curl, Harold Kroto, and Richard Smally discovered that carbon exists in a new form, with 60 atoms covalently bonded in the shape of a ball (Figure 14.3).

EXAMPLE 14.2

- Is the 60-carbon molecule a macromolecular form of carbon?
- Would you expect its melting point to be as high as that of graphite?

Solution

- No, although a large molecule, it is not macromolecular.
- Its melting point is much lower.

**Figure 14.3** The 60-Carbon Molecule

The 60-carbon molecule in the shape of a geodesic dome is named after the architect who designed the dome, Buckminster Fuller. The molecule's nickname "Buckyball" is catchier than its full name—Buckminster fullerene.

EXAMPLE 14.3

How many pairs of ions are included in a tiny cube of rock salt, if 250,000 sodium ions occur on each edge in the three perpendicular directions?

Solution

The cube contains $(2.5 \times 10^5)^3 = 1.6 \times 10^{16}$ sodium ions. There are also 1.6×10^{16} chloride ions in this tiny particle of NaCl. (Remember that 1.00 mol, or 58.5 g, of NaCl includes 6.02×10^{23} formula units of NaCl, about 39 million times as many as in this tiny cube.)

380**CHAPTER 14 ■ Solids, Liquids, and Energies of Physical and Chemical Changes**

An ionic substance is composed of individual positive and negative ions, which form a three-dimensional lattice. The attraction of one ion is not limited to any single other ion but extends to all the oppositely charged ions around it. Thus, the attractive forces throughout the lattice are strong, and, therefore, the structure is hard to break up. Ionic substances are solids at room temperature.

Practice Problem 14.3 How many iodine molecules and how many iodine atoms are included in a cube of solid I₂ with 250,000 molecules on each edge?

Molecular solids are relatively easy to melt or sublime, but network or ionic solids have very high melting or sublimation points. In general, the weaker the force holding the particles together, the easier it is to get them apart. The strong forces (chemical bonds) that hold network or ionic solids together take a great deal of energy to overcome in order to get a substance into the liquid or the gaseous state.

In macromolecules such as diamond and silica, covalent bonds link millions of atoms into a giant molecule, rather than linking only a few atoms into each of many small molecules. Because the atoms are held together by strong forces, the solid is difficult to “get apart.” Diamond and graphite are still solids at temperatures up to 3500°C. Ionic compounds, made up of oppositely charged ions with ionic bonds extending throughout the solid, also have high melting points (typically at least 500°C). In contrast, solids composed of molecules, held to one another by (weak) intermolecular forces (Section 13.6), are much more easily melted or sublimed.

The four types of crystalline solids are summarized in Table 14.2.

EXAMPLE 14.4

State the type of bonding or force holding together each of the following solids, and indicate whether the melting point is low or high:

- (a) Silica, SiO₂ (b) KCl (c) Ammonia

Solution

- (a) (Network) covalent bonding, high melting point
(b) Ionic bonding, high melting point
(c) Hydrogen bonding (a type of intermolecular force), very low melting point

Table 14.2 Types of Crystalline Solids

Type	Units	Relative Melting and Boiling Points
Molecular	Small molecules	Very low to moderate
Ionic	Ions	High to very high
Network	Atoms covalently bonded throughout	Very high
Metallic	Metal atoms bonded by mobile valence electrons	Low to very high

Practice Problem 14.4 Three solids have the following melting points: 90°C, 801°C, and 1475°C. Which one is molecular?

The Liquid State

Solids have strong forces holding the particles in their proper positions. Only molecular solids (and some metals) can be melted at temperatures anywhere near room temperature or below. The energy involved in disrupting the covalent or ionic bonds of other types of solids makes the melting points of such solids very high, up to hundreds or even thousands of degrees Celsius (Table 14.3). The weaker intermolecular forces involved in molecular solids allow most of them to be melted at temperatures below about 200°C. Substances that exist as liquids at these relatively low temperatures are composed of molecules, uncombined atoms (noble gases), or weakly bonded atoms (metals such as mercury).

The molecules of a liquid are in contact with one another, as in molecular solids, but the regularity of their arrangement does not extend very far. We might think of liquids as being like a crowd of commuters in a railroad station and solids being more like an army of soldiers on parade. The molecules in a liquid are not arranged in any regular pattern, although some may form pairs or

Table 14.3 Melting Points of Various Types of Solids

Solid	Formula	Melting Point (°C)
<i>Molecular</i>		
Aspirin	C ₉ H ₈ O ₄	135
Benzoic acid	HC ₆ H ₅ CO ₂	122.4
Carbon tetrabromide	CBr ₄	90.1
Carbon tetrachloride	CCl ₄	-23
Carbon tetrafluoride	CF ₄	-184
Helium	He	-272.2 (at 26 atm)
Naphthalene	C ₁₀ H ₈	80.22
Tetrasulfur tetranitride	S ₄ N ₄	179 (sublimes)
Water	H ₂ O	0.00
<i>Ionic</i>		
Aluminum oxide	Al ₂ O ₃	2045
Magnesium oxide	MgO	2800
Potassium carbonate	K ₂ CO ₃	891
Sodium chloride	NaCl	801
<i>Macromolecular</i>		
Diamond	C	>3550
Graphite	C	3652 (sublimes)
Quartz	SiO ₂	1610
<i>Metallic</i>		
Cesium	Cs	28.4
Iron	Fe	1535
Mercury	Hg	-38.87
Sodium	Na	97.8
Tungsten	W	3410

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small groups. Molecules in a liquid are able to slip and slide past one another, giving liquids their **fluidity**. In contrast, molecules (or other particles) of solids cannot move past one another, giving solids their unyielding structures.

A material is a solid because the energy available to its particles is not sufficient to overcome the relatively strong attractive forces holding the individual particles together. The molecules of liquids exhibit attractive forces strong enough to hold them in close proximity to one another but not to hold them relatively motionless. Gases, of course, have very weak intermolecular forces relative to their energies, and their molecules are almost completely independent of one another.

**Snapshot Review**ChemSkill Builder
14.2, 14.3

- The rigidity and constant volume of solids results from the relatively strong forces holding the particles together. In liquids, the forces are not quite as strong, leading to the ability of liquids to assume the shape of their containers.

- A. What types of particles can constitute a solid?
- B. Amorphous solids are sometimes called “supercooled liquids.” List their similarities to crystalline solids and to liquids.

14.2 Changes of Phase

Any process of changing state (or phase) for a sample of matter is called a **phase change**. When a solid changes to a liquid as a result of a rise in temperature, the process is called **melting**, or **fusion**. The process of changing a liquid to a gas is called **evaporation**, or **vaporization**. A gas in contact with its liquid is often called a **vapor**. Changing a solid directly into a gas is called **sublimation**. Changing a liquid to a solid is called **freezing**, and changing a gas to either a solid or a liquid is called **condensation**. These states and changes are summarized in Figure 14.4.

As an example of these phase changes, we will investigate the vaporization process in some detail. It takes energy to cause a liquid to evaporate. We can put a pan of water on a stove and add heat to it to cause rapid vaporization. Coming out of a swimming pool on a hot, breezy day makes us aware that energy is used to evaporate a liquid. The breeze causes evaporation, which uses energy, thereby lowering our temperatures. Even on a hot day, we grab for a towel to stop the evaporation and resulting cooling.

A process called **distillation** is often used to purify liquids. The liquid is heated to vaporize it, and then the vapor is cooled to condense it back to a liquid in a different place (Figure 14.5). Impurities that are less easily vaporized are left behind in the original container, and those that are more easily vaporized distill first and are discarded before the desired product distills.

On a molecular level, the change from a liquid to a gas is accompanied by a separation of the molecules—from close proximity to far apart. Only the most energetic of the liquid molecules have sufficient energy to overcome the attractive forces and go into the gas phase. Thus, the process of vaporization leaves behind the less energetic molecules. As we learned in Section 12.10, the absolute

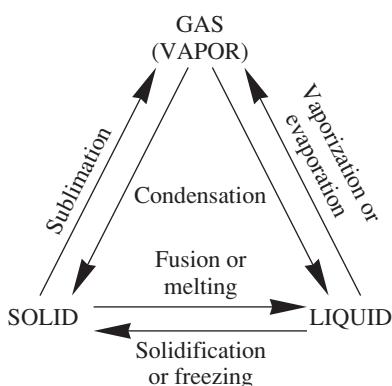


Figure 14.4 Terminology of Phase Changes

14.2 ■ Changes of Phase

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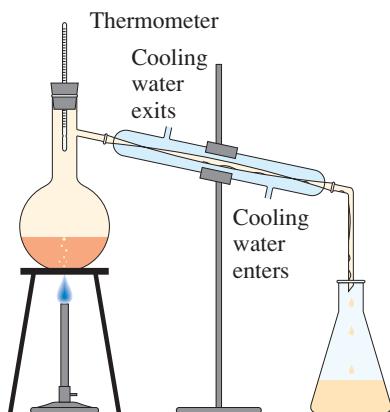


Figure 14.5 Distillation Apparatus



Figure 14.6 Water Boiling at Room Temperature Under Reduced Pressure

The evaporation has cooled the water sufficiently for some of it to turn to frost.

temperature is directly proportional to the average kinetic energy of gas molecules. The same is also true for liquid (and solid) molecules. Thus, when the highest energy molecules go into the gas phase, the molecules left in the liquid phase have less energy, on average, and therefore, the liquid has a lower temperature unless energy is added from the surroundings. In addition, if the gas molecules do work, such as pushing back the atmosphere, additional energy is required. If no energy is added from the surroundings, this energy must come from the molecules themselves. That is, the gas molecules also lose energy, and therefore, the gas is cooled.

In a closed system at constant temperature, as liquid molecules escape into the gas phase, the pressure of the vapor builds up. More and more gas molecules are present, and they can condense back to liquid. Thus, the rate of condensation increases. When the rate of condensation matches the rate of evaporation, a condition called **physical equilibrium** is attained. The rate of evaporation of liquid molecules is equal to the rate of condensation of gas molecules. Two opposite processes are occurring at equal rates, and no net change is taking place. Specifically, the pressure of the vapor is constant under these conditions and is called the **vapor pressure** of the substance at that temperature.

If the temperature of the system is increased, the number of liquid molecules with sufficient energy to escape into the gas phase will increase, but the number of gas molecules available to condense will not immediately be affected. Therefore, the rate of evaporation will exceed the rate of condensation until the number of molecules in the gas phase builds up, and a new and higher vapor pressure results. (If all the liquid evaporates, no equilibrium is possible.)

The vapor pressure of a pure liquid is determined solely by the temperature. (Section 12.6 showed that the vapor pressure of water is determined by its temperature alone.) If the surface area for evaporation is larger, so also is the surface area for condensation. If there is more volume for the gas to occupy, more molecules will be able to evaporate before the rate of condensation equals the rate of evaporation, but it will take that many more molecules to build up to the same vapor pressure. The volume and shape occupied by the liquid also have no effect on the vapor pressure of a pure liquid.

Boiling occurs when the vapor pressure of the liquid equals the pressure of the surroundings. At that point, bubbles appear within the liquid itself. The **boiling point** of a liquid is the temperature at which the vapor pressure of the liquid equals the pressure on the system. The **normal boiling point** is the boiling point at a pressure of 1.00 atm. For example, when liquid water at 100°C and 1.00 atm is heated, it boils. Liquids can boil at temperatures other than their normal boiling points if the pressure on them is different from 1.00 atm. For example, water can boil at 25°C if the pressure above it is about 24 torr (Figure 14.6). In contrast, pressure cookers are used to allow water to boil at a higher temperature, so that food in the cooker will cook faster.

Snapshot Review

- ☐ When the forces between the particles change in relationship to the energy available to them (by a change in temperature, for example), the phase can change to reflect the new circumstances. For example, the forces holding a solid together at one temperature might not be sufficient to hold it together at a much higher temperature, so the solid melts.



- Liquids and molecular solids can be in equilibrium with their molecules in the gas phase because some molecules in any sample have relatively high energies.
- A. Explain how a coating of ice on a sidewalk can eventually disappear even if the temperature never rises above 0°C.

14.3 Measurement of Energy Changes

When we add energy to a sample of matter, we generally expect the sample to warm up. The sample does warm up, unless it happens to be a pure substance at its melting, sublimation, or boiling point (Section 14.2). Thus there are two types of calculations required.

Specific Heat Calculations

The amount of heat required to warm a sample of matter is given by the equation

$$\text{Heat} = mc\Delta t$$

where m is the mass, c is the specific heat capacity, usually called the **specific heat**, and Δt is the *change* in temperature in either degrees Celsius or kelvins. The Greek capital delta (Δ) is used to mean “change in.” The change in temperature is defined as the *final* temperature minus the *initial* temperature. The SI unit of energy is the **joule** (J).

Specific heats of some substances are given in Table 14.4.

Table 14.4 Specific Heat Capacities of Selected Substances

Substance, Formula	Specific Heat Capacity (J/g·°C)
<i>Covalent molecules</i>	
Carbon dioxide, CO ₂	0.852
Carbon monoxide, CO	1.04
Hydrogen, H ₂	14.4
Nitrogen, N ₂	1.04
Oxygen, O ₂	0.922
Water, gaseous, H ₂ O(g)	2.042
Water, liquid, H ₂ O(ℓ)	4.184
Water, solid, H ₂ O(s)	2.089
<i>Metals</i>	
Aluminum, Al	0.90
Chromium, Cr	0.45
Cobalt, Co	0.46
Copper, Cu	0.385
Gold, Au	0.129
Iron, Fe	0.442
Lead, Pb	0.13
Magnesium, Mg	1.0
Silver, Ag	0.24
Sodium, Na	0.293
Tin, Sn	0.22
Zinc, Zn	0.388

EXAMPLE 14.5

- (a) Calculate the daily rate per person at a resort if the cost for four people for five nights is \$3630.
(b) Calculate the specific heat of water if 83.68 J is required to raise the temperature of 4.000 g of water by 5.000°C.

Solution

(a) Cost = (number of people)(rate)(number of nights)
3630 dollars = (4 people)(rate)(5 nights)

$$\text{Rate} = \frac{3630 \text{ dollars}}{(4 \text{ people})(5 \text{ nights})} = \frac{181.50 \text{ dollars}}{\text{person}\cdot\text{night}}$$

(b) $c = \frac{\text{heat}}{m\Delta t} = \frac{83.68 \text{ J}}{(4.000 \text{ g})(5.000^\circ\text{C})} = 4.184 \text{ J/g}\cdot^\circ\text{C}$

Note that the unit for specific heat, like that for the room rate in part (a), has two different units in its denominator (g and °C).

Practice Problem 14.5 Calculate the specific heat of ice if 128 J is required to raise the temperature of 4.00 g of ice by 15.3°C.

EXAMPLE 14.6

- (a) Calculate the amount of money that will be charged to house 18 students for four nights in a guest house at a rate of 33 dollars per student per night.
- (b) Calculate the quantity of energy required to raise the temperature of 14.5 g of water by 31.3°C . The specific heat of water is $4.184 \text{ J/g} \cdot ^{\circ}\text{C}$.

Solution

$$(a) \text{Cost} = 18 \text{ students} \left(\frac{33 \text{ dollars}}{\text{student} \cdot \text{night}} \right) 4 \text{ nights} = 2376 \text{ dollars}$$

$$(b) \text{Heat} = 14.5 \text{ g} \left(\frac{4.184 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}} \right) 31.3^{\circ}\text{C} = 1900 \text{ J} = 1.90 \text{ kJ}$$

EXAMPLE 14.7

Calculate the number of joules required to heat 123 g of water from 14.7°C to 31.1°C .

Solution

The equation to use is

$$\text{Heat} = mc\Delta t$$

The mass of the water is given in the problem. The *change* in temperature is the final temperature minus the initial temperature:

$$\Delta t = t_2 - t_1 = 31.1^{\circ}\text{C} - 14.7^{\circ}\text{C} = 16.4^{\circ}\text{C}$$

The specific heat of the water, as calculated in Example 14.5 and listed in Table 14.4, is $4.184 \text{ J/g} \cdot ^{\circ}\text{C}$. Thus, the heat required is

$$\text{Heat} = (123 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(16.4^{\circ}\text{C}) = 8440 \text{ J} = 8.44 \text{ kJ}$$

Practice Problem 14.7 Calculate the number of joules required to heat 123 g of iron from 14.7°C to 31.1°C . Does heating the iron take more energy than heating the same mass of water?

EXAMPLE 14.8

Calculate the final temperature after 1485 J of energy is added to 16.7 g of water at 23.4°C .

Solution

The equation is rearranged to give the *change in temperature*:

$$\Delta t = \frac{\text{heat}}{mc} = \frac{1485 \text{ J}}{(16.7 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})} = 21.3^{\circ}\text{C}$$

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Energy added to a system is defined as *positive*, and energy released from a system is defined as *negative*.

A process in which energy is added to a system is said to be an *endothermic process*. A process in which energy is released from a system is said to be an *exothermic process*.

The final temperature is 21.3°C greater than the initial temperature. That is, since $\Delta t = t_2 - t_1$,

$$t_2 = \Delta t + t_1 = 21.3^{\circ}\text{C} + 23.4^{\circ}\text{C} = 44.7^{\circ}\text{C}$$

Energy added to a system is defined as *positive*, and energy released from a system is defined as *negative*. A process in which energy is added to a system is said to be an **endothermic process**. A process in which energy is released from a system is said to be an **exothermic process**.

EXAMPLE 14.9

Calculate the final temperature after 987 J of energy is removed from 14.9 g of water at 22.0°C .

Solution

In this case, because energy is removed from the system, we use -987 J in the equation:

$$\Delta t = \frac{\text{heat}}{mc} = \frac{-987\text{ J}}{(14.9\text{ g})(4.184\text{ J/g}\cdot^{\circ}\text{C})} = -15.8^{\circ}\text{C}$$

The final temperature is

$$t_2 = \Delta t + t_1 = -15.8^{\circ}\text{C} + 22.0^{\circ}\text{C} = 6.2^{\circ}\text{C}$$

That the temperature is lowered when energy is removed from the system should not be surprising.

When heat is transferred from one object to another, and none is transferred to or from the surroundings, the heat is equal to zero.

When heat is transferred from one object to another, with no energy gained from or lost to anything else (the surroundings), the total change in energy is the sum of the changes in energy of the two objects. For example, if a piece of hot metal is placed in a sample of cold water, the water is warmed and the metal is cooled. Both the metal and the water will reach the same temperature. The heat transferred to or from the surroundings is zero. Thus,

$$\text{Heat} = 0 = (m_{\text{water}})(c_{\text{water}})(\Delta t_{\text{water}}) + (m_{\text{metal}})(c_{\text{metal}})(\Delta t_{\text{metal}})$$

This relationship may be used in the lab to find the specific heat of a metal.

EXAMPLE 14.10

A 12.5-g sample of a metal at 67.7°C is placed in 27.6 g of water at 10.3°C , and the final temperature of the system is 15.4°C . Calculate the specific heat of the metal. Which of the metals in Table 14.4 is it?

Solution

$$\text{Heat} = 0 = (m_{\text{water}})(c_{\text{water}})(\Delta t_{\text{water}}) + (m_{\text{metal}})(c_{\text{metal}})(\Delta t_{\text{metal}})$$

14.3 ■ Measurement of Energy Changes**387**

The change in the temperature of the water is $15.4^{\circ}\text{C} - 10.3^{\circ}\text{C} = 5.1^{\circ}\text{C}$. The change in the temperature of the metal is $15.4^{\circ}\text{C} - 67.7^{\circ}\text{C} = -52.3^{\circ}\text{C}$. Note that both the water and the metal wind up at 15.4°C . Note also that the change in temperature of the metal is negative; it cooled down. Substituting into the equation yields

$$0 = (27.6 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C})(5.1^{\circ}\text{C}) + (12.5 \text{ g})(c_{\text{metal}})(-52.3^{\circ}\text{C})$$

$$c_{\text{metal}} = 0.90 \text{ J/g}\cdot^{\circ}\text{C}$$

The metal in the table with the heat capacity closest to $0.90 \text{ J/g}\cdot^{\circ}\text{C}$ is aluminum.

Practice Problem 14.10 A 186-g sample of a metal at 74.0°C is placed in 251 g of water at 18.0°C , and the final temperature of the system is 26.4°C . Calculate the specific heat of the metal. Which of the metals in Table 14.4 could it be?

EXAMPLE 14.11

Calculate the final temperature after 6.79 g of a metal ($c = 0.892 \text{ J/g}\cdot^{\circ}\text{C}$) at 67.4°C is placed in 196 g of water at 19.6°C .

Solution

$$\text{Heat} = 0 = (m_{\text{water}})(c_{\text{water}})(\Delta t_{\text{water}}) + (m_{\text{metal}})(c_{\text{metal}})(\Delta t_{\text{metal}})$$

Let t_f represent the final temperature of *both* the metal and the water:

$$0 = (m_{\text{water}})(c_{\text{water}})(t_f - t_{\text{water}}) + (m_{\text{metal}})(c_{\text{metal}})(t_f - t_{\text{metal}})$$

Substituting the known quantities gives

$$0 = (196 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C})(t_f - 19.6^{\circ}\text{C}) + (6.79 \text{ g})(0.892 \text{ J/g}\cdot^{\circ}\text{C})(t_f - 67.4^{\circ}\text{C})$$

$$0 = (196)(4.184)(t_f - 19.6^{\circ}\text{C}) + (6.79)(0.892)(t_f - 67.4^{\circ}\text{C})$$

The equation is simplified using the distributive property of algebra, each product having three significant digits:

$$0 = 820.1t_f - 16,070^{\circ}\text{C} + 6.057t_f - 408.2^{\circ}\text{C}$$

$$826.2t_f = 16,480^{\circ}\text{C}$$

$$t_f = 19.9^{\circ}\text{C}$$

The algebraic simplification is based on the equality

$$wx(y - z) = wxy - wxz$$

Practice Problem 14.11 Calculate the final temperature after 11.3 g of a metal ($c = 0.44 \text{ J/g}\cdot^{\circ}\text{C}$) at 60.0°C is placed in 97.2 g of water at 19.0°C .

Change of Phase Calculations

When energy is added to or removed from a pure substance and that substance *changes phase* as a result, the *temperature does not change*. That is, when a pure substance melts, solidifies, sublimes, evaporates, or condenses, it does so

388**CHAPTER 14 ■ Solids, Liquids, and Energies of Physical and Chemical Changes****Table 14.5** Selected Heats of Phase Change

Substance	Phase Change (at 1 atm)	Temperature (°C)	Heat Involved (J/g)
Ammonia	Boiling	-33	1380
Carbon dioxide	Sublimation	-90	3680
CCl ₂ F ₂ (a refrigerant)	Boiling	-29.8	165
CHClF ₂ (a refrigerant)	Boiling	-40.8	234
Sulfur dioxide	Boiling	-10	402
Water	Melting	0	335
Water	Boiling	100	2260

at a given temperature (under constant pressure). For example, when energy is added to liquid water at 100°C and 1.00 atm, the water boils. However, as long as some liquid water remains, the water and vapor are still at 100°C. The added energy is converted to potential energy as the molecules go from their relative closeness in the liquid phase to their well-separated states in the gas phase. This energy is called the **enthalpy of vaporization**, or less precisely the **heat of vaporization**.

The amount of heat associated with the phase change of a pure substance depends on the nature of the substance and the quantity of substance in the sample. For example, the **enthalpy of fusion**, or **heat of fusion**, of water—the heat necessary to change water from solid to liquid—is 335 J/g. The unit for this value includes no *degree* because the temperature does not change when solid water melts. The heat of any process in Figure 14.4 has the opposite sign of the opposing process. Thus the heat of solidification of water is -335 J/g. In general, the heat term is named according to the name of the process. For example:

Process	Name of Heat Term	More Precise Name
Fusion (melting)	Heat of fusion	Enthalpy of fusion
Vaporization (evaporation)	Heat of vaporization	Enthalpy of vaporization
Sublimation	Heat of sublimation	Enthalpy of sublimation

Some selected values of heats of phase change are presented in Table 14.5.

EXAMPLE 14.12

Calculate the energy required to melt 16.4 g of ice at 0°C.

Solution

The heat of fusion of water at 0°C is 335 J/g (from Table 14.5).

$$\text{Heat} = (16.4 \text{ g})(335 \text{ J/g}) = 5.49 \times 10^3 \text{ J} = 5.49 \text{ kJ}$$

Practice Problem 14.12 Calculate the heat required to vaporize 16.4 g of water at 100°C. Compare this quantity of heat to that required to melt the same mass of ice (Example 14.12).

14.3 ■ Measurement of Energy Changes**389****ITEM OF INTEREST**

Water and steam are very useful for heating buildings. The high specific heat of water makes it useful for baseboard heating of homes and small buildings. It has the highest heat capacity of any entry in Table 14.4 except hydrogen, and it is liquid over a useful range.

The high heat of vaporization and the reasonable normal boiling point of water make steam useful for steam heating of large buildings. As steam condenses, it gives off 2260 J of heat per gram. (Carbon dioxide has a higher heat of sublimation, but its low sublimation point makes it suitable for refrigeration of ice cream trucks rather than for heating of buildings.)

Sodium is used as a heat transfer agent in cooling nuclear reactors. It has a relatively high specific heat and an acceptable liquid range for the purpose. (It melts just below 100°C.)

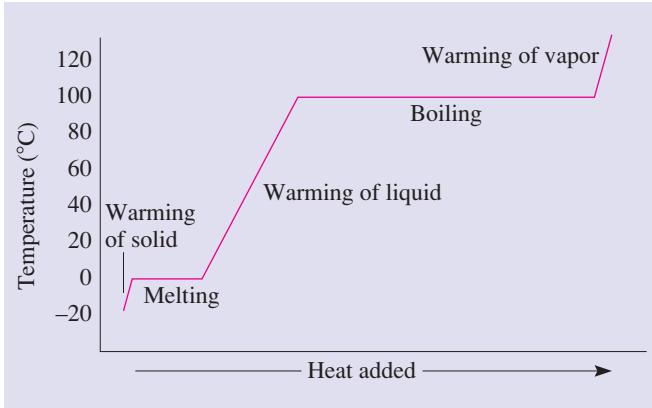
When we add heat to a substance that is not at a temperature at which a phase change will occur, its temperature rises. Suppose that the temperature rises to the temperature of a phase change. Then, the phase change will occur at constant temperature until it is complete, after which the temperature will rise again. For example, if we add heat to ice at -20°C , the ice will warm to 0°C . At that temperature, melting begins, and the temperature stays at 0°C until all the ice has melted. Then the temperature of the liquid water rises as we add even more heat. After the temperature of the liquid reaches the boiling point, the addition of more heat causes it to boil. Further heating increases the temperature of the vapor. We can draw a graph that shows what happens as we heat a pure substance. Such a graph is called a **heating curve** (Figure 14.7).

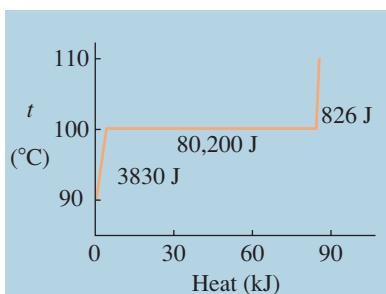
How do we calculate the energy required to raise the temperature of a substance and cause it to change phase? We do separate calculations for each step and then sum the results.

EXAMPLE 14.13

Calculate the energy required to change a 17.1-g sample of water from 87.7°C to steam at 121.0°C and 1.00 atm. Use data from Tables 14.4 and 14.5.

Figure 14.7 Heating Curve
for Water



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The water in the liquid phase will be heated to 100.0°C. It will then boil, producing water vapor at 100.0°C. Finally, the water vapor produced will be heated to 121.0°C. We do one calculation for each of these three steps:

For heating the liquid water:

$$\text{Heat} = mc\Delta t = (17.1 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(100.0^\circ\text{C} - 87.7^\circ\text{C}) = 880.0 \text{ J}$$

To vaporize the water:

$$\text{Heat} = mc_{\text{vap}} = (17.1 \text{ g})(2260 \text{ J/g}) = 38,650 \text{ J}$$

For heating the water vapor:

$$\text{Heat} = mc\Delta t = (17.1 \text{ g})(2.042 \text{ J/g}\cdot^\circ\text{C})(121.0^\circ\text{C} - 100.0^\circ\text{C}) = 733.3 \text{ J}$$

Sum the energies:

$$\text{Total heat} = 880.0 \text{ J} + 38,650 \text{ J} + 733.3 \text{ J} = 40,300 \text{ J} = 40.3 \text{ kJ}$$

Note that we cannot even combine the calculations for the two heating steps because liquid water and water vapor have different heat capacities.

Practice Problem 14.13 Calculate the quantity of energy that is removed when 40.0 g of water at 14.4°C is changed to ice at -16.3°C.

**Snapshot Review**

ChemSkill Builder
8.1, 8.3

- The energy necessary to change the temperature of a substance is given by

$$\text{Heat} = mc\Delta t$$

- If a substance changes phase as energy is added or removed, the heat of phase change is the heat per gram (see Table 14.5) times the mass of the sample.

- A. Calculate the heat necessary to raise the temperature of 50.0 g of water from 85.6°C to 100.0°C.
 B. Calculate the heat necessary to vaporize 50.0 g of water at 100°C.
 C. Calculate the heat necessary to change 50.0 g of water at 85.6°C to water vapor at 100.0°C.

In all steps of a heating or cooling curve problem, the signs must be the same.

14.4 Enthalpy Changes in Chemical Reactions

Heat, symbolized q , is different from other kinds of energy. All other kinds of energy can be converted entirely to heat, but heat cannot be converted entirely to any other form of energy. We classify all other kinds of energy as **work**, symbolized w . Thus, the change in energy of a system, ΔE , is merely the heat added to the system plus the work added to the system:

$$\Delta E = q + w$$

14.4 ■ Enthalpy Changes in Chemical Reactions**391**

Energy added to a system is *defined* as positive; energy removed is *defined* as negative.

This equation is merely an expression of the law of conservation of energy. By convention, energy, heat, and work added to a system are regarded as positive, but any of these removed from a system is regarded as negative. *Be sure to get the sign right.*

EXAMPLE 14.14

- A certain acid-base reaction in solution produces 117 kJ of heat but does no work. What is the sign of q ?
- All of the heat is used to warm the solution. What is the sign of q for the warming process?
- What is the value of q for the overall process?

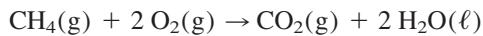
Solution

- Because heat is given off by the reaction, q is negative.
- Because the heat is absorbed by the solution, this q is positive.
- The overall q is zero because no heat was added to or taken from the surroundings. All the heat from the reaction went into the warming process.

Because we cannot measure the heat produced by a chemical reaction directly, we measure it by determining its effect on something. For example, the heat produced by burning 3.00 mol of methane (natural gas) might be measured by determining the increase in temperature of a certain mass of water warmed by the heat. In such an experiment, we must try to ensure that *all* of the heat produced by the combustion reaction is used to warm the water and that none escapes to the surroundings.

EXAMPLE 14.15

Burning 2.00 mol of CH₄ warms 10.0 kg of water by 42.5°C. Calculate the heat produced in the combustion process:

**Solution**

The heat added to the water is

$$\text{Heat} = mc\Delta t = (10,000 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(42.5^\circ\text{C}) = 1.78 \times 10^6 \text{ J} = 1780 \text{ kJ}$$

That is the magnitude of the heat produced by the reaction. Because the reaction *produced* the heat, $q = -1780 \text{ kJ}$ for the reaction.

Practice Problem 14.15 Burning 0.250 mol of C₂H₆ warms 5.65 kg of water by 16.5°C. Calculate the heat produced in the combustion process.

Table 14.6 Standard Enthalpies of Formation at 298 K

	State	ΔH_f (kJ/mol)
AgCl	s	-127.0
AgBr	s	-99.6
AgI	s	-62.3
Al ₂ O ₃	s	-1670
Au(OH) ₃	s	-418
B ₂ H ₆	g	31
BF ₃	g	-1110
B ₂ O ₃	s	-1277
BaO	s	-558.6
BaCO ₃	s	-1217
BaSO ₄	s	-1465
CO	g	-110.5
CO ₂	g	-393.5
CaO	s	-635.5
CaCO ₃	s	-1207
CaCl ₂	s	-795.0
Ca(OH) ₂	s	-986.6
CaSO ₄	s	-1431
Cr ₂ O ₃	s	-1141
CuO	s	-157
Cu ₂ S	s	-79.5
Fe ₂ O ₃	s	-822.2
H ₂ O	ℓ	-285.9
H ₂ O	g	-241.8
H ₂ SO ₄	ℓ	-811.3
HBr	g	-36.2
HCl	g	-92.13
HF	g	-269
HI	g	25.9
H ₂ S	g	-20.15
HgO	s	-90.8
KCl	s	-435.9
NF ₃	g	-127
NH ₃	g	-46.19
N ₂ H ₄	g	50.42
NH ₄ Cl	s	-315.4
N ₂ O	g	81.55
NO	g	90.37
NO ₂	g	33.8
NaCl	s	-411.0
NaHCO ₃	s	-710.4
Na ₂ CO ₃	s	-1430.1
PH ₃	g	23
P ₂ O ₅	s	-1531
SO ₂	g	-296.9
SO ₃	g	-395.2
SiO ₂	s	-878.2
SiCl ₄	g	-609.6
SiF ₄	g	-1511.6
WO ₃	s	-843.1
ZnO	s	-348
ZnS	s	-203

Once the value for a particular reaction has been determined, it can be used to calculate values for other experiments. For example, if we burn the same gas under the same conditions, we will get the same quantity of heat. Twice as much gas will yield twice as much heat, and so on. Moreover, we can find out information about other reactions.

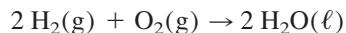
Enthalpy Change

Enthalpy change, ΔH , is equal to the heat involved in a process when the process is done under a constant pressure and involves no work except perhaps expansion (or contraction) against the atmosphere. When these conditions are not met, ΔH is a more fundamental quantity than heat. For example, ΔH is a **state function**, which means that the change in its value is independent of the path in going from the initial state to the final state. Another example of a state function is change in volume. For example, if a gas starts out occupying 2.5 L and finally occupies 4.5 L, $\Delta V = 2.0$ L no matter if the gas is first expanded to 8.6 L, then contracted to 3.7 L, then expanded to 4.5 L, or if some other path were followed. (Heat, in contrast, does depend on the path, except when $q = \Delta H$.) The ΔH value is important in both theoretical and practical terms in chemistry.

The ΔH value of a certain process conventionally is called the enthalpy of that process. For example, the enthalpy change of the vaporization process is called the enthalpy of vaporization, $\Delta H_{\text{vaporization}}$. The enthalpy change for the fusion (the melting) process is ΔH_{fusion} . The enthalpy of combustion of a substance is, by definition, the enthalpy change accompanying the burning of the substance *in excess oxygen*. Essentially, however, enthalpy change is a single function that can be applied to many different processes, and the name used as a subscript to ΔH is the name of the particular process.

Enthalpy of Formation

One particularly useful type of process for us to consider is the formation of a substance in its standard state from its elements in their standard states. **Standard state** is the state in which the substance is most stable. For example, the standard state of elemental oxygen is O₂(g), not O(g) or O₃(g). Thus, the equation for the formation reaction of water is



The enthalpy change for this reaction can be called the **enthalpy of formation** of water, $\Delta H_f(\text{H}_2\text{O})$. Table 14.6 shows standard enthalpies of formation. Table 14.7 is a separate table for unbranched hydrocarbons.

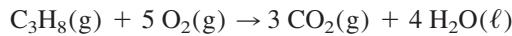
Values of ΔH for many reactions can be determined experimentally; for other reactions, measuring ΔH is impossible because the process is too slow or for some other reason. Values of ΔH_f are useful because we can calculate the ΔH for any reaction by subtracting the sum of the ΔH_f values of the reactants of the reaction from the sum of the ΔH_f values of the products of the reaction:

$$\Delta H = \text{sum of } \Delta H_f(\text{products}) - \text{sum of } \Delta H_f(\text{reactants})$$

The ΔH_f of an element in its standard state is zero because converting an element in its standard state to the element in its standard state does not involve any change. That “reaction” will have a ΔH of zero.

14.4 ■ Enthalpy Changes in Chemical Reactions**393****EXAMPLE 14.16**

Calculate ΔH for the complete combustion of 1.00 mol of propane, C_3H_8 , a major component of lighter fluid.

Solution

Values of ΔH_f are obtained from Tables 14.6 and 14.7. For the products,

$$\Delta H_f = 3 \text{ mol } CO_2 \left(\frac{-393 \text{ kJ}}{1 \text{ mol } CO_2} \right) + 4 \text{ mol } H_2O \left(\frac{-286 \text{ kJ}}{1 \text{ mol } H_2O} \right) = -2323 \text{ kJ}$$

For the reactants,

$$\Delta H_f = 1 \text{ mol } C_3H_8 \left(\frac{-105 \text{ kJ}}{1 \text{ mol } C_3H_8} \right) + 5 \text{ mol } O_2 \left(\frac{0 \text{ kJ}}{1 \text{ mol } O_2} \right) = -105 \text{ kJ}$$

$$\Delta H = \Delta H_f(\text{prod}) - \Delta H_f(\text{react}) = (-2323 \text{ kJ}) - (-105 \text{ kJ}) = -2220 \text{ kJ}$$

(Note that the value of ΔH_f of O_2 is not in Table 14.6 because we know that ΔH_f of every uncombined element in its standard state is zero.)

Practice Problem 14.16 Calculate ΔH for the complete combustion of 1.00 mol of heptane, C_7H_{16} .

ΔH_f of an element in its standard state is zero by definition.

Be sure to distinguish between ΔH_f and ΔH for a reaction.

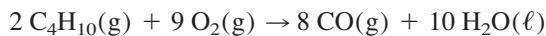
Be especially careful about the signs when doing these calculations!

We can multiply the number of kilojoules per mole by the number of moles undergoing reaction to get the number of kilojoules for any given quantity of reactant or product involved. Thus, for Example 14.16, if 2.50 mol of C_3H_8 had been involved, the enthalpy change would have been

$$2.50 \text{ mol} \left(\frac{-2220 \text{ kJ}}{1 \text{ mol}} \right) = -5550 \text{ kJ}$$

EXAMPLE 14.17

Calculate the enthalpy change for the combustion of 1.00 mol of butane (boiled gas), C_4H_{10} , to give CO and H_2O . Use the following equation:

**Solution**

For the products,

$$\Delta H_f = 8 \text{ mol } CO \left(\frac{-110 \text{ kJ}}{1 \text{ mol } CO} \right) + 10 \text{ mol } H_2O \left(\frac{-286 \text{ kJ}}{1 \text{ mol } H_2O} \right) = -3740 \text{ kJ}$$

For the reactants,

$$\Delta H_f = 2 \text{ mol } C_4H_{10} \left(\frac{-126 \text{ kJ}}{1 \text{ mol } C_4H_{10}} \right) + 9 \text{ mol } O_2 \left(\frac{0 \text{ kJ}}{1 \text{ mol } O_2} \right) = -252 \text{ kJ}$$

Table 14.7 Enthalpies of Formation at 25°C of Unbranched Hydrocarbons

Compound	ΔH_f (kJ/mol)
CH ₄	-74.5
C ₂ H ₆	-83.7
C ₃ H ₈	-105
C ₄ H ₁₀	-126
C ₅ H ₁₂	-146
C ₆ H ₁₄	-167
C ₇ H ₁₆	-187
C ₈ H ₁₈	-208

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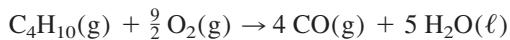
For this equation,

$$\Delta H = \Delta H_f(\text{prod}) - \Delta H_f(\text{react}) = (-3740 \text{ kJ}) - (-252 \text{ kJ}) = -3488 \text{ kJ}$$

However, the equation involves 2 mol C₄H₁₀, and the problem requires 1.00 mol.

$$1.00 \text{ mol} \left(\frac{-3488 \text{ kJ}}{2 \text{ mol}} \right) = -1740 \text{ kJ}$$

Practice Problem 14.17 Repeat Example 14.17, using the following equation, and compare the results:



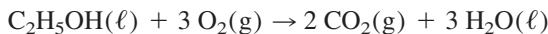
We can use ΔH_{comb} to calculate ΔH_f values.

EXAMPLE 14.18

Calculate the value of ΔH_f of 1.000 mol of ethyl alcohol, C₂H₅OH, from its enthalpy of combustion, -1371 kJ/mol.

Solution

The equation for the combustion reaction is



$$\Delta H_{\text{comb}} = 2 \Delta H_f(\text{CO}_2) + 3 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_2\text{H}_5\text{OH})$$

In this problem, the unknown value happens to be on the right side of the equation, but the equation is as straightforward to solve as if we had been given ΔH_f and asked to calculate ΔH_{comb} . Per mole of C₂H₅OH:

$$-1371 \text{ kJ} = 2(-393 \text{ kJ}) + 3(-286 \text{ kJ}) - \Delta H_f(\text{C}_2\text{H}_5\text{OH})$$

$$\Delta H_f(\text{C}_2\text{H}_5\text{OH}) = -273 \text{ kJ}$$

Practice Problem 14.18 Calculate the value of ΔH_f for 1 mol of acetylene, C₂H₂, from its enthalpy of combustion, -1300 kJ/mol.

We must know the equation corresponding to an enthalpy of combustion value.

Hess's Law

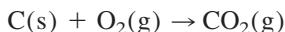
Another way to calculate values of ΔH for reactions involves manipulating equations for other reactions with known ΔH values. When chemical equations are added to yield a different chemical equation, the corresponding ΔH values are added to get the ΔH for the desired equation. This principle is called **Hess's law**. For example, we can calculate the ΔH for the reaction of carbon with oxygen gas to yield carbon dioxide from the values for the reaction of carbon with

What do you use if ΔH_f values are not available? Some combination of other ΔH values.

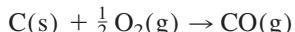
14.4 ■ Enthalpy Changes in Chemical Reactions**395**

oxygen to yield carbon monoxide and that of carbon monoxide plus oxygen to yield carbon dioxide:

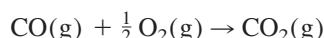
Desired:

 **ΔH (kJ)**

Given:

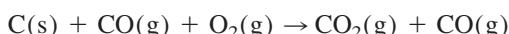


-110

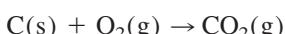


-283

Adding the two chemical equations given:



Eliminating CO from both sides results in the desired equation:



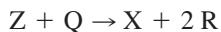
Therefore, adding these two ΔH values will give the ΔH desired:

$$\Delta H = (-110 \text{ kJ}) + (-283 \text{ kJ}) = -393 \text{ kJ}$$

Note that we have not used enthalpies of formation explicitly in this process. Enthalpy changes of *any* type of reaction will do.

EXAMPLE 14.19

Calculate the enthalpy change of the general reaction



from the following data:

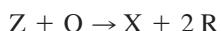
	ΔH (kJ)
$\text{Z} + \text{Q} \rightarrow \text{E} + 2 \text{D}$	27.1
$\text{E} + 2 \text{D} \rightarrow \text{X} + 2 \text{R}$	-13.7

Solution

Adding the two equations will result in the elimination of D and E, and yield the desired equation. We then merely add the corresponding ΔH values:

$$\Delta H = (27.1 \text{ kJ}) + (-13.7 \text{ kJ}) = 13.4 \text{ kJ}$$

Practice Problem 14.19 Calculate the enthalpy change of the general reaction



from the following data:

	ΔH (kJ)
$\text{Z} + \text{Q} \rightarrow \text{E} + 2 \text{D}$	-41.7
$\text{E} + 2 \text{D} \rightarrow \text{J} + \text{A}$	+17.7
$\text{J} + \text{A} \rightarrow \text{X} + 2 \text{R}$	+10.6

Using Hess's law is straightforward if the equations given are in a form in which simply adding them yields the equation desired. More often, however, to get the desired equation, we must multiply or divide a given equation by a small

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When we multiply or divide an equation by any number, we also multiply or divide the ΔH value by that number. When we reverse an equation we change the sign of the ΔH value.

integer. When we do so, we must also multiply or divide the corresponding ΔH value by that same integer. Sometimes the given equation must be reversed, whereupon the sign of the corresponding ΔH must be changed. Sometimes, both of these processes are necessary. We decide which of these steps to take by looking at the desired equation to see where we want each reactant and product, and how many moles of each we want.

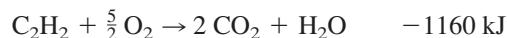
EXAMPLE 14.20

Given the ΔH values for equations I, II, and III, below, calculate ΔH for the following reaction:

	$C_2H_2 + 2 H_2 \rightarrow C_2H_6$	ΔH (kJ)
I	$2 C_2H_2 + 5 O_2 \rightarrow 4 CO_2 + 2 H_2O$	-2320
II	$2 C_2H_6 + 7 O_2 \rightarrow 4 CO_2 + 6 H_2O$	-3040
III	$2 H_2 + O_2 \rightarrow 2 H_2O$	-572

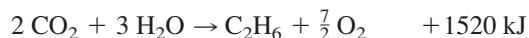
Solution

Because we need 1 mol of C_2H_2 on the left of the required equation, and we have 2 mol there in equation I, we divide equation I by 2, including its ΔH value:

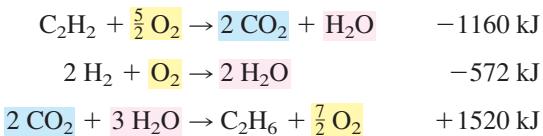


We also need 2 mol of H_2 on the left, so we add equation III unchanged.

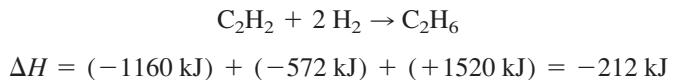
We need 1 mol of C_2H_6 on the right, so we reverse equation II and also divide it by 2. Reversing the equation requires that we change the sign of ΔH , and we also divide the given magnitude of ΔH by 2:



Adding the equations and their corresponding ΔH values gets us the solution:



The highlighted substances cancel out, leaving

**Snapshot Review**

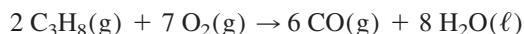
ChemSkill Builder 8.6

- The enthalpy of a reaction can be calculated in two ways: (1) from the enthalpies of formation of products and reactants and (2) by combining enthalpies of any reactions (using Hess's law).

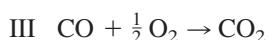
■ Summary

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- A. Calculate the enthalpy change for the incomplete combustion of 1.00 mol of C₃H₈ from ΔH_f values:



- B. Determine ΔH for equation III below from those of equations I and II,
(a) by Hess's law and (b) by use of ΔH_f values:

**Key Terms**

Key terms are defined in the Glossary.

amorphous solid (14.1)

boiling point (14.2)

condensation (14.2)

crystalline solid (14.1)

distillation (14.2)

endothermic process (14.3)

enthalpy change (14.4)

enthalpy of formation (14.4)

enthalpy of fusion (14.3)

enthalpy of vaporization (14.3)

evaporation (14.2)

exothermic process (14.3)

fluidity (14.1)

freezing (14.2)

fusion (14.2)

heat (14.4)

heating curve (14.3)

heat of fusion (14.3)

heat of vaporization (14.3)

Hess's law (14.4)

ionic solid (14.1)

joule (14.3)

melting (14.2)

metallic solid (14.1)

molecular solid (14.1)

network solid (14.1)

normal boiling point (14.2)

phase change (14.2)

physical equilibrium (14.2)

specific heat (14.3)

standard state (14.4)

state function (14.4)

vapor (14.2)

vaporization (14.2)

vapor pressure (14.2)

work (14.4)

Symbols/Abbreviations

Δ (change in) (14.3)

ΔH_f (enthalpy of formation) (14.4)

q (heat) (14.4)

ΔE (change in energy) (14.4)

J (joule) (14.3)

w (work) (14.4)

ΔH (change in enthalpy) (14.4)

Summary

Compared with the molecules of gases, the particles that make up liquids and solids are (1) closer together, (2) more strongly held together, and (3) for solids, not necessarily molecules. The forces that hold solids together include chemical bonds and intermolecular forces—dipole moments, van der Waal forces, and hydrogen bonding. In general, the stronger the attractive forces are, the higher the boiling point and melting point of the substance and the more energy it takes to get the substance to melt or vaporize. Intermolecular forces are

not as strong as chemical bonds, such as the ionic bonds that hold the ions in sodium chloride together or the covalent bonds that hold the atoms in diamond together.

A crystalline solid is characterized by a regularly repeating arrangement of the particles that make it up. The particles may be ions, covalently bonded atoms (in macromolecules), small molecules held to one another by intermolecular forces, or metal atoms held to one another by metallic bonding. In contrast, liquids at room temperature are composed of molecules. The molecules

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are not regularly arranged over long distances (on a molecular level) but change their relative positions rather easily, giving a liquid its fluidity. (Section 14.1)

Substances can change phase—from solid to liquid or from gas to liquid, for example. It takes energy to change a substance from solid to liquid, solid to gas, or liquid to gas, but the same quantity of energy is released in the reverse process. On a submicroscopic level, energy is needed to overcome the high attractive forces between particles in the solid state to get to the somewhat lower attractions in the liquid state or the negligible attractions in the gas state.

A liquid exerts a certain vapor pressure as a given fraction of its molecules on the liquid surface escape into the gas phase. The relative rates of escape of molecules from the liquid phase and of their return to it determine how many molecules per unit volume will be in the gas phase, and these rates are determined by the nature of the liquid and its temperature. Vapor pressure increases with increasing temperature (but not in direct proportion) for any substance in the liquid state. Thus, the vapor pressure of a pure liquid is governed by temperature alone. Boiling occurs when the vapor pressure equals the pressure of the surrounding atmosphere, and the normal boiling point is the boiling point when that pressure is equal to 1.00 atm. (Section 14.2)

When energy is added to a pure substance, either its temperature will rise or it will change phase (unless it

undergoes a chemical reaction). Alternatively, both a temperature rise and a phase change may occur (one at a time). The quantity of energy required to raise the temperature of a substance is given by the equation

$$\text{Heat} = mc\Delta t$$

where m is the mass, c is the specific heat capacity, and Δt is the change in temperature. Any one of these four quantities may be calculated if the other three are known. Note that the change in temperature involves an initial and a final temperature, either of which may be unknown.

When a pure substance changes phase, it does so at constant temperature. The quantity of energy involved is simply the mass times the heat required per gram (called the enthalpy of fusion, enthalpy of vaporization, or enthalpy of sublimation, for example). When energy is added to a system, the sign on the quantity of energy is plus; when energy is removed from the system, the sign is minus. (Section 14.3)

The enthalpy change (ΔH) for any reaction is equal to the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants. Alternatively, values of ΔH can also be obtained from ΔH values of other reactions using Hess's law, which involves adding their chemical equations and the corresponding ΔH values. (Section 14.4)

Items for Special Attention

- In the phrase *normal boiling point*, the word *normal* means “at 1 atm.”
- For a solid or liquid to change to a gas, the forces holding the particles together must be overcome. The stronger the forces holding the solid together, the more energy is required to melt or sublime it. Also, in general, the stronger the forces holding the solid together, the higher is the sublimation point or melting point.
- Heat capacities have units with degrees Celsius (or kelvins) in the denominator, but heats of phase change do

not because the temperature does not change when a pure substance changes phase.

- Be especially careful about the signs and the units when doing the calculations in this chapter.
- Be careful to distinguish between ΔH_f and ΔH for a reaction. For example, the equation $\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$ uses enthalpy of formation values only to calculate ΔH of a reaction. It does not use enthalpies of combustion or any other enthalpy values. Hess's law can be used with other kinds of data.

Answers to Snapshot Reviews

- 14.1 A. A solid can consist of atoms held together by intermolecular forces, atoms covalently bonded from one end to another, molecules, ions, or metal atoms held together by metallic bonding (not covered in this course).
B. The rigidity of amorphous solids is similar to that of crystalline solids, but their internal structures are more like that of liquids.

- 14.2 A. The ice can slowly sublime—pass directly from the solid to the gas phase.
14.3 A. $\Delta H = mc\Delta t$
 $= (50.0 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(100.0^\circ\text{C} - 85.6^\circ\text{C})$
 $= 3012 \text{ J} = 3.012 \text{ kJ}$
B. $\Delta H = (50.0 \text{ g})(2260 \text{ J/g}) = 113,000 \text{ J} = 113 \text{ kJ}$
C. Merely add the ΔH values of the prior two problems:
 $\Delta H = \Delta H_A + \Delta H_B$
 $= 3.012 \text{ kJ} + 113 \text{ kJ} = 116 \text{ kJ}$

■ Problems

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- 14.4 A. For 2 mol C₃H₈:

$$\begin{aligned}\Delta H &= 6 \Delta H_f(\text{CO}) + 8 \Delta H_f(\text{H}_2\text{O}) - 2 \Delta H_f(\text{C}_3\text{H}_8) \\ &= 6(-110 \text{ kJ}) + 8(-286 \text{ kJ}) - 2(-105 \text{ kJ}) \\ &= -2738 \text{ kJ}\end{aligned}$$

For 1 mol C₃H₈:

$$1 \text{ mol C}_3\text{H}_8 \left(\frac{-2738 \text{ kJ}}{2 \text{ mol C}_3\text{H}_8} \right) = -1370 \text{ kJ}$$

- B. (a) Reverse equation II and add:

$$-393 \text{ kJ} + (+110 \text{ kJ}) = -283 \text{ kJ}$$

- (b) Equation I is the equation representing ΔH_f of CO₂, and equation II represents ΔH_f of CO. Therefore, for equation III,

$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

gives the same value.

Self-Tutorial Problems

- 14.1 List the types of forces that hold particles of various types of solids together, and give an example of a solid that is held together by each type.

- 14.2 Explain how we know that gases at room temperature are not composed of ions.

- 14.3 Which of the phases is characterized by having strong intermolecular forces among molecules that (a) are permanently located in or near one site? (b) are not permanently located in or near one site?

- 14.4 (a) What is the difference between condensation of a gas to a liquid and vaporization of a liquid to a gas?
(b) Which process is endothermic?
(c) What is the difference between the heat of vaporization and the heat of condensation?

- 14.5 (a) What is the difference between sublimation of a solid and condensation of a gas to a solid?
(b) Which process is endothermic?
(c) What is the difference between the heat of sublimation and the heat of condensation of a gas to a solid?

- 14.6 If 12.8 g of a metal at 74.2°C is placed in 20.2 g of water at 26.2°C and it warms the water to 31.7°C, what is the final temperature of the metal?

- 14.7 If it takes 7.30 kJ of energy to warm 63.0 g of water from 18.2°C to 45.9°C, how much energy is required to cool 63.0 g of water from 45.9°C to 18.2°C?

- 14.8 Calculate the final temperature if the initial temperature of a system is 25.0°C and the temperature change is (a) 6.3°C and (b) -6.3°C.

- 14.9 Identify the initial temperature, the final temperature, and the change in temperature for each of the following cases:
(a) Water is warmed from 21.2°C to 33.1°C.

- (b) Water is warmed 33.1°C from 21.2°C.

- (c) Water is warmed by 33.1°C to 54.3°C.

- (d) Water is warmed 33.1°C to 54.3°C.

- (e) Water is warmed 54.3°C from 33.1°C.

- (f) Water is changed from 33.1°C to 21.2°C.

- 14.10 The specific heat of water vapor is 2.042 J/g·°C, and that of water is 4.184 J/g·°C. The heat of vaporization of water is 2260 J/g.

- (a) Calculate the heat required to warm 16.9 g of water from 87.4°C to 100.0°C.
(b) Calculate the heat required to vaporize the water.
(c) Calculate the heat required to warm the resulting water vapor to 122.2°C.
(d) Calculate the total heat required for all three processes.

- 14.11 What name can be given to the enthalpy change for each of the following processes?

- (a) CO₂(s) → CO₂(g)
(b) H₂O(ℓ) → H₂O(g)
(c) C(s) + O₂(g) → CO₂(g) (two answers)
(d) C₃H₈(g) + 4 O₂(g) → 3 CO₂(g) + 2 H₂O(ℓ)
(e) 3 C(s) + 2 H₂(g) → C₃H₈(g)

- 14.12 What types of calculations would we have to make to find the energy required to change 14.8 g of ice at -15.0°C to water vapor at 119°C?

- 14.13 What characteristics should be chosen for a refrigerant used to transfer heat from inside a refrigerator to outside the refrigerator?

- (a) High ΔH_{vap} or low ΔH_{vap} ? (b) High molar mass or low molar mass?

Problems

14.1 Nature of the Solid and Liquid States

- 14.14 Explain why solid LiF and solid CF₄ melt at such widely different temperatures: 870°C and -184°C, respectively.

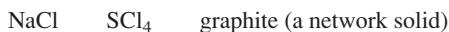
- 14.15 Which has the higher melting point—an ionic compound in which the ions have single charges or an analogous ionic compound in which each ion has a double charge?

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14.16 Carbon dioxide, CO_2 , sublimes at -78°C and silicon dioxide, SiO_2 , melts at 1713°C . What type of solid is each of these?

14.17 Glass softens over a wide range of temperature. Ice melts at a precise temperature. Explain the difference.

14.18 Which of the following substances should we expect to have the lowest melting point?



14.19 Should we expect Br_2 or ICl , which have the same total number of electrons and approximately the same molar mass, to have a higher normal boiling point? Explain.

14.20 Which of the noble gases should we expect to have the lowest normal boiling point?

14.21 Suppose we could look at one atom of a substance in a certain phase and when we looked along a certain line from that atom, we saw many atoms of the same element occurring at regular intervals. Each such atom had the same other atoms surrounding it as the original atom. In what phase is the substance?

14.22 Diphosphorus trioxide, P_2O_3 , melts at 23.8°C , and aluminum oxide, Al_2O_3 , melts at 2045°C . What type of solid is each of these?

14.23 Should we expect HCl or HI to have a higher normal boiling point? Explain.

14.24 Explain why, under ordinary conditions, elemental bromine exists as a liquid, fluorine and chlorine both exist as gases, and iodine exists as a solid.

14.25 Which element that exists as diatomic molecules has the lowest melting point?

14.26 Which of the following compounds is highest boiling?

**14.2 Changes of Phase**

14.27 (a) Determine from the graph of Figure 14.7 what will happen first to liquid water at 100°C as heat is added to it.

(b) Repeat part (a) for liquid water at 0°C .

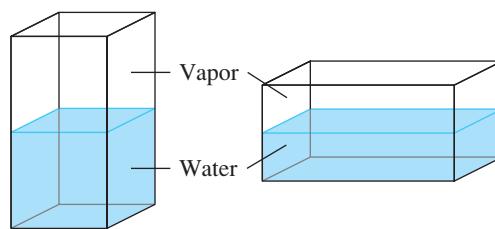
14.28 (a) Determine from the graph of Figure 14.7 what will happen first to liquid water at 100°C as heat is removed from it.

(b) Repeat part (a) for liquid water at 0°C .

14.29 Which of the following will increase the vapor pressure of water?

- Increasing the surface area of the liquid
- Increasing the temperature
- Increasing the pressure of dry air over the liquid
- Increasing the volume of the liquid
- Increasing the volume occupied by the vapor

14.30 A sealed rectangular box is half-filled with water and has water vapor in the upper half at a pressure equal to the vapor pressure of water at the temperature. Will the pressure change if the box is placed horizontally, thereby changing the surface area of the water? (See the accompanying illustrations.)



14.31 What will happen to a water-steam mixture at 100°C if no energy is added or removed?

14.32 Suppose all the liquid water in a closed container evaporates. Is it certain that the pressure of the water vapor in the container is equal to the vapor pressure of water?

14.3 Measurement of Energy Changes

14.33 (a) Calculate the heat required to warm 35.0 g of water from 10.5°C to 41.6°C .

(b) Calculate the heat required to cool 35.0 g of water from 41.6°C to 10.5°C .

14.34 (a) Calculate the heat required to warm 23.1 g of ice from -20.0°C to -10.0°C .

(b) Calculate the heat required to cool 23.1 g of ice from -10.0°C to -20.0°C .

14.35 Calculate the final temperature after 127 J of heat is added to 51.5 g of iron at 23.0°C .

14.36 Calculate the specific heat of a metal if 46.0 g of the metal at 78.0°C warms 32.0 g of water at 23.1°C to 36.1°C . Which metal in Table 14.4 is this metal most likely to be?

14.37 How much energy is required to raise the temperature of 23.9 g of iron by 41.7°C ?

14.38 Calculate the final temperature after 415 J of heat is added to 123.0 g of magnesium at 22.2°C .

14.39 How much energy is required to raise the temperature of 40.9 g of zinc by 38.1°C ?

14.40 How much energy is required to raise the temperature of 40.9 g of zinc from 17.6°C to 55.7°C ?

14.41 Calculate the specific heat of a metal if 90.6 g of the metal at 75.0°C warms 224 g of water at 15.0°C to 17.5°C . Which metal in Table 14.4 is this metal most likely to be?

14.42 Calculate the final temperature after 25.0 g of chromium at 54.5°C is placed in 215 g of water at 19.0°C .

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- 14.43 Calculate the final temperature after 10.7 g of aluminum at 72.3°C is placed in 117 g of water at 14.6°C.
- 14.44 Calculate the final temperature after 2.47 g of zinc at 60.1°C is placed in 29.4 g of water at 16.4°C.
- 14.45 Calculate the final temperature after 29.4 g of cobalt at 15.9°C is placed in 94.3 g of water at 61.4°C.
- 14.46 How much energy is required to raise the temperature of 10.0 g of chromium from 41.3°C to 104.0°C?
- 14.47 Calculate the final temperature after 14.9 g of an alloy of metals ($c = 0.650 \text{ J/g} \cdot ^\circ\text{C}$) at 81.6°C is placed in 88.8 g of water at 15.5°C.
- 14.48 A certain reaction emits 3.95 kJ of heat. What temperature change will 250.0 g of water at 16.0°C undergo if the heat from the reaction is added to it?
- 14.49 Calculate the heat required to change 27.7 g of ice at -15.9°C to liquid water at 25.0°C.
- 14.50 Calculate the heat required to change 255 g of liquid water at 88.5°C to water vapor at 125.0°C.
- 14.51 Calculate the final temperature after 17.0 g of water at 20.0°C is mixed with (a) 17.0 g water at 50.0°C (b) 34.0 g of water at 50.0°C.

14.4 Enthalpy Changes in Chemical Reactions

- 14.52 Write an equation corresponding to the ΔH for the
- Sublimation of ice
 - Formation of carbon monoxide
 - Formation of carbon dioxide
 - Combustion of carbon
 - Which two of the preceding are the same?
- 14.53 Write an equation to which each of the following corresponds:
- $\Delta H_{\text{sublimation}}(\text{CO}_2)$
 - $\Delta H_f(\text{CO})$
 - $\Delta H_{\text{combustion}}(\text{CO})$
 - $\Delta H_{\text{fusion}}(\text{H}_2\text{O})$
 - $\Delta H_f(\text{HCl})$
 - $\Delta H_{\text{combustion}}(\text{CH}_4)$
- 14.54 Write a balanced chemical equation corresponding to the reaction with enthalpy change given as (a) $\Delta H_f(\text{C}_8\text{H}_{18})$ and (b) $\Delta H_{\text{combustion}}(\text{C}_8\text{H}_{18})$.
- 14.55 Which of the following processes represents the reaction corresponding to the enthalpy of formation of AgCl ? Explain.
- $\text{AgCl}(s) \rightarrow \text{Ag}(s) + \frac{1}{2} \text{Cl}_2(g)$
 - $\text{Ag}(s) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{AgCl}(s)$
 - $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$
 - $\text{Ag}(s) + \text{AuCl}(s) \rightarrow \text{Au}(s) + \text{AgCl}(s)$
- 14.56 (a) Write a balanced chemical equation for the complete combustion of formaldehyde, CH_2O . (b) Its enthalpy of combustion is -561 kJ/mol. Calculate its enthalpy of formation. (c) Calculate the enthalpy change when 68.3 g of the compound is burned.

- 14.57 Calculate the enthalpy of formation of CH_2O from the following data:

	$\Delta H (\text{kJ})$
$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	-561
$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$	+286
$\text{CO}_2 \rightarrow \text{C} + \text{O}_2$	+393

- 14.58 Calculate ΔH for the reaction of 14.9 g of CuO according to the equation



- 14.59 Calculate the enthalpy of combustion at 25°C of 125 g of CO.

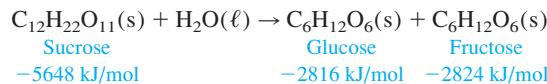
- 14.60 Given the following information:

$\text{R} + \text{X} \rightarrow \text{Q} + \text{Z}$	$\Delta H^\circ = -27.0 \text{ kJ}$
$\text{Q} + \text{Z} \rightarrow \text{T}$	$\Delta H^\circ = 43.0 \text{ kJ}$

calculate ΔH° for each of the following reactions:

- $\text{R} + \text{X} \rightarrow \text{T}$
- $\text{Q} + \text{Z} \rightarrow \text{R} + \text{X}$
- $2 \text{ Q} + 2 \text{ Z} \rightarrow 2 \text{ R} + 2 \text{ X}$

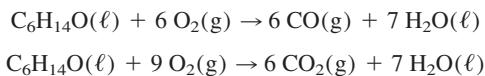
- 14.61 Calculate the enthalpy change for the following reaction of sucrose and water to give glucose and fructose, from their enthalpies of *combustion*, given below each substance in the following equation:



- 14.62 The value of ΔH for the reaction $\text{X} + \text{Q} \rightarrow \text{Z}$ is 13.3 kJ. What is the value of ΔH for each of the following reactions?

- $2 \text{ X} + 2 \text{ Q} \rightarrow 2 \text{ Z}$
- $\text{Z} \rightarrow \text{Q} + \text{Y}$

- 14.63 Which of the following equations represents the enthalpy of combustion of $\text{C}_6\text{H}_{14}\text{O}$? Explain why.



- 14.64 Which of the following equations

- $\text{C}_{(\text{graphite})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- $\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- $\text{C}_{(\text{graphite})} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)}$
- $\text{C}_{(\text{diamond})} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)}$
- $\text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

have enthalpy changes equal to

- $\Delta H_f^\circ(\text{CO}_2)$
- $\Delta H_{\text{combustion}}^\circ(\text{C})$
- $\Delta H_{\text{combustion}}^\circ(\text{CO})$
- $\Delta H_f^\circ(\text{CO})$

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- 14.65 The value of $\Delta H_{\text{combustion}}(\text{C}_6\text{H}_6)$ is -3266 kJ . Calculate its ΔH_f .

- 14.66 Calculate ΔH for the reaction of 4.000 mol of octane, C_8H_{18} , with excess O_2 to form CO_2 and H_2O .

- 14.67 Given the following reactions with their enthalpy changes at 25°C :

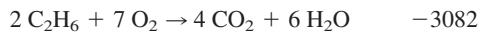
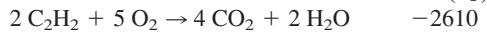


calculate the enthalpy of reaction of NO_2 to form N_2O_4 . Is N_2O_4 apt to be stable with respect to NO_2 at 25°C ? Explain your answer.

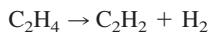
- 14.68 From the following data, calculate the enthalpy of hydrogenation of C_2H_2 to C_2H_6 :



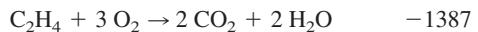
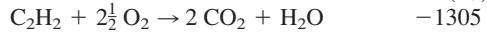
$$\Delta H \text{ (kJ)}$$



- 14.69 From the following data, calculate the enthalpy of dehydrogenation of 23.4 g of C_2H_4 to C_2H_2 :

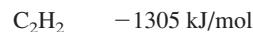
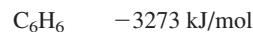
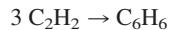


$$\Delta H \text{ (kJ)}$$



- 14.70 (a) What quantity of heat is yielded to the surroundings when (a) 0.660 mol of C_8H_{18} is completely burned at constant pressure in 8.25 mol of oxygen gas at 25°C , producing CO_2 and H_2O at 25°C ? (b) If 15.00 mol of O_2 had been present, what quantity of heat would have been produced?

- 14.71 Given the following enthalpies of combustion, calculate the enthalpy change for the reaction of 25.0 g of C_2H_2 according to the equation



- 14.72 From the following data, calculate the enthalpy of hydrogenation of C_2H_2 to C_2H_6 :



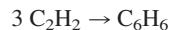
$$\Delta H \text{ (kJ)}$$



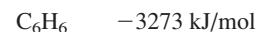
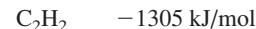
- 14.73 (a) Use the answer from the prior problem, to determine the enthalpy of hydrogenation of 51.7 g of C_2H_2 .
 (b) Repeat the calculation using the preliminary result to Problem 14.68.
 (c) Explain the results.

- 14.74 Determine the ΔH for the reaction of 50.0 g of SO_3 with MgO at 25°C . Values of ΔH_f are -602 kJ/mol for MgO , -395 kJ/mol for SO_3 , and -1280 kJ/mol for MgSO_4 .

- 14.75 Consider the following reaction:



Given the following enthalpies of combustion:



calculate the enthalpy change for:

- (a) The reaction of 15.0 g of C_2H_2
 (b) The production of 15.0 g of C_6H_6
 (c) Compare and explain the results of parts (a) and (b).
 (d) The reaction of 0.750 mol of C_2H_2
 (e) The production of 0.750 mol of C_6H_6
 (f) Compare and explain the results of (d) and (e).

General Problems

- 14.76 Energy is emitted when a pure substance freezes, but the substance has the same temperature after being frozen as before. Because the kinetic energy of the substance is directly proportional to the absolute temperature, both solid and fluid have the same kinetic energy. Where did the emitted energy come from?

- 14.77 Explain why both NH_3 and AsH_3 boil higher than PH_3 .

- 14.78 The *molar* heat capacity of a substance is the number of joules required to raise the temperature of a *mole* of the substance by 1°C . (Note the difference between this use

of the word *molar* and that in Chapter 11.) Calculate the molar heat capacity of (a) liquid water and (b) gold.

- 14.79 If 985 J of energy is added to a certain solution, the solution is warmed.
 (a) Does it make any difference if the added energy is electrical, chemical, or heat energy?
 (b) If a chemical reaction supplies energy to the solution, does the reaction have a positive, negative, or zero ΔH ?

■ General Problems

- (c) Does adding heat to the solution represent a positive, negative, or zero ΔH ?
- (d) Does the overall process have a positive, negative, or zero ΔH ?
- 14.80** Calculate the molar heat capacity (see Problem 14.78) of each element in Table 14.4. What can you generalize about the molar heat capacities of gaseous elements and those of metallic elements?
- 14.81** Label the portions of the heating curve in Figure 14.7 to show the areas in which the energy input goes into kinetic energy of the molecules and the areas in which the energy goes into potential energy.
- 14.82** It takes energy to boil a pure liquid substance, but the substance has the same temperature after being boiled as before. Because the kinetic energy of the substance is directly proportional to the absolute temperature, both liquid and vapor have the same kinetic energy. What happened to the energy that was used to change the liquid to vapor?
- 14.83** Calculate the energy required to convert 50.5 g of water at 23.5°C to ice at -4.2°C.
- 14.84** Relative humidity is defined as 100% times the ratio of the humidity at a given temperature to the maximum humidity that the air can have at that temperature (its vapor pressure):
- $$\text{Relative humidity} = \frac{\text{actual pressure of water vapor}}{\text{vapor pressure}} \times 100\%$$
- On a certain day, the relative humidity is 87%. If the temperature falls with no change in the concentration of water vapor in the air, what happens to the relative humidity?
- 14.85** (a) Calculate the final temperature after 0.690 kJ of energy is added to 50.0 mL of 0.250 M NaCl solution (density 1.01 g/mL, $c = 4.10 \text{ J/g}\cdot\text{°C}$) at 25.0°C.
 (b) Calculate the number of kilojoules of heat produced when 0.0125 mol of NaOH(aq) is allowed to react with 0.0125 mol of HCl(aq).
- $$\Delta H_{\text{neutralization}} = -55.2 \text{ kJ/mol of water formed}$$
- (c) Calculate the final temperature when 25.0 mL of 0.5000 M HCl at 25.0°C reacts with 25.0 mL of 0.5000 M NaOH at 25.0°C.
- 14.86** Potassium fluoride and calcium oxide have the same crystal structure. Which one should melt at the higher temperature? Explain why.
- 14.87** Magnesium oxide and sodium chloride have the same crystal structure. Which one should melt at the higher temperature? Explain why.
- 14.88** A certain mass of steam at 100°C is bubbled into 15.00 g of water at 15.3°C. When the process is ended, there is 15.60 g of water at 39.4°C.
- (a) What mass of steam is used in this experiment?
 (b) How much energy is supplied to the cold water?

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- (c) As it cooled, how much energy did the hot water (formed by condensation of the steam at 100°C) supply to the cold water?
- (d) How much energy did the condensation process supply to the cold water?
- (e) What is the heat of vaporization of water per gram at 100°C?
- 14.89** A certain mass of ice at 0°C is placed in 35.0 g of water at 27.3°C. When the process is ended, there is 40.6 g of water at 12.5°C.
- (a) What mass of ice is used in this experiment?
 (b) How much energy is provided by the warm water?
 (c) As it warmed, how much energy did the cold water (formed by melting of the ice at 0°C) accept from the hot water?
 (d) How much energy did the melting process accept from the water?
 (e) What is the heat of fusion of ice per gram at 0°C?
- 14.90** A certain mass of steam at 100°C is bubbled into 25.0 g of water at 22.2°C. When the process is ended, there is 26.0 g of water at 46.0°C. What is the heat of vaporization of water per gram at 100°C?
- 14.91** A certain mass of ice at 0°C is placed in 25.0 g of water at 76.6°C. When the process is ended, there is 29.0 g of water at 11.9°C. What is the heat of fusion of water per gram at 0°C?
- 14.92** In a certain experiment, when 1.75 mol of carbon reacted with oxygen to form a mixture of CO and CO_2 at 25°C and constant pressure, 546 kJ of heat was liberated, and no carbon remained. Calculate the number of moles of oxygen that reacted.
- 14.93** Given the following data, calculate ΔH for the reaction of 175 g of SO_2 according to the following equation:
- $$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$$
- (a) using Hess's law and (b) using another method.
- $$\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \quad \Delta H = -299 \text{ kJ}$$
- $$\text{S(s)} + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) \quad \Delta H = -395 \text{ kJ}$$
- 14.94** What is the final temperature of a 35.0-g sample of ice that is initially at -15°C after 2.10 kJ of energy is added to it. (See Tables 14.4 and 14.5 for specific heats and heats of phase change.)
- 14.95** What is the final temperature of a 41.3-g sample of water that is initially at 19°C after 14.4 kJ of energy is removed from it. (See Tables 14.4 and 14.5 for specific heats and heats of phase change.)
- 14.96** Calculate the final temperature when 100.0 mL of 1.000 M HCl at 25.0°C reacts with 100.0 mL of 1.000 M NaOH at 25.0°C (density of final solution = 1.01 g/mL, $c = 4.10 \text{ J/g}\cdot\text{°C}$).

$$\Delta H_{\text{neutralization}} = -55.2 \text{ kJ/mol of water formed}$$

404**CHAPTER 14 ■ Solids, Liquids, and Energies of Physical and Chemical Changes**

- 14.97 It took 12.9 kJ to vaporize a 3.50-g sample of a certain substance to its gaseous form at 1.00 atm. Which substance of Table 14.5 was involved?

- 14.98 When 0.200 mol NaOH dissolved in 50.00 mL of solution at 25.0°C is treated with 50.00 mL of HCl solution also at 25.0°C, the temperature rises to 31.3°C. Assuming that the specific heat of the solution is 4.15 J/g·°C and the mass of the solution is 111 g, calculate the number of moles of HCl in the second solution.

$$\Delta H_{\text{neutralization}} = -55.2 \text{ kJ}/(\text{mol H}_2\text{O formed})$$

- 14.99 Explain why a carbon dioxide fire extinguisher sprays “snowlike” solid CO₂ when discharged, even though it is at room temperature before being used.

- 14.100 A substance at its boiling point was placed in thermal contact with a water bath containing 533 g of water at 26.5°C, upon which the substance vaporized to fill a 1.50-L vessel with gas at 1.44 atm. Both the gas and the water ended up at 20.0°C. Which of the gases in Table 14.5 was involved?

- 14.101 Calculate the heat produced when 4.00 gal of octane, C₈H₁₈, reacts with oxygen to form carbon monoxide and water at 25°C. (The density of octane is 0.7025 g/mL; 1.000 gal = 3.785 L. The complete combustion of octane yields 5450 kJ/mol, and the combustion of CO yields 283.0 kJ/mol.)

- 14.102 Calculate the energy required to convert 30.7 g of water at 88.0°C and 1.00 atm to water vapor at 113.0°C and 1.00 atm.

- 14.103 (a) Draw a cooling curve for the change of 1.00 mol of water vapor at 107°C to ice at -5°C.
(b) Calculate the enthalpy change for the process.

- 14.104 Calculate the enthalpy of combustion of 1.00 mol of CO at 75°C. The value at 25°C is -283.0 kJ/mol.

(Hint: Use Hess's law, including equations for heating or cooling the reactants and products of the combustion reaction.)

- 14.105 A certain solid has regularly repeating molecules along the x, y, and z axis in its structure. What can you say about its melting point?

- 14.106 Water molecules are linked by hydrogen bonds, but H₂S, H₂Se, and H₂Te molecules are not. Plot the normal boiling points of these three compounds (H₂S, -60.7°C; H₂Se, -30°C; H₂Te, -2°C) versus the atomic number of the central atom, and extend the best straight line through the heavier three to atomic number 8. Predict what the normal boiling point of water would be in the absence of hydrogen bonding.

- 14.107 HF molecules are linked by hydrogen bonds, but HCl, HBr, and HI molecules are not. Plot the normal boiling points of these compounds (HF, -83.1°C; HCl, -114.8°C; HBr, -67.0°C; HI, -50.8°C) versus the atomic number of the halogen, and extend the best straight line through the heavier three to atomic number 9. Predict what the normal boiling point of HF would be in the absence of hydrogen bonding.

- 14.108 Given the ΔH values for equations I, II, III, and IV, calculate ΔH for reactions V and VI.

	ΔH (kJ)
I C ₄ H ₆ + $\frac{11}{2}$ O ₂ → 4 CO ₂ + 3 H ₂ O	-2600
II 2 C ₄ H ₁₀ + 13 O ₂ → 8 CO ₂ + 10 H ₂ O	-5760
III H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	-286
IV C ₄ H ₈ + 6 O ₂ → 4 CO ₂ + 4 H ₂ O	-2710
V C ₄ H ₆ + H ₂ → C ₄ H ₈	
VI C ₄ H ₆ + 2 H ₂ → C ₄ H ₁₀	



Various solutions

15

Solutions

- 15.1 The Solution Process
- 15.2 Saturated, Unsaturated, and Supersaturated Solutions
- 15.3 Percent by Mass
- 15.4 Molality
- 15.5 Mole Fraction
- 15.6 Colligative Properties

Review Clues

- Section 15.1** Sections 1.1, 12.10
Section 15.3 Appendix 1, Chapter 11
Section 15.4 Chapter 11
Section 15.6 Chapter 11, Section 12.6

Objectives

- 15.1** To explain, using the energetics of the solution process, how to predict which types of solvents are most likely to dissolve a given solute
- 15.2** To determine if more or less solute can be held in a given solution from its concentration, the solubility of the solute at various temperatures, and the temperature
- 15.3** To do calculations with percent by mass as a measure of concentration
- 15.4** To do calculations using molality—a temperature-independent measure of concentration
- 15.5** To do calculations using mole fraction—another temperature-independent measure of concentration, in which solute and solvent are not defined
- 15.6** To do calculations using some of the properties of solutions that depend on the concentrations of the dissolved particles, rather than their nature

The concept of solutions was introduced in Chapter 1, and molarity was considered in Chapter 11. Molarity is defined in terms of volume of solution, and volume can change with temperature, even if the masses of solvent and solute do not change. When dealing with solution concentrations in systems at varying temperatures, we need concentration units that do not vary with temperature. Three such units are introduced here.

This chapter first considers the nature of the solution process (Section 15.1) and the quantity of solute that can dissolve in a given quantity of solvent (Section 15.2). Covered next are three temperature-independent measures of concentration—percent by mass (Section 15.3), molality (Section 15.4), and mole fraction (Section 15.5). Finally, colligative properties of solutions are considered in Section 15.6.

15.1 The Solution Process

Solutions of two substances may be any of the types shown in Table 15.1. Most solutions discussed in this book are solutions of a solid, liquid, or gas in a liquid (most often water).

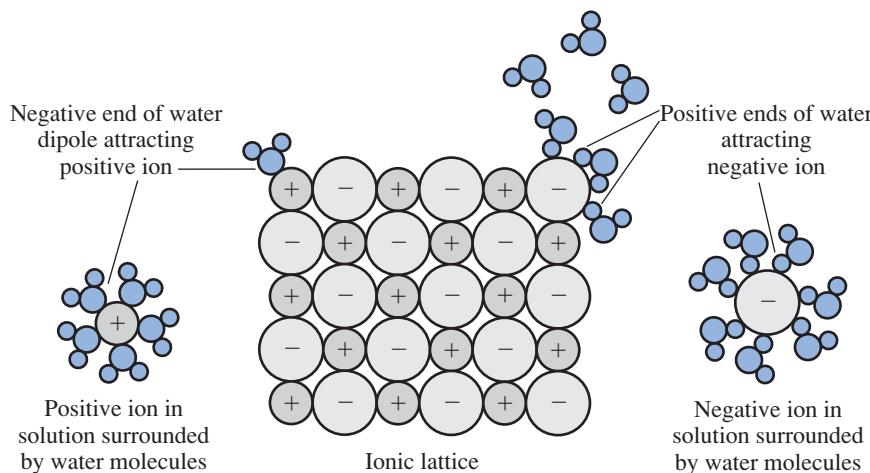
Substances dissolve in one another because the solution they form is more stable than a heterogeneous mixture of the individual substances. That statement implies that the attractions between the solvent molecules and the solute particles (atoms, molecules, or ions) are at least as great as the attractive forces between the particles of the solute or the molecules of the solvent. For an ionic solid to dissolve in a liquid, attractions between the solvent molecules and the ions of the solid must overcome the large attractions between the oppositely charged ions. The solvent molecules generally must have dipoles to be able to exert significant attractions on the charged ions. Thus, solutes with polar molecules are able to dissolve some ionic substances, but those with nonpolar molecules cannot. In contrast, nonpolar solutes are more apt to dissolve in nonpolar solvents. The solvent-solvent interactions cannot be too strong, otherwise the solvent-solute interactions will not be able to overcome them. (That is, if a solute is to dissolve in a polar solvent, considerable forces of attraction between the solvent molecules must be overcome. The solute-solvent attractions must be strong enough to do that. Nonpolar solutes do not have sufficient attractions for

Table 15.1 Types of Solutions Containing Two Substances

Type	Example
Solid in solid	Brass (zinc in copper)
Solid in liquid	Sugar water
Solid in gas	Moth balls in nitrogen (or in air)
Liquid in solid	Mercury in silver (dental amalgam)
Liquid in liquid	Martini (no olive)
Liquid in gas	Water in nitrogen (or in air)
Gas in solid	Hydrogen in platinum
Gas in liquid	Club soda
Gas in gas	Oxygen in nitrogen (a mixture like air)

15.1 ■ The Solution Process**407****Figure 15.1** Dissolving Action of Water on an Ionic Solid

All of the ions at the surface of the solid are affected by water molecules. However, the ones at the edges and corners are affected more because there are more water molecules in the vicinity and fewer ions of opposite charge. The ions in solution have the most water molecules around them.



Like dissolves like.

polar solvents to do the job.) Thus, a general rule emerges: “Like dissolves like.” That is, polar solvents are more likely to dissolve ionic and polar solutes, and nonpolar solvents are more likely to dissolve nonpolar solutes.

When sodium chloride dissolves in water, the H_2O molecules orient their dipoles around the Na^+ and Cl^- ions so that their oppositely charged ends are adjacent to each ion (Figure 15.1). Each sodium or chloride ion in solution is surrounded by many water molecules, lessening the attractions between the ions. Silver chloride, AgCl , does not dissolve in water. Evidently, the ion-dipole attractions are not sufficient to overcome the ion-ion attractions of this solid lattice. The nonpolar solvent benzene, C_6H_6 , cannot dissolve either of these ionic compounds.

EXAMPLE 15.1

Which solvent—liquid ammonia (NH_3) or benzene (C_6H_6)—is more likely to dissolve each of the following solutes? (a) H_2O (b) C_6H_{12} (c) AgCl

Solution

- H_2O is more likely to dissolve in NH_3 because both substances are polar and capable of hydrogen bonding.
- C_6H_{12} is more likely to dissolve in the nonpolar solvent, C_6H_6 .
- AgCl is more likely to dissolve in the polar solvent, NH_3 .

Practice Problem 15.1 Which type of solvent—polar, nonpolar, or hydrogen bonding—is most likely to dissolve methyl alcohol, CH_3OH ?



ChemSkill Builder 15.1

Snapshot Review

- The attractions between solvent molecules and particles of solute must be sufficient to overcome the attractions of the solvent molecules for

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CHAPTER 15 ■ Solutions

one another and the solute particles for one another in order for significant dissolving to occur.

□ Like dissolves like.

- A. What type of solvent should be chosen to try to dissolve naphthalene, $C_{10}H_8$, a type of moth repellent?

15.2 Saturated, Unsaturated, and Supersaturated Solutions

Most solutes will dissolve only to a certain extent in a given solvent at a certain temperature. For example, only 6.35 g of boric acid, H_3BO_3 (used to bathe infected eyes), will dissolve in 100 g of water at 30°C. If we add more than 6.35 g of H_3BO_3 to the water at that temperature, the excess quantity H_3BO_3 will not dissolve. We state that the **solubility** of H_3BO_3 in water at 30°C is 6.35 g per 100 g of water.

A solution containing as much solute as it can stably hold at a given temperature is said to be a **saturated solution**. If the solution contains less solute, it is said to be an **unsaturated solution**. Thus, a solution containing 2.00 g of H_3BO_3 in 100 g of water at 30°C is unsaturated.

A change in temperature affects the solubility of a solute in a given solvent (Figure 15.2). Most solid solutes get more soluble in liquid solvents as the temperature is raised, but gases dissolved in liquids get less soluble. If we have a saturated solution of such a solid solute at a high temperature and we lower the solution's temperature, we expect that the excess solute will crystallize from the solution at the lower temperature. For example, at 100°C, the solubility of H_3BO_3 in water is 27.6 g per 100 g of water. If a solution containing 27.6 g of H_3BO_3 in 100 g of water at 100°C is cooled to 30°C, only 6.35 g of the H_3BO_3 will continue to be soluble, and 21.25 g of H_3BO_3 will crystallize from the solution. (This type of process, called **recrystallization**, is often used to purify solid substances.)

When we cool saturated solutions of certain solutes, such as sodium acetate, the solute often has difficulty forming the first crystal, resulting in an unstable solution. More solute is in the solvent than is stable at the lower temperature. This type of solution is called a **supersaturated solution**. If a supersaturated solution is shaken or the inner surface of the container is scratched with a glass rod, the excess solute may crystallize out. A more certain way to get a supersaturated solution to crystallize is to add to it a tiny crystal of the solid solute, on which the excess solute can crystallize (Figure 15.3).

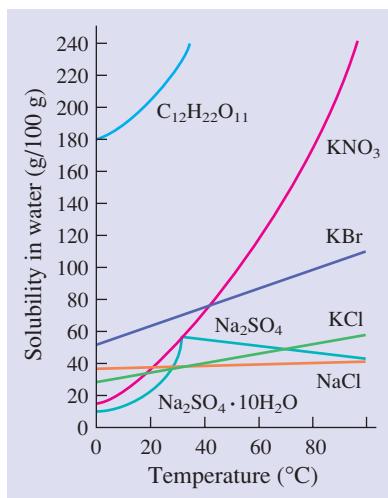


Figure 15.2 Variation of Solubility with Temperature of Various Solutes in Water

EXAMPLE 15.2

The number of grams of sodium acetate that will dissolve in 100 g of water is 119 g at 0°C and 170 g at 100°C.

- If 170 g of sodium acetate is placed in 100 g of water at 0°C, how much will dissolve?
- Is the resulting system homogeneous or heterogeneous?
- Ignoring any excess solid solute that may be present, is the solution saturated, unsaturated, or supersaturated?
- If the system is then raised to 100°C, is it homogeneous or heterogeneous?

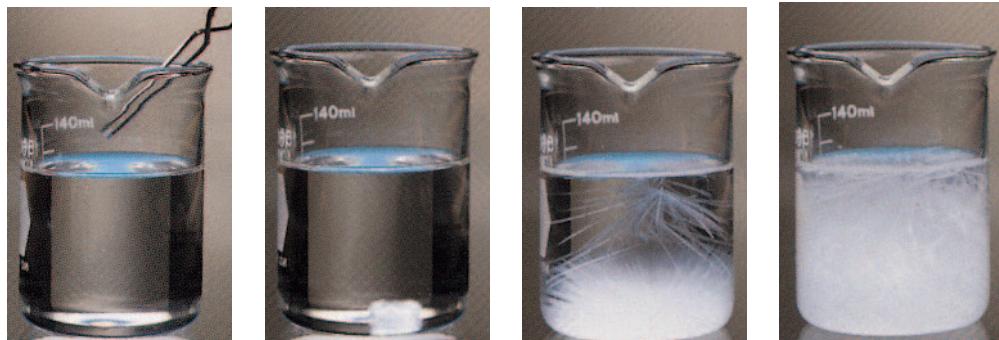
15.2 ■ Saturated, Unsaturated, and Supersaturated Solutions**409**

Figure 15.3 Crystallization of a Solute from a Supersaturated Solution Until the Solution Holds No Excess Solute

As time passes, crystals grow from the supersaturated solution.

- (e) Is the solution saturated, unsaturated, or supersaturated?
- (f) If the system is then carefully cooled back to 0°C, and no crystals appear, is the system homogeneous or heterogeneous?
- (g) Is the solution saturated, unsaturated, or supersaturated?

Solution

- (a) Only 119 g of sodium acetate will dissolve in 100 g of water at 0°C.
- (b) The system is heterogeneous—a mixture of the solution and the excess solid.
- (c) The solution part is saturated; it holds as much solute as it stably can hold at 0°C.
- (d) When the system is heated to 100°C, all 170 g of solute will dissolve, and the system is homogeneous.
- (e) The solution is saturated; it holds 170 g in 100 g of water, which is the maximum it can hold stably *at this temperature*.
- (f) Homogeneous. Because no solute crystallizes, the system is still a solution.
- (g) The solution is supersaturated because the 170 g of solute that it holds is more than the 119 g that would be stable at this temperature. If a small crystal of sodium acetate is added, the excess sodium acetate will crystallize out (see Figure 15.3).

Practice Problem 15.2

- (a) What would your answer to part (e) of Example 15.2 be if only 161 g of sodium acetate had been used?
- (b) What would your answer to part (d) be if 90.0 g of water had been used?

A solution of a gas in a liquid with which it does not react is a little different. At any given temperature, the solubility of the gas in the liquid is directly proportional to the partial pressure of the gas. This statement is known as **Henry's law**. Mathematically,

$$\text{Concentration of gas} = kP$$

where k is the Henry's law constant. Thus, to specify a saturated solution of a gas in a liquid, we must specify both the temperature and the partial pressure of the gas.



Snapshot Review

- A saturated solution holds the maximum quantity of solute that will dissolve in a given quantity of solvent at a particular temperature. The easiest way to tell that there is a saturated solution is to have excess solute present that will not dissolve.
 - Supersaturated solutions, containing more solute than is stable at the temperature of the system, are inherently unstable.
 - The concentration of a gas in a liquid is directly proportional to the partial pressure of the gas.
- A. A tiny crystal of solid sodium acetate is added to three aqueous solutions of sodium acetate. Classify each original solution as saturated, unsaturated, or supersaturated.
- The added sodium acetate just sits there.
 - The added sodium acetate causes more solid sodium acetate to form.
 - The added sodium acetate dissolves.
- B. A certain gas is saturated at 0.0100 M in water under a given set of conditions. What would its solubility be if the pressure of the gas were tripled, all other conditions remaining the same?

15.3 Percent by Mass

The 100 g and 100% are definitions, not measurements, and can be used to as many significant digits as necessary.

The **percent by mass** of a solute is simply the number of grams of solute in exactly 100 g of *solution*. It can be calculated as exactly 100% times the mass of the solute divided by the mass of the entire solution:

$$\text{Percent by mass} = \left(\frac{\text{mass of solute}}{\text{total mass}} \right) \times 100\%$$

(The words “percent solute” usually mean “percent by mass of solute”.) Thus a 10.00% aqueous saline solution has 10.00 g of NaCl in 100.00 g of solution. The mass of the water can be calculated from its percentage (90.00%) or by subtraction of the mass of the salt from the total mass:

$$100.00 \text{ g total} - 10.00 \text{ g NaCl} = 90.00 \text{ g H}_2\text{O}$$

Six factors could be used for calculations involving that solution:

$$\begin{array}{ccc} \left(\frac{10.00 \text{ g salt}}{100.00 \text{ g total}} \right) & \left(\frac{90.00 \text{ g water}}{100.00 \text{ g total}} \right) & \left(\frac{10.00 \text{ g salt}}{90.00 \text{ g water}} \right) \\[10pt] \left(\frac{100.00 \text{ g total}}{10.00 \text{ g salt}} \right) & \left(\frac{100.00 \text{ g total}}{90.00 \text{ g water}} \right) & \left(\frac{90.00 \text{ g water}}{10.00 \text{ g salt}} \right) \end{array}$$

EXAMPLE 15.3

Calculate the mass of NaCl in 46.6 g of 3.00% by mass saline solution.

15.3 ■ Percent by Mass**411****Solution**

$$46.6 \text{ g solution} \left(\frac{3.00 \text{ g NaCl}}{100.0 \text{ g solution}} \right) = 1.40 \text{ g NaCl}$$

Practice Problem 15.3 Calculate the mass of NaCl required to make a 3.00% by mass saline solution with 46.6 g of water.

EXAMPLE 15.4

State exactly how to prepare 200.0 g of 4.000% by mass NaCl solution.

Solution

First calculate the mass of NaCl required:

$$200.0 \text{ g solution} \left(\frac{4.000 \text{ g NaCl}}{100.0 \text{ g solution}} \right) = 8.000 \text{ g NaCl}$$

The mass of water required is thus $200.0 \text{ g solution} - 8.000 \text{ g NaCl} = 192.0 \text{ g}$ water. Therefore we dissolve 8.000 g NaCl in 192.0 g water to make our solution.

Often solutions are prepared by dilution of more concentrated solutions of the same solute. (These dilution problems are similar to those involving molarity, presented in Chapter 11.) When we dilute a solution, the mass of the solute does not change, but the masses of the solvent and the solution do, and thus the percentage of each component changes.

EXAMPLE 15.5

Calculate the mass of 10.00% stock solution required to prepare 0.8000 kg of 4.000% solution.

Solution

For the final solution:

$$0.8000 \text{ kg solution} \left(\frac{1000 \text{ g solution}}{1 \text{ kg solution}} \right) \left(\frac{4.000 \text{ g solute}}{100.0 \text{ g solution}} \right) = 32.00 \text{ g solute}$$

For the initial solution:

$$32.00 \text{ g solute} \left(\frac{100.0 \text{ g solution}}{10.00 \text{ g solute}} \right) = 320.0 \text{ g solution}$$

Thus 320.0 g of 10.00% stock solution (containing 32.00 g of solute) is diluted with

$$800.0 \text{ g final solution} - 320.0 \text{ g initial solution} = 480.0 \text{ g water}$$

Practice Problem 15.5 Calculate the mass of 0.650% solution that can be prepared by diluting 25.0 g of 3.00% stock solution.

EXAMPLE 15.6

A nurse needs 525 g of 2.00% sterile saline solution (NaCl). He has two sterile stock solutions of NaCl: 5.000% and 0.5000% by mass, but no sterile water. How can he make the required solution?

Solution

$$525 \text{ g solution} \left(\frac{2.00 \text{ g NaCl}}{100.0 \text{ g solution}} \right) = 10.5 \text{ g NaCl required}$$

Let x = the mass of the 5.000% solution.

Then $525 - x$ = the mass of the 0.5000% solution.

$$\frac{x(5.000)}{100.0} + \frac{(525 - x)(0.5000)}{100.0} = 10.5$$

$$0.05000x + 2.625 - 0.005000x = 10.5$$

$$0.0450x = 7.875$$

$$x = 175 \text{ g of 5.000\% solution}$$

$$525 - x = 350 \text{ g of 0.5000\% solution}$$



Snapshot Review



ChemSkill Builder 15.2

- Percent by mass is the number of grams of solute in exactly 100 g of solution. Note that unlike molarity (Chapter 11), the denominator of this ratio is a mass, not a volume.
 - Be sure to distinguish between mass of solvent and mass of solution.
- A. Calculate the percent by mass of glucose in a solution containing 11.1 g of glucose in 100.0 g of water.
 - B. State how to prepare 125.0 g of a 2.500% dextrose solution in water.

15.4 Molality

The concept of molarity was defined and used in Chapter 11. Molarity is based on the volume of the solution, which may change with temperature. That is, if the solution is heated, its volume increases and its molarity decreases, even if the components of the solution do not change. Because chemists sometimes need to measure concentrations in experiments in which different temperatures

15.4 ■ Molality**413**

Molality is the number of moles of solute per kilogram of solvent.

must be used, they developed other ways to express concentrations. **Molality** is the number of moles of solute per kilogram of solvent:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

Molality is symbolized *m*. The unit of molality is **molal**, and the symbol for molal is *m*. The great similarities in name and meaning between molarity and molality can be confusing. However, the concepts differ in two ways: For molality, (1) *mass* is used, not volume; and (2) the *solvent* is measured, not the solution. Be sure to use M (capital) to represent molar, and *m* (lowercase) to represent molal.

EXAMPLE 15.7

Calculate the molality of a solution prepared by dissolving 29.4 g of NaCl in 212.7 g of water.

Solution

The number of moles of solute and the number of kilograms of solvent are calculated first:

$$29.4 \text{ g NaCl} \left(\frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}} \right) = 0.5026 \text{ mol NaCl}$$

$$212.7 \text{ g H}_2\text{O} \left(\frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}} \right) = 0.2127 \text{ kg H}_2\text{O}$$

The number of moles of NaCl is then divided by the number of kilograms of H₂O to obtain the molality:

$$m = \frac{0.5026 \text{ mol NaCl}}{0.2127 \text{ kg H}_2\text{O}} = 2.36 \text{ m}$$

Practice Problem 15.7 Calculate the molality of a solution prepared by dissolving 28.2 g of C₃H₇OH in 207 mL of water (density = 1.00 g/mL).

EXAMPLE 15.8

The solubility of MgSO₄ in water at 0°C is 26 g per 100.0 g of water. Express this solubility as a molality.

Solution

$$\begin{aligned} 26.0 \text{ g MgSO}_4 &\left(\frac{1 \text{ mol MgSO}_4}{120.4 \text{ g MgSO}_4} \right) \left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) = \frac{2.16 \text{ mol MgSO}_4}{1 \text{ kg H}_2\text{O}} \\ &= 2.16 \text{ m MgSO}_4 \end{aligned}$$

Many problems involving molality are similar to those involving molarity.

EXAMPLE 15.9

Calculate the number of moles of solute in a 1.37 m solution containing 0.200 kg of solvent.

Solution

Because molality is a ratio, it may be used as a factor:

$$0.200 \text{ kg} \left(\frac{1.37 \text{ mol solute}}{1 \text{ kg solvent}} \right) = 0.274 \text{ mol solute}$$

Practice Problem 15.9 Calculate the mass of HClO_4 needed to make a 5.13 m solution in 239 g of water.

EXAMPLE 15.10

Calculate the mass of solvent required to make a 1.70 m solution that contains 0.435 mol of solute.

Solution

The inverse of the ratio expressing the molality may also be used as a factor:

$$0.435 \text{ mol solute} \left(\frac{1 \text{ kg solvent}}{1.70 \text{ mol solute}} \right) = 0.256 \text{ kg solvent}$$

Practice Problem 15.10 Calculate the number of grams of water that must be mixed with 14.7 g of acetaldehyde, $\text{C}_2\text{H}_4\text{O}$, to make 1.68 m $\text{C}_2\text{H}_4\text{O}$.

EXAMPLE 15.11

What is the molality of a solution prepared by mixing a 1.21 m solution of KCl containing 3.11 mol of solute with a 1.89 m solution of KCl containing 1.18 mol of solute?

Solution

The total number of moles of KCl is 4.29 mol. The number of kilograms of solvent must be calculated for each solution and then added to get the number of kilograms of solvent in the final solution:

$$3.11 \text{ mol KCl} \left(\frac{1 \text{ kg solvent}}{1.21 \text{ mol KCl}} \right) = 2.570 \text{ kg solvent}$$

$$1.18 \text{ mol KCl} \left(\frac{1 \text{ kg solvent}}{1.89 \text{ mol KCl}} \right) = 0.6243 \text{ kg solvent}$$

15.5 ■ Mole Fraction**415**

The total mass of solvent is 3.194 kg, so the molality is

$$m = \frac{4.29 \text{ mol KCl}}{3.194 \text{ kg solvent}} = 1.34 \text{ m}$$

Practice Problem 15.11 Calculate the molality of a certain solute if a 0.512 m solution of the solute is combined with a 0.216 m solution of the solute. The first solution contains 1.34 kg of solvent, and the second solution contains 2.13 kg of the same solvent.

**Snapshot Review**

ChemSkill Builder 15.2

- The molality is the number of moles of solute per *kilogram* of solvent. Note the differences between molality and molarity.
- A 6.17 m solution would have how many millimoles of solute per gram of solvent?
 - Calculate the molality of 41.5 g of naphthalene, C₁₀H₈, in 400.0 g of benzene, C₆H₆.

15.5 Mole Fraction

The **mole fraction** of a component of a solution is simply the number of moles of that component divided by the total number of moles in the solution. The mole fraction of component A is symbolized by X_A. A mole fraction is similar to a percentage in that it represents a part of a whole. The sum of the mole fractions of all the components of a solution is equal to 1, just as the sum of the percentages of all components of a whole must be 100%. With mole fraction, solute and solvent are not differentiated; every component is treated the same. A mole fraction has no units because it is obtained by dividing moles by moles.

EXAMPLE 15.12

Calculate the mole fraction of methyl alcohol, CH₃OH, in a solution composed of 1.46 mol of methyl alcohol and 2.19 mol of ethyl alcohol, C₂H₅OH.

Solution

The mole fraction is

$$X_{\text{CH}_3\text{OH}} = \frac{1.46 \text{ mol}}{1.46 \text{ mol} + 2.19 \text{ mol}} = 0.400$$

Practice Problem 15.12 Calculate the mole fraction of CH₂O and of C₃H₇OH in a solution containing equal masses of both. (*Hint:* Assume some mass, say 10.00 g of each.)

EXAMPLE 15.13

Show that the sum of the mole fractions of the components of the solution of Example 15.12 is equal to 1.

Solution

The mole fraction of the ethyl alcohol is

$$X_{C_2H_5OH} = \frac{2.19 \text{ mol}}{1.46 \text{ mol} + 2.19 \text{ mol}} = 0.600$$

Adding this mole fraction to that of methyl alcohol (obtained in Example 15.12) gives

$$0.400 + 0.600 = 1.000$$

Practice Problem 15.13 Which, if either, of the two substances in Example 15.12 is regarded as the solute?

EXAMPLE 15.14

Calculate the molality of a solution of methyl alcohol, CH_3OH , in water in which the alcohol has a mole fraction of 0.133.

Solution

Choose a quantity that makes at least one number of moles easy to calculate.

Because both concentration units are intensive, we can choose any quantity of solution we wish (or we can solve using algebraic unknowns). It is generally easiest to assume a quantity in which one or more numbers of moles is easiest to determine; in this case we will choose 1.000 mol total. Thus we have 0.133 mol CH_3OH and 0.867 mol water. We merely change the water to kilograms to determine the molality.

$$0.867 \text{ mol H}_2\text{O} \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 15.6 \text{ g} = 0.0156 \text{ kg}$$

$$\frac{0.133 \text{ mol CH}_3\text{OH}}{0.0156 \text{ kg H}_2\text{O}} = 8.53 \text{ m}$$

Practice Problem 15.14 Calculate the mole fractions of a 1.27 m solution of methyl alcohol in water.

**Snapshot Review**

- The mole fraction of a substance in a solution is the number of moles of the substance divided by the total number of moles in the solution.
- A. Calculate the mole fraction of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (table sugar), if 1.16 mol is dissolved in 55.6 mol of water (1.00 kg).

15.6 Colligative Properties

Certain physical properties of solutions depend on the concentrations of the particles (molecules or ions) dissolved in the solution, rather than the nature of these solute particles. In this section, we will consider four such **colligative properties**. The word “colligative” means “depending on the number of particles.”

Vapor-Pressure Lowering

The vapor pressure of a pure substance is dependent only on the nature of the substance and the temperature (Chapter 14). If we add a solute to the substance, its vapor pressure is lowered because the molecules of the substance cannot evaporate from the surface as rapidly as they could in the absence of the solute. The **vapor-pressure lowering** depends on the *concentration* of the solute particles, not on their nature. **Raoult’s law** states that the vapor pressure of a component of an ideal solution is equal to the mole fraction of the component times its vapor pressure when it is a pure substance. That is, for component Z:

$$P_Z = X_Z P_Z^\circ$$

where P_Z is the vapor pressure of the component in the solution and P_Z° is its vapor pressure when it is a pure substance. Many solutions follow Raoult’s law approximately. An **ideal solution** is defined as a solution that follows Raoult’s law exactly.

EXAMPLE 15.15

The vapor pressure of ethyl alcohol at a certain temperature is 79.3 torr. Calculate the vapor pressure of the ethyl alcohol in solution at that temperature if 0.175 mol of glucose is dissolved in 0.909 mol of the alcohol.

Solution

The mole fraction of the alcohol is

$$X_{\text{alcohol}} = \frac{0.909 \text{ mol}}{1.084 \text{ mol}} = 0.8386$$

The vapor pressure of the alcohol in the solution is

$$P_{\text{alcohol}} = X_{\text{alcohol}} P_{\text{alcohol}}^\circ = (0.8386)(79.3 \text{ torr}) = 66.5 \text{ torr}$$

Practice Problem 15.15 Calculate the vapor pressure of benzene in a solution in which the mole fraction of benzene is 0.820. The vapor pressure of pure benzene is 123 torr at this temperature.

EXAMPLE 15.16

Calculate the vapor-pressure *lowering* of the alcohol in Example 15.15.

Solution

The lowering of the vapor pressure may be defined as the vapor pressure of the pure substance minus its vapor pressure in the solution. It is symbolized ΔP .

$$\Delta P = P^\circ - P = 79.3 \text{ torr} - 66.5 \text{ torr} = 12.8 \text{ torr}$$

Note that vapor-pressure lowering, *not* vapor pressure, is directly proportional to the mole fraction of *solute*. (See Problem 15.96) For a solution of a **nonvolatile** (nonevaporating) solute in a **volatile** (easily evaporated) solvent, the greater the number of moles of *solute* present, the smaller is the mole fraction of the solvent. The smaller the mole fraction of the solvent, the lower is the vapor pressure of the solvent. Because the solute does not evaporate, the lower the vapor pressure of the solvent, the lower is the vapor pressure of the solution and the larger is the vapor-pressure lowering. That is, the smaller the value of P , the larger is the value of ΔP .

EXAMPLE 15.17

Calculate the total pressure of benzene and toluene over a solution of 0.661 mol benzene and 0.227 mol toluene at 25°C. Their vapor pressures when pure are 96.0 torr and 27.0 torr, respectively.

Solution

Each substance follows Raoult's law. Therefore

$$P_{\text{benzene}} = P_{\text{benzene}}^\circ X_{\text{benzene}}$$

$$P_{\text{toluene}} = P_{\text{toluene}}^\circ X_{\text{toluene}}$$

$$P_{\text{benzene}} = 96.0 \text{ torr} [(0.661 \text{ mol})/(0.661 + 0.227 \text{ mol})] = 71.46 \text{ torr}$$

$$P_{\text{toluene}} = 27.0 \text{ torr} [(0.227 \text{ mol})/(0.661 + 0.227 \text{ mol})] = 6.902 \text{ torr}$$

The total pressure is 78.4 torr.

Practice Problem 15.17 A mixture of carbon tetrachloride and chloroform at 20°C has a total pressure of 111 torr. If the mole fraction of chloroform is 0.402 and the vapor pressure of pure chloroform (CHCl_3) is 160 torr, what is the vapor pressure of pure carbon tetrachloride at that temperature?

EXAMPLE 15.18

Calculate the mole fraction of benzene in the vapor phase of the system in Example 15.17.

Solution

The partial pressures in a gas mixture are proportional to their ratio of moles (Section 12.6, p. 332). Therefore, the ratio of moles of benzene to moles of

15.6 ■ Colligative Properties**419**

toluene is $71.46/6.902$. The ratio of moles of benzene to total moles in the gas phase is $71.46/78.36 = 0.912$, which is equal to the mole fraction.

Note that the mole fraction of the more volatile substance has increased in the gas phase (from 0.744 in the liquid phase to 0.912). The process of distillation is based on this fact.

Practice Problem 15.18 A mixture of carbon tetrachloride, with mole fraction 0.300, and chloroform (CHCl_3) at 30°C has a total pressure of 215 torr. If the mole fraction of chloroform in the vapor phase is 0.800, what is the vapor pressure of each pure substance at that temperature?

Freezing-Point Depression

Addition of a solute to a solvent will cause the freezing point of the solvent to be lowered. The solute particles interfere with the process of making the orderly array of molecules characteristic of a crystalline solid. Antifreeze is added to car radiators to lower the freezing point of the water to prevent the coolant in the radiator from freezing in the winter. A salt is spread on icy sidewalks to make the freezing point of the water lower than the external temperature and thus melt the ice (Figure 15.4). In general, the more solute added per kilogram of solvent, the *greater* is the freezing-point depression and the *lower* is the freezing point. That is, the **freezing-point depression**, Δt_f , is directly proportional to the molality of the solute particles; the proportionality constant is symbolized as k_f :

$$\Delta t_f = k_f m$$

where

$$\Delta t_f = t_{\text{solvent}} - t_{\text{solution}}$$

The freezing point of a solution is always lower than that of the pure solvent, and the freezing-point depression may be defined as negative ($\Delta t_f = t_{\text{solution}} - t_{\text{solvent}}$). Because the value of Δt_f is referred to as a depression, however, its value is usually given without a minus sign. That practice will be followed in this book.

The value of k_f depends on the nature of the *solvent* and is independent of the solute used (as long as the solute does not ionize). The nature of the solute does not affect the freezing-point depression. Some k_f values and freezing points of substances frequently used as solvents are given in Table 15.2. Note that each value of k_f in the table is for that particular solvent and that the solute dissolved



Figure 15.4 Product for Common Use of Freezing-Point Depression

Calcium chloride is often used to melt ice on sidewalks. (It is less harmful to plants than is sodium chloride.)

Table 15.2 Some Freezing-Point Depression Data

Solvent	Formula	Freezing Point (°C)	k_f (°C/m)
Benzene	C_6H_6	5.5	5.12
Naphthalene	C_{10}H_8	80.22	6.85
Phenol	$\text{C}_6\text{H}_5\text{OH}$	43	7.40
Water	H_2O	0.00	1.86

in it does not make any difference in the value. (However, for ionic solutes, the total molality of cations *and* anions must be considered.)

EXAMPLE 15.19

Calculate the freezing point of a solution containing 0.135 mol of a nonionic solute in 2.50 kg of benzene.

Solution

The freezing-point depression is proportional to the molality. The molality is

$$m = \frac{0.135 \text{ mol}}{2.50 \text{ kg}} = 0.0540 \text{ m}$$

The value of k_f is found in Table 15.2. Then,

$$\Delta t_f = k_f m = (5.12^\circ\text{C}/\text{m})(0.0540 \text{ m}) = 0.2765^\circ\text{C}$$

The freezing point of the solution is equal to the freezing point of the solvent, pure benzene, minus the freezing-point depression (Δt_f):

$$t_{\text{solution}} = t_{\text{solvent}} - \Delta t_f = 5.5^\circ\text{C} - 0.2765^\circ\text{C} = 5.2^\circ\text{C}$$

Be sure to differentiate between the freezing point and the freezing-point depression, as well as between the freezing point of the solvent and the freezing point of the solution.

Practice Problem 15.19 Calculate the freezing point of a 0.250 m solution of benzene, C_6H_6 , in naphthalene.

The molar mass of a solute may be determined from the number of grams of solute dissolved in a given mass of solvent and the freezing-point depression of the solution. The freezing-point depression yields the number of moles of solute per kilogram of solvent, and the mass data yield the number of grams per kilogram of solvent. Dividing the number of grams per kilogram by the number of moles per kilogram yields the number of grams per mole—the molar mass.

EXAMPLE 15.20

A solution containing 1.66 g of nonionic solute in 171 g of water freezes at -0.602°C . Calculate the molar mass of the solute.

Solution

The molality of the solution is determined from the freezing-point depression and the value of k_f for water. The freezing-point depression for this solution is 0.602°C

$$m = \frac{\Delta t}{k_f} = \frac{0.602^\circ\text{C}}{1.86^\circ\text{C}/\text{m}} = 0.3237 \text{ m}$$

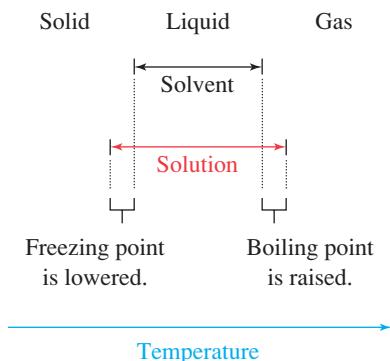
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Figure 15.5 Liquid Range of a Nonvolatile Solvent and Its Solution

The freezing point of the solution is lower than that of the solvent, and the boiling point of the solution is higher than that of the solvent. The liquid range has been extended on both ends.

Be sure to distinguish between boiling point and boiling-point elevation.

The number of moles of solute in 1.00 kg of solvent is therefore 0.3237 mol. The mass of solute per 1.00 kg of solvent is calculated next:

$$1.00 \text{ kg H}_2\text{O} \left(\frac{1.66 \text{ g solute}}{0.171 \text{ kg H}_2\text{O}} \right) = 9.708 \text{ g solute}$$

The molar mass is the ratio of the number of grams in a kilogram to the number of moles in a kilogram:

$$\text{Molar mass} = \frac{9.708 \text{ g}}{0.3237 \text{ mol}} = 30.0 \text{ g/mol}$$

Boiling-Point Elevation

The presence of a nonvolatile solute causes the boiling point of a solution to be raised in comparison with the boiling point of the pure solvent. The antifreeze added to water in car radiators causes the liquid in the radiator to boil at a temperature higher than 100°C, which is important in summertime to avoid engine overheating and radiator boilover. Like the freezing-point depression, the **boiling-point elevation** is directly proportional to the molality of the solute particles. In this case, however, the effect is positive; the boiling point is *raised*. Thus, the presence of a solute makes the liquid range of a solution longer, extending it at both the freezing-point end and the boiling-point end. That is, the solution is in the liquid state over a wider range of temperatures than is the pure solvent (Figure 15.5). The equation that relates boiling-point elevation to molality is the same as the one for freezing-point depression, except that the constant is k_b . However, even for a given solvent, the values of k_f and k_b are different. Some boiling-point elevation data are given in Table 15.3.

EXAMPLE 15.21

Calculate the boiling-point elevation for a 0.650 m solution of fructose, fruit sugar, $\text{C}_6\text{H}_{12}\text{O}_6$, in water. Fructose is nonvolatile and nonionic.

Solution

The boiling-point elevation constant for water is 0.512°C/m (see Table 15.3). Thus,

$$\Delta t_b = k_b m = (0.512^\circ\text{C}/\text{m})(0.650 \text{ m}) = 0.333^\circ\text{C}$$

Table 15.3 Some Boiling-Point Elevation Data

Solvent	Formula	Normal Boiling Point (°C)	k_b (°C/m)
Benzene	C_6H_6	80.1	2.53
Carbon tetrachloride	CCl_4	-22.99	5.03
Chloroform	CHCl_3	61.2	3.63
Water	H_2O	100.0	0.512

Practice Problem 15.21 Calculate the boiling-point elevation for a 0.650 m solution of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, in water. Ethylene glycol is the main constituent of permanent antifreeze.

EXAMPLE 15.22

Calculate the boiling point of a 0.650 m solution of fructose in water at 1.000 atm.

Solution

The boiling-point elevation was calculated in Example 15.21. The boiling point is therefore

$$t_{\text{solution}} = t_{\text{solvent}} + \Delta t_b = 100.0^\circ\text{C} + 0.333^\circ\text{C} = 100.3^\circ\text{C}$$

Note the difference between boiling point and boiling-point elevation.

Practice Problem 15.22 Calculate the boiling point of 0.650 m solution of naphthalene (a nonvolatile solute) in benzene.

Osmotic Pressure

When a solution is separated from its solvent by a semipermeable membrane, the solvent molecules can pass through the membrane but the solute particles cannot. The word “semipermeable” in this context means “porous to some molecules and not to others.” The rate of passage of solvent molecules from pure solvent to solution is greater than the rate of their passage in the other direction because the presence of the solute particles reduces the number of solvent molecules at the membrane. Therefore, if all other factors are equal, the liquid will rise on the solution side as more of the solvent passes through the membrane to that side than in the other direction (Figure 15.6). The more concentrated the solute, the higher the liquid level rises on the solution side. The effect can be best measured by seeing how much external pressure it takes to keep the liquid levels even on the two sides. (That way, the concentration of the solution is not changed.) That pressure is equal to the **osmotic pressure** of the solution. The osmotic pressure is governed by an equation analogous to the ideal gas law equation:

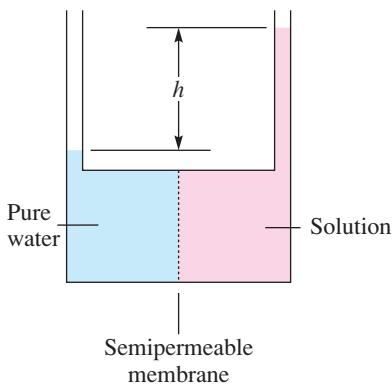


Figure 15.6 Osmotic Pressure

Because water molecules can pass through the semipermeable membrane from the pure water side to the solution side more easily than in the other direction, the level of pure water falls and that of the solution rises. The difference in the heights of the levels, h , corresponds to the osmotic pressure of the solution.

$$\pi V = nRT$$

where π is the osmotic pressure, V is the volume of the solution, n is the number of moles of solute, R is the gas constant, and T is the absolute temperature. If 0.0821 L·atm/mol·K is used for the value of R and the volume is given in liters, then π is in atmospheres. This equation can be rearranged to relate the osmotic pressure to *molarity*—the number of moles of solute per liter of solution (M):

$$\pi = \frac{nRT}{V} = \left(\frac{n}{V} \right) RT = MRT \quad \text{Thus,} \quad M = \frac{n}{V} = \frac{\pi}{RT}$$

ITEM OF INTEREST

A process called *reverse osmosis* is used to remove salts from seawater to make drinking water for human consumption. If a pressure greater than the osmotic pressure is applied to the solution side of an apparatus such as shown in Figure 15.6, water is forced from the solution (the seawater) to the pure solvent (water) side. This process is used industrially for water purification.

EXAMPLE 15.23

Calculate the osmotic pressure of a 0.0150 M solution of glucose, C₆H₁₂O₆, in water at 25°C.

Solution

$$\begin{aligned}\pi &= \frac{nRT}{V} = \left(\frac{n}{V}\right)RT \\ &= (0.0150 \text{ M})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K}) = 0.367 \text{ atm}\end{aligned}$$

Practice Problem 15.23 Calculate the concentration of sucrose in water at 25°C that would yield an osmotic pressure of 68.3 torr.

Example 15.23 shows that osmotic pressure is rather high, even for a very dilute solution.

Osmotic pressure is extremely important in biological systems. For example, in trees, it helps in moving liquids from the root systems to the tops. Water returns from human tissue to blood capillaries because of the greater concentration of solutes in the blood. The use of saline solution when replacing blood in accident victims must be carefully controlled so that the fluid's osmotic pressure is the same as that of blood.

EXAMPLE 15.24

Calculate the height of a column of water that can be supported by a pressure of 1.00 torr.

Solution

Since 1.00-torr pressure can support a column of mercury to a height of 1.00 mm, it can support a column of water 13.6 mm high, since mercury has a density 13.6 times that of water. That is an easily measurable distance.

**Snapshot Review**

- Vapor-pressure *lowering*, freezing-point *depression*, boiling-point *elevation*, and *osmotic pressure* all depend on the number of solute particles in a given quantity of solution.

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CHAPTER 15 ■ Solutions

- Vapor-pressure lowering is calculated with mole fraction; freezing-point depression and boiling-point elevation are calculated with molality; and osmotic pressure is calculated with molarity.
- Calculate the vapor-pressure lowering of benzene in a solution with mole fraction naphthalene 0.222. $P_{\text{benzene}}^{\circ} = 95.0 \text{ torr}$.
 - Calculate the freezing-point depression of benzene in a solution of 0.222 m naphthalene. $k_f = 5.12^\circ\text{C}/\text{m}$.
 - Calculate the osmotic pressure of 0.222 M sucrose in water at 25°C.

Key Terms

Key terms are defined in the Glossary.

boiling-point elevation (15.6)
colligative properties (15.6)
freezing-point depression (15.6)
Henry's law (15.2)
ideal solution (15.6)
molal (15.4)
molality (15.4)

mole fraction (15.5)
nonvolatile (15.6)
osmotic pressure (15.6)
percent by mass (15.3)
Raoult's law (15.6)
recrystallization (15.2)

saturated solution (15.2)
solubility (15.2)
supersaturated solution (15.2)
unsaturated solution (15.2)
vapor-pressure lowering (15.6)
volatile (15.6)

Symbols/Abbreviations

ΔP (vapor-pressure lowering) (15.6)
 Δt_b (boiling-point elevation) (15.6)
 Δt_f (freezing-point depression) (15.6)
 k_b (boiling-point elevation constant) (15.6)

k_f (freezing-point depression constant) (15.6)
 m (molal) (15.4)
 m (molality) (15.4)

P° (vapor pressure of pure substance) (15.6)
 π (osmotic pressure) (15.6)
 X_A (mole fraction of component A) (15.5)

Summary

Substances dissolve in solvents to form solutions because the attractions between solute particles and solvent particles are at least as strong as those holding the solute or solvent particles together. In general, nonpolar solutes tend to dissolve in nonpolar solvents, and polar and ionic solutes tend to dissolve in polar solvents (Section 15.1).

Most solutes have a certain limit to their solubility in a given solvent at a given temperature. A solution at that concentration is said to be saturated. If less of the solute is dissolved in the solvent at that temperature, the solution is unsaturated. If more is dissolved, the solution is supersaturated. A change in temperature changes the

solubility of a solute in a given solvent. Raising the temperature makes most solids more soluble in liquids but makes all gases less soluble in liquids. Greater pressure makes gases more soluble.

Supersaturated solutions are not stable; the excess solute is likely to crystallize out of solution if the solution is shaken, if the inside of the container is scratched, or especially if a crystal of the solute is added. Supersaturated solutions are typically prepared by dissolving a large quantity of solute in a given quantity of solvent at a high temperature, then carefully cooling the resulting solution. If the solute has difficulty crystallizing, a supersaturated solution may result (Section 15.2).

■ Items for Special Attention

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Percent by mass is a measure of concentration, defined as 100.0% times the mass of a component of the solution divided by the total mass of the solution. It is a temperature-independent concentration unit. It is often used for solutions in applied chemistry situations, such as medical laboratories and hospitals (Section 15.3).

Molality (m) is a temperature-independent measure of concentration, defined as the number of moles of solute per kilogram of solvent. It differs from molarity (M) in that it is based on a *mass of solvent*, rather than a volume of solution. Like molarity, molality can be used as a factor to solve problems (Section 15.4). Molality is also used in problems involving freezing-point depression and boiling-point elevation.

A third temperature-independent measure of concentration is mole fraction. It does not distinguish between solute and solvent. The mole fraction is defined as the number of moles of one component, say component A, divided by the total number of moles in the solution:

$$X_A = \frac{\text{number of moles of A}}{\text{total number of moles}}$$

(Section 15.5).

The presence of a solute affects some of the physical properties of a solution, but the identity of the solute makes little difference in the colligative properties. Vapor-pressure lowering, freezing-point depression, boiling-point elevation, and osmotic pressure are four such properties.

The vapor pressure of a solvent in the presence of a nonvolatile solute is given by Raoult's law:

$$P_A = X_A P_A^\circ$$

where P_A is the vapor pressure of the solvent in the solution, X_A is the mole fraction of A, and P_A° is the vapor pressure of the solvent when pure. Because X_A must be

lower than 1 in a solution of A, P_A must be lower than P_A° ; a vapor-pressure lowering has resulted because of the presence of the solute.

The freezing point of a solvent is lowered by the presence of a solute, and the boiling point of a solution is raised by the presence of a nonvolatile solute. The freezing-point depression and the boiling-point elevation are both directly proportional to the molality of the solute particles. Determining the molality therefore allows us to calculate the freezing point or boiling point of a solution; conversely, determining the freezing point or boiling point allows us to calculate the molality. With the molality and other data, we are able to calculate the number of moles and the molar mass.

Osmotic pressure is another property due to dissolved substances. The presence of solute particles lowers the ability of solvent molecules to pass through a semipermeable membrane. Osmotic pressure is very important in biological systems, and an application of the theory behind osmotic pressure allows for the purification of seawater. The osmotic pressure of a solution, π , is proportional to the molarity (the number of moles per liter):

$$\pi V = nRT$$

or

$$\pi = \left(\frac{n}{V} \right) RT = MRT$$

where R is the ideal gas law constant. Osmotic pressure measurement is a very sensitive means of determining the number of moles of solute in a given volume of solution and, together with other data, the molar mass (Section 15.6).

Items for Special Attention

- Be careful to distinguish between the mass of solution and the mass of solvent in percent by mass and molality problems. Percent by mass uses the former, and molality the latter.
- Molarity and molality are very similar; be careful not to confuse them. Also, be sure to use M to represent molar and m to represent molal.
- Osmotic pressure is a colligative property.
- Be sure to remember the difference between *vapor pressure* and *vapor-pressure lowering*, between *freezing point* and *freezing-point depression*, and between *boiling point* and *boiling-point elevation*.
- Vapor-pressure lowering calculations involve mole fraction; freezing-point depression and boiling-point elevation calculations use molality; and osmotic pressure is calculated with molarity.

Answers to Snapshot Reviews

- 15.1 A. A nonpolar solvent.
15.2 A. (a) Saturated (b) Supersaturated (c) Unsaturated
B. 0.0300 M (Because the partial pressure has tripled, the solubility triples.)
15.3 A. Percent glucose = $\left(\frac{11.1 \text{ g glucose}}{111.1 \text{ g solution}} \right) \times 100\% = 9.99\% \text{ glucose}$
B. $125.0 \text{ g solution} \left(\frac{2.500 \text{ g dextrose}}{100.00 \text{ g solution}} \right) = 3.125 \text{ g dextrose}$
 $125.0 \text{ g solution} - 3.125 \text{ g dextrose} = 121.9 \text{ g water}$
Dissolve 3.125 g dextrose in 121.9 g water.
15.4 A. 6.17 mmol/g (Multiplying both numerator and denominator by 1000 yields moles per kilogram.)

B. $41.5 \text{ g C}_{10}\text{H}_8 \left(\frac{1 \text{ mol C}_{10}\text{H}_8}{128 \text{ g C}_{10}\text{H}_8} \right) = 0.3242 \text{ mol C}_{10}\text{H}_8$
 $\frac{0.3242 \text{ mol C}_{10}\text{H}_8}{0.4000 \text{ kg benzene}} = 0.811 \text{ m}$

- 15.5 A. $\frac{1.16 \text{ mol}}{56.76 \text{ mol}} = 0.0204$
15.6 A. Because the mole fraction of naphthalene is 0.222, that of benzene is 0.778.
 $P = P^\circ X = (95.0 \text{ torr})(0.778) = 73.91 \text{ torr}$
 $\Delta P = 95.0 \text{ torr} - 73.91 \text{ torr} = 21.1 \text{ torr}$
B. $\Delta t = k_f m = (5.12^\circ\text{C/m})(0.222 \text{ m}) = 1.14^\circ\text{C}$
C. $\pi = (n/V)RT$
 $= (0.222 \text{ M})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})$
 $= 5.43 \text{ atm}$

Self-Tutorial Problems

- 15.1 A 15.00-g sample of a solid substance is placed in 100.0 g of water at 25°C, and all of the solid dissolves. Then another 2.00 g of the substance is added, and all of it dissolves. A final 2.00 g is added, and none of it dissolves.
(a) Is the first solution saturated, unsaturated, or supersaturated?
(b) Is the second solution saturated, unsaturated, or supersaturated?
(c) What can we tell about the final solution in contact with solid?
- 15.2 Using Figure 15.2, determine whether KNO_3 or KCl is more soluble in water at (a) 10°C and (b) 40°C.
- 15.3 List the differences between molarity and molality.
- 15.4 List as many similarities and differences as possible between mole fraction and percent composition by mass.
- 15.5 (a) How can the molarity of a solution be changed without changing the quantity of any of the components?
(b) Can molality be changed in the same way?
- 15.6 Calculate the molality of a solution of 12.0 g of NaCl in 125 g of water.
- 15.7 In a solution of formaldehyde and water, the formaldehyde is 25.0% by mass. Calculate the percentage of water.
- 15.8 In a solution of ethyl alcohol in water, the mole fraction of H_2O is equal to 0.930. Calculate the mole fraction of ethyl alcohol.

- 15.9 In a solution of CH_2O and CH_3OH in water, the mole fraction of H_2O is equal to 0.911 and that of CH_3OH is 0.0450. Calculate the mole fraction of CH_2O .
- 15.10 Calculate the mole fraction of KCl in a solution of 43.0 g in 275 g of water.
- 15.11 Which measure of concentration is used with (a) vapor-pressure lowering, (b) freezing-point depression, (c) boiling-point elevation, and (d) osmotic pressure?
- 15.12 Calculate the vapor-pressure lowering at 50°C of a solution of each of the following in water. Each has a mole fraction 0.150. (Hint: See Table 15.3) (a) sucrose, table sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) (b) antifreeze [$\text{C}_2\text{H}_4(\text{OH})_2$] (c) glucose ($\text{C}_6\text{H}_{12}\text{O}_6$).
- 15.13 Consider a 1.00 m solution and a 2.00 m solution of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, a nonvolatile solute, in water.
(a) Which solution has the greater boiling-point elevation?
(b) Which one has the higher boiling point?
- 15.14 Consider a 1.00 m solution and a 2.00 m solution of CH_3OH in water. (a) Which solution has the greater freezing-point depression? (b) Which one has the higher freezing point?
- 15.15 Calculate the percent by mass of the solution of Problem 15.10.

Problems**15.1 The Solution Process**

- 15.16 Explain why NH_3 is soluble in water but C_6H_6 is not.
- 15.17 Explain why C_8H_{18} (octane) is soluble in C_6H_6 , but Na_2SO_4 is not.

- 15.18 Explain why CH_3OH (methyl alcohol) is soluble in water, but C_6H_6 is not.
- 15.19 Explain why AgBr is soluble in liquid ammonia.

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- 15.20** Sucrose (table sugar), $C_{12}H_{22}O_{11}$, has many covalently bonded $—OH$ groups in its molecule. Explain why sucrose is so soluble in water.
- 15.21** (a) When water dissolves $MgCl_2(s)$, which end, if either, of a water molecule's dipole is expected to be nearer to a Mg^{2+} ion?
 (b) To a Cl^- ion?
 (c) When water dissolves liquid formaldehyde, which part of a water molecule is expected to be nearer to the oxygen atom of the CH_2O molecule? Why?

15.2 Saturated, Unsaturated, and Supersaturated Solutions

- 15.22** Explain how to prepare 500 mL of a saturated solution of a given salt in water.
- 15.23** Using Figure 15.2, propose an explanation for the sudden change in solubility of Na_2SO_4 as its solution warms up near 50°C.
- 15.24** A tiny crystal of a solid substance is added to an aqueous solution of the same substance. What would happen if the original solution was (a) unsaturated, (b) supersaturated, or (c) saturated?
- 15.25** If 3 tsp of table sugar is placed in a glass of iced tea, it does not all dissolve right away. Examine Figure 15.2 and conclude if the sugar ($C_{12}H_{22}O_{11}$) is not very soluble or does not dissolve very quickly.
- 15.26** Which compound in Figure 15.2 changes solubility most with increasing temperature?
- 15.27** Which solute in Figure 15.2 has the solubility that is least temperature-dependent?
- 15.28** From Figure 15.2, determine the solubility of KNO_3 in water at 80°C.
- 15.29** From Figure 15.2, determine whether a solution of 25.0 g of $NaCl$ in 100 g of water at 50°C is saturated, unsaturated, or supersaturated.
- 15.30** From Figure 15.2, determine whether each of the following solutions is saturated, unsaturated, or supersaturated:
 (a) 80 g KBr in 100 g of water at 50°C
 (b) 70 g KBr in 100 g of water at 33°C
 (c) 85 g KBr in 100 g of water at 80°C

15.3 Percent by Mass

- 15.31** Calculate the mass of $NaCl$ required to make a 2.00% by mass saline solution with 55.7 g of water.
- 15.32** Calculate the mass of $NaCl$ in 156.2 g of 15.50% by mass saline solution.
- 15.33** From Figure 15.2, calculate the approximate percent by mass of saturated $NaCl$ at 0°C.
- 15.34** Calculate the mass of 5.00% stock solution required to prepare 75.0 g of 1.75% solution.

- 15.35** Calculate the mass of 1.25% solution that can be prepared by diluting 15.5 g of 20.0% stock solution.
- 15.36** State exactly how to prepare 200.0 g of 1.750% by mass of KNO_3 solution.
- 15.37** Calculate the percent by mass of solute in a solution prepared by diluting 15.95 g of 15.00% stock solution with 100.00 g of water.

15.4 Molality

- 15.38** Calculate the molality of a solution of 6.17 g of acetic acid, $HC_2H_3O_2$, in 72.3 g of water.
- 15.39** Calculate the molality of a solution containing 0.527 mol of MgF_2 and 700.0 g of water.
- 15.40** Calculate the number of moles of solute in a 2.73 m solution that was made with 139 g of water.
- 15.41** Calculate the mass of solvent in a 1.33 m solution containing 0.707 mol of solute.
- 15.42** Calculate the number of moles of Na^+ ions in a 0.507 m solution of Na_2SO_4 containing 1.33 kg of water.
- 15.43** Calculate the molality of a solution of 17.4 g of $NaCl$ in 135 g of water.
- 15.44** Calculate the molality of chloride ions in a solution of 6.75 g of $AlCl_3$ in 195 g of water.
- 15.45** Calculate the molality of 1.000 kg of solution containing 1.62 mol of glycerine, $C_3H_5(OH)_3$, in water.
- 15.46** Calculate the number of moles of $MgCl_2$ needed to make a solution with 14.9 g of water that is 0.600 m in Cl^- .
- 15.47** Calculate the mass of solvent in a 1.18 m solution containing 0.697 mol of solute.
- 15.48** A solution of 0.515 mol of an organic compound in 182 g of benzene occupies 207 mL. Calculate its molarity and its molality.
- 15.49** A solution of 0.515 mol of an inorganic compound in 182 g of water occupies 191 mL. Calculate its molarity and its molality.
- 15.50** Explain why the molarity and molality of Problem 15.48 are so different but those of Problem 15.49 are so similar.
- 15.51** Calculate the molarity and molality of 268.3 mL of a solution containing 0.5142 mol of $CsCl$ and 197.5 g of water.
- 15.52** A solution of density 1.03 g/mL contains 0.363 mol of an inorganic compound (MM = 73.2 g/mol) in 417 g of water. Calculate its molarity and its molality.
- 15.53** Calculate the molality of an aqueous solution 7.50% by mass ethylene glycol, $C_2H_4(OH)_2$.
- 15.54** Calculate the percent by mass of a 3.00 m solution of benzoic acid, $HC_6H_5CO_2$, in benzene, C_6H_6 .
- 15.55** A solution of density 0.903 g/mL contains 0.255 mol of an organic compound (MM = 165 g/mol) in 298 g of benzene. Calculate its molarity and its molality.

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- 15.56 Calculate the mole fraction of water in each of the following solutions:
- 1.50 mol of $\text{C}_2\text{H}_4(\text{OH})_2$, 2.50 mol of CH_2O , and 6.00 mol of H_2O
 - 1.50 g of $\text{C}_2\text{H}_4(\text{OH})_2$, 2.50 g of CH_2O and 6.00 g of H_2O
- 15.57 Calculate the mole fraction of water in each of the following solutions:
- 95.5 g H_2O and 1.25 mol CH_3OH
 - 49.2 g $\text{C}_2\text{H}_5\text{OH}$ and 74.8 g H_2O
- 15.58 Calculate the mole fraction of ammonia in a 7.50 m aqueous solution of ammonia.
- 15.59 Calculate the mole fractions of a solution 15.7% by mass methyl alcohol (CH_3OH) in water.
- 15.60 Calculate the percent by mass of an alcohol-water solution with a mole fraction of water equal to 0.912. The alcohol is $\text{C}_2\text{H}_5\text{OH}$.
- 15.61 Calculate the mole fraction of glycerine in 715 g of solution containing 1.50 mole of glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$, in water.
- 15.62 Calculate the molality of alcohol in water if the mole fraction of alcohol is 0.180.
- 15.63 Calculate the mole fraction of NaCl in a solution containing 12.6 g NaCl and 21.3 g KCl in 122 g of water.
- 15.64 Calculate the molality of CH_2O in CH_3OH , with $X_{\text{CH}_2\text{O}} = 0.200$.

15.6 Colligative Properties

- 15.65 Calculate the vapor pressure of benzene, C_6H_6 , at 25°C in an ideal solution containing 1.66 mol of benzene and 0.313 mol of toluene. The vapor pressure of pure benzene is 96.0 torr.
- 15.66 Calculate the vapor pressure of toluene, C_7H_8 , at 25°C in an ideal solution containing 1.66 mol of benzene and 0.313 mol of toluene. The vapor pressure of pure toluene is 27.0 torr.
- 15.67 Calculate the total vapor pressure at 25°C above a solution containing 1.66 mol benzene and 0.313 mol toluene, using the data of Problems 15.65 and 15.66.
- 15.68 (a) The temperature of a sample of pure water is -1°C . Is the sample in the liquid or solid state?
(b) If the freezing point of a sample of water is depressed to -3°C by the addition of CaCl_2 , in what state will the sample be at -1°C ?
(c) Explain why a salt is used on icy streets and sidewalks.

CHAPTER 15 ■ Solutions

- 15.69 At 25°C, the vapor pressure of pure benzene, C_6H_6 , is 96.0 torr, and that of pure ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, is 44.0 torr. Assuming ideal behavior, calculate the vapor pressure at 25°C of a solution that contains an equal mass of each.
- 15.70 A solution of a nonionic solute in benzene freezes at 4.02°C . Calculate its molality.
- 15.71 A solution of a nonionic solute in naphthalene freezes at 74.12°C . Calculate its molality.
- 15.72 Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is nonvolatile and nonionic. For a 3.15 m solution of sucrose in water, calculate:
(a) The freezing point of the solution
(b) The boiling point of the solution at 1.0000 atm
- 15.73 An aqueous solution freezes at -1.51°C . Calculate the molality of the nonionic solute.
- 15.74 Calculate the freezing point of (a) 0.529 m benzene in naphthalene and (b) 0.529 m naphthalene in benzene.
- 15.75 The freezing point of pure ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, which is used as a permanent antifreeze, is -11.5°C . Would a solution of 17.3 g of water in 1.00 kg of ethylene glycol freeze below -11.5°C , at -11.5°C , or above -11.5°C ? Explain.
- 15.76 Calculate the freezing-point depression of an 0.800 m solution of (a) CH_3OH in water, (b) $\text{C}_2\text{H}_5\text{OH}$ in water, and (c) $\text{C}_3\text{H}_7\text{OH}$ in water.
- 15.77 Calculate the number of moles of nonionic solute in 125 g of water if the solution freezes at -1.02°C .
- 15.78 Fructose, fruit sugar, $\text{C}_6\text{H}_{12}\text{O}_6$, is nonvolatile and nonionic. For a 2.46 m solution of fructose in water, calculate:
(a) The freezing point of the solution
(b) The boiling point of the solution at exactly 1 atm
- 15.79 At 30°C, the vapor pressure of methanol, CH_3OH , is 0.211 atm. What is the mole fraction of CH_3OH in a solution in which the partial pressure of CH_3OH is 0.157 atm at 30°C?
- 15.80 An aqueous solution freezes at -0.908°C . Calculate the molality of the nonionic solute.
- 15.81 Calculate the freezing point of (a) 0.200 m benzene in naphthalene and (b) 0.200 m naphthalene in benzene.
- 15.82 Calculate the osmotic pressure of a 0.0100 M solution of glucose in water at 25°C.
- 15.83 Calculate the osmotic pressure in torr of a 0.1033 M solution of sucrose (table sugar) in water at 25°C.

■ General Problems

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General Problems

- 15.84** Calculate the concentration of a 7.500% solution of NaCl in water in (a) molality (b) mole fraction NaCl.
- 15.85** An aqueous solution of glucose ($C_6H_{12}O_6$) has a mole fraction of glucose equal to 0.175. Calculate its percent by mass glucose.
- 15.86** Calculate the percent glucose ($C_6H_{12}O_6$) by mass in a 4.68 m solution in water.
- 15.87** A solution contains 7.04 g of CH_2O and 80.0 g of C_2H_5OH .
 - Calculate the percent of CH_2O in the solution.
 - Calculate the molality of CH_2O in C_2H_5OH .
 - Calculate the molality of C_2H_5OH in CH_2O .
 - Calculate the mole fraction of each component.
 - What does identifying the solvent have to do with determining the percent by mass or the mole fractions?
- 15.88** A solution contains 42.7 g of ethylene glycol, $C_2H_4(OH)_2$, and 89.6 g of H_2O .
 - Calculate the percent of $C_2H_4(OH)_2$.
 - Calculate the molality of $C_2H_4(OH)_2$ in the water.
 - Calculate the molality of H_2O in the $C_2H_4(OH)_2$.
 - Calculate the mole fraction of each component.
 - What does identifying the solvent have to do with determining the percent by mass or the mole fractions?
- 15.89** A 14.5-g sample of a nonionic solute is dissolved in 50.0 g of water. The solution freezes at $-2.50^\circ C$. Calculate the molar mass of the solute.
- 15.90** Calculate the number of moles of solute in 400.0 g of water if the solution boils at $104.0^\circ C$ and 1.00 atm.
- 15.91** Which compound in Figure 15.2 could be purified best by recrystallization (dissolving it in hot water and cooling the solution)?
- 15.92** Add the appropriate boxes and connectors to Figure 12.10 to illustrate the calculation of mole-related quantities from (a) vapor-pressure depression data, (b) freezing-point lowering data, (c) boiling-point elevation data, and (d) osmotic pressure data.
- 15.93** Calculate the total pressure of an ideal solution consisting of 1.13 mol of benzene and 1.87 mol of toluene. The vapor pressures of the pure components are 105 torr and 34.0 torr, respectively.
- 15.94** Calculate the total pressure of an ideal solution consisting of 0.678 mol of benzene and 0.414 mol of toluene. The vapor pressures of the pure components are 105 torr and 34.0 torr, respectively.
- 15.95** A 4.73-g sample of a nonionic solute is dissolved in 50.5 g of water. The solution freezes at $-1.73^\circ C$. Calculate the molar mass of the solute.
- 15.96** (a) For an ideal solution of one nonvolatile solute in one solvent, show that
- $$\Delta P_{\text{solvent}} = X_{\text{solute}} P_{\text{solvent}}^{\circ}$$
- (b) Compare this equation to that for P_{solvent} given in the text, and state explicitly why these two equations must be used with extreme care.
- 15.97** Calculate the freezing point of 60.0 mL of an aqueous solution of density 1.01 g/mL if its osmotic pressure at $25^\circ C$ is 27.1 torr. The molar mass of the solute is 78.0 g/mol.
- 15.98** A solution contains a solute with molar mass 94.5 g/mol. The solution is 1.77 m and also 1.70 M. Calculate the density of the solution.
- 15.99** Which of the following 0.250 m solutions has the greatest freezing-point depression? (a) KCl (b) CH_2O (c) $CaCl_2$
- 15.100** Which of the following 0.150 m solutions has the greatest boiling-point elevation? (a) $Mg(NO_3)_2$ (b) $NaNO_3$ (c) $C_2H_4(OH)_2$
- 15.101** Determine the molality of chloride ions in a 10.0% $AlCl_3$ solution in water.
- 15.102** Calculate the molarity of a 2.50% aqueous NaCl solution whose density is 1.03 g/mL.
- 15.103** Calculate the freezing point of an aqueous solution that boils at $102.60^\circ C$ at 1.00 atm.
- 15.104** The molality of a solution can be calculated from its molarity if the density of the solution is known. In such a calculation, we must keep track not only of the units involved but of the materials to which the units apply. Calculate the molality of a 0.503 M $Sn(NO_3)_2$ solution that has a density of 1.083 g/mL.
- 15.105** The percent composition of a solute is 93.75% C and 6.25% H. If a solution containing 18.6 g of this substance in 86.6 g of benzene freezes at $-2.90^\circ C$, calculate the molecular formula of the substance.
- 15.106** The molality of a solution can be calculated from its molarity if the density of the solution is known. In such a calculation, we must keep track not only of the units involved but of the materials to which the units apply. Calculate the molality of a 0.333 M $CaCl_2$ solution that has a density of 1.031 g/mL.
- 15.107** Calculate the molar mass of a nonionic solute if a solution containing 6.11 g in 250.0 g of water freezes at $-1.151^\circ C$.
- 15.108** Calculate the molar mass of a nonionic solute if a solution containing 1.61 g in 81.4 g of benzene freezes at $4.3^\circ C$.
- 15.109** Calculate the molality of methyl alcohol, CH_3OH , in ethyl alcohol, C_2H_5OH , in which the mole fraction of methyl alcohol is 0.319.

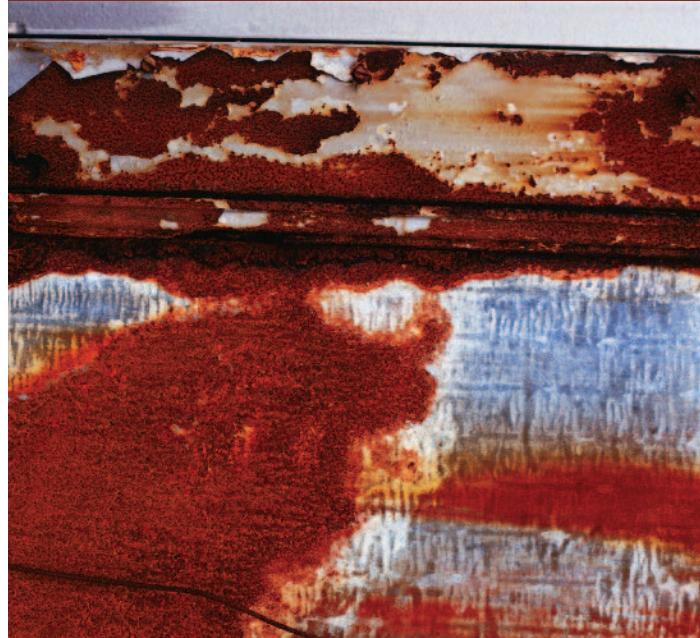
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- 15.110 The vapor pressure of pure benzene, C_6H_6 , at 50°C is 268 torr. How many moles of nonvolatile solute per mole of benzene is needed to prepare a solution having a vapor pressure of 231 torr at 50°C ?
- 15.111 The boiling point at 1.00 atm of a solution containing 1.71 g of a nonionic solute and 8.14 g of water is 100.44°C . Calculate the molar mass of the solute.
- 15.112 The percent composition of a nonionic substance is 40.0% C, 6.7% H, and 53.3% O. If a solution containing 9.298 g of this substance in 340.7 g of water freezes at -0.41°C , calculate the molecular formula of the substance.
- 15.113 Calculate the mole fraction of CH_3OH in a solution containing 70.0% by mass of CH_3OH and 30.0% of CH_2O .
- 15.114 Calculate the mole fraction of $\text{C}_2\text{H}_5\text{OH}$ in a solution containing 45.0% by mass of $\text{C}_2\text{H}_5\text{OH}$ in CH_3OH .
- 15.115 Calculate the vapor-pressure depression of an aqueous solution of density 1.02 g/mL if its osmotic pressure at 25°C is 98.0 torr. The molar mass of the nonvolatile solute is 125 g/mol.
- 15.116 The density of 10.00% by mass KCl solution in water is 1.06 g/mL. Calculate the molarity, molality, and mole fraction of KCl in this solution.
- 15.117 The boiling point at 1.00 atm of a solution containing 70.2 g of a nonionic solute and 482 g of water is 101.32°C . Calculate the molar mass of the solute.
- 15.118 Addition of 42.0 g of a nonvolatile solute to 2.15 mol of benzene lowers the vapor pressure of the benzene from

CHAPTER 15 ■ Solutions

105.0 torr to 95.1 torr. Calculate the molar mass of the solute.

- 15.119 The vapor pressure of pure chloroform at 40°C is 366 torr, and that of pure carbon tetrachloride is 143 torr. If a solution with mole fraction 0.180 in chloroform is allowed to evaporate, the vapor phase is separated from the solution and condensed, and the resulting solution is allowed to evaporate, what would be the mole fraction of the vapor phase after the second evaporation?
- 15.120 A saturated solution of ammonia in water is about 15 M at 25°C and 1.0 atm. Calculate the ratio of moles of ammonia per liter of this solution to moles per liter of ammonia gas at 25°C and 1.00 atm.
- 15.121 A solution is described as 55.2 m CH_3OH in water. Calculate the molality of water in CH_3OH .
- 15.122 A solution is described as 16.5 m acetone, $\text{C}_3\text{H}_6\text{O}$, in ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$. Calculate the molality of ethyl alcohol in $\text{C}_3\text{H}_6\text{O}$.
- 15.123 Calculate the molality of methyl alcohol, CH_3OH , in an aqueous solution in which the mole fraction of methyl alcohol is 0.191.
- 15.124 Calculate the percent by mass of a solution prepared from a 12.00% solution and a 2.00% solution of the same solute by combining (a) equal masses of the two solutions, (b) samples of each solution containing equal masses of water.



Rust

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Oxidation Numbers

- 16.1 Assigning Oxidation Numbers
- 16.2 Using Oxidation Numbers in Naming Compounds
- 16.3 Periodic Variation of Oxidation Numbers
- 16.4 Balancing Oxidation-Reduction Equations

Review Clues

- Section 16.1** Sections 5.1, 5.3, 5.5
- Section 16.2** Section 6.2
- Section 16.3** Sections 5.3, 6.1
- Section 16.4** Sections 8.2, 8.3, Chapter 9

Objectives

- 16.1** To assign oxidation numbers to elements based on the formula of a compound or polyatomic ion
- 16.2** To use oxidation numbers in naming compounds
- 16.3** To predict possible oxidation numbers of an element from its position in the periodic table and to use those numbers to predict possible formulas for its compounds
- 16.4** To use a systematic method to balance equations in which oxidation numbers change

In Chapter 5, we learned to write formulas for ionic compounds from the charges on the ions and to recognize the ions from the formulas of the compounds. For example, we know that aluminum chloride is AlCl_3 and that VCl_2 contains V^{2+} ions. We cannot make comparable deductions for covalent compounds because they have no ions; there are no charges to balance. To make similar predictions for species with covalent bonds, we need to use the concept of oxidation number, also called oxidation state. A system with some arbitrary rules allows us to predict formulas for covalent compounds from the positions of the elements in the periodic table and also to balance equations for complicated oxidation-reduction reactions.

Section 16.1 introduces the concept of oxidation number and how to calculate the oxidation number of an element from the formula of the compound or ion of which it is a part. Section 16.2 describes how to use the oxidation numbers to name compounds, formalizing and extending the rules given in Chapter 6. Section 16.3 shows how to predict possible oxidation numbers from the position of the element in the periodic table and how to use these oxidation numbers to write probable formulas for covalent compounds. Section 16.4 presents a systematic method for balancing equations in which oxidation numbers change.

16.1 Assigning Oxidation Numbers

The **oxidation number**, also known as the **oxidation state**, of an atom in a compound (or in a free element or polyatomic ion) is defined as the number of electrons possessed by a free (an uncombined) atom of the element— N_{free} —minus the number that is assigned to the atom in the compound (or element or ion)— N_{combined} :

$$\text{Oxidation number} = N_{\text{free}} - N_{\text{combined}}$$

Alternatively, we can often use the numbers of *valence* electrons in the free atom and in the atom in the compound to calculate the oxidation number.

For compounds of monatomic ions, the number of electrons assigned to each ion is easy to calculate, and the oxidation number turns out to be equal to the charge on the ion. For example, in magnesium chloride, the magnesium ion has 10 electrons remaining after transferring 2 electrons to the chlorine atoms. Because an uncombined magnesium atom has 12 electrons, the oxidation number of magnesium in this compound is $12 - 10 = +2$. Each chlorine atom started out with 17 electrons and has gained 1 electron to form the chloride ion in the compound, so the oxidation number of chlorine is $17 - 18 = -1$. Alternatively, the number of valence electrons in magnesium went from 2 to 0, yielding a +2 oxidation number. The number in chlorine went from 7 to 8, for a -1 oxidation number. In each case, the oxidation number is equal to the charge on the ion.

In this text, the sign of the oxidation number is written first to distinguish oxidation numbers from charges on ions, which we write with the sign second. For example, the oxidation number of sodium in Na^+ is +1 and the charge on the ion is $1+$.

We do not really need oxidation numbers when working with compounds of monatomic ions; we can use the charges to write formulas, and we can predict the charges from the periodic table or deduce them from the formulas. When working with compounds with covalent bonds and polyatomic ions (which also

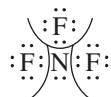
16.1 ■ Assigning Oxidation Numbers

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"Control" of the electrons in a covalent bond is arbitrarily assigned to the more electronegative element of the bond.

contain covalent bonds), however, we need oxidation numbers. Oxidation numbers for such species must be assigned by allocating the shared electrons in the covalent bonds to one or the other of the atoms, or equally to both if the atoms are the same. If the atoms are identical, they each control half of the shared electrons. If they are different, we arbitrarily allocate all the electrons in the bond to the more electronegative of the atoms involved (see Figure 5.4). In most cases, that will be the atom farther to the right or farther toward the top of the periodic table. The electrons are assigned to the more nonmetallic of the elements involved in the bond. For example, in NF_3 the bonds are covalent, so there are no charges. Because nitrogen lies closer to the metal area of the periodic table, each fluorine atom is assigned "control" of the shared electrons. This control is not complete; if the fluorine atoms really had complete control of the electrons, they would be fluoride ions. This compound is covalent. However, the concept of control is useful for the purposes of assigning oxidation numbers.

We can assign oxidation numbers from the electron dot diagram of a compound, such as NF_3 :



The nitrogen atom, when uncombined, has 5 valence electrons. In the compound, the shared electrons are "controlled" by the fluorine atoms, so the nitrogen atom retains "control" of only the unshared pair of electrons. It "controls" only 2 electrons. Its oxidation state is $5 - 2 = +3$. The uncombined fluorine atom has 7 valence electrons; but in the compound, each fluorine atom "controls" 8, so its oxidation number is $7 - 8 = -1$.

	Nitrogen	Fluorine
N_{free}	5	7
minus $N_{\text{controlled}}$	-2	-8
Oxidation number	$+3$	-1

Note that an oxidation number, like the charge on an ion, is assigned to *each atom* in a compound. Thus, *each* fluorine atom in NF_3 has an oxidation number of -1 .

In most cases, assigning oxidation numbers from formulas by drawing electron dot diagrams is more time-consuming than necessary. The following set of rules speeds the assignment of oxidation numbers for the elements in most cases. If these rules do not work for assigning oxidation numbers in a particular case, the electron dot method may be used.

Rules for Assigning Oxidation Numbers

1. The total of the oxidation numbers of all the atoms (not simply all the elements) is equal to the charge on the atom, molecule, or ion. Thus, for any compound, the sum of the oxidation numbers totals zero because the net charge on any compound is zero. The sum of the oxidation numbers of the atoms of any polyatomic ion is equal to the charge on that ion.
2. The oxidation number of any uncombined element is zero. Because the element is not combined with any other element, there is either one atom alone or a group of identical atoms. Because the atoms are alike, the electrons are shared equally, and the number "controlled" is equal to the number in the free

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CHAPTER 16 ■ Oxidation Numbers

atom. For example, the oxidation number of sodium as a free element and that of fluorine in F_2 are determined from their valence electrons as follows:

	Sodium as Free Element	Fluorine in F_2
N_{free}	1	7
minus $N_{\text{controlled}}$	−1	−7
Oxidation number	$\overline{0}$	$\overline{0}$

Thus, this rule is actually a corollary to rule 1; the oxidation number is equal to the charge on the species, zero in these cases.

3. The oxidation number of a monatomic ion is equal to the charge on the ion. This rule is also a corollary of rule 1. If the sum of all the oxidation numbers is equal to the charge and there is only one oxidation number because there is only one atom, then that oxidation number must equal the charge on the monatomic ion.
4. The oxidation number of any alkali metal atom *in any of its compounds* is always equal to +1.
5. The oxidation number of any alkaline earth metal atom *in any of its compounds* is always equal to +2.
6. The oxidation number of hydrogen in its compounds is equal to +1, except in its binary compounds with an alkali metal, an alkaline earth metal, or aluminum, when it is −1. (The H^- ion is named the *hydride ion*.)
7. The oxidation number of oxygen in its compounds is generally −2 (except in peroxides, −1, superoxides, $-\frac{1}{2}$, and its two compounds with fluorine).
8. The oxidation number of a halogen atom in its compounds is −1, except for chlorine, bromine, or iodine when combined with oxygen or another halogen that is above it in the periodic table.

The examples that follow illustrate these rules.



ENRICHMENT

In peroxides, the oxidation number of oxygen is −1, and in superoxides, it is $-\frac{1}{2}$. The only common superoxides are those of hydrogen and the alkali metals from potassium through francium. Peroxides occur with hydrogen, sodium, barium, and chromium, and in these compounds, each of these elements exists in its highest oxidation state.

In oxygen's rarely encountered compounds with fluorine (OF_2 and O_2F_2) the oxygen atoms have oxidation states of +2 and +1, respectively.

However, the oxidation number of oxygen is −2 in most of its compounds.

EXAMPLE 16.1

Determine the oxidation numbers of phosphorus and chlorine in phosphorus pentachloride, PCl_5 .

16.1 ■ Assigning Oxidation Numbers**435****Solution**

In this compound, the oxidation number of each chlorine atom is -1 (rule 8). To make the total of all the oxidation numbers for PCl_5 equal zero, the phosphorus must have an oxidation number of $+5$. To do this calculation systematically, let x equal the oxidation number of phosphorus in PCl_5 . Then

$$\begin{array}{cccc} & x + 5(-1) = 0 & & \\ \text{Oxidation} & & \text{Number of} & \text{Oxidation} & \text{Charge} \\ \text{number of} & & \text{chlorine} & \text{number of} & \text{on the} \\ \text{phosphorus} & & \text{atoms} & \text{each chlorine atom} & \text{molecule} \\ & & & & \\ & x = +5 & & & \end{array}$$

Practice Problem 16.1 Determine the oxidation number of carbon in CO .

EXAMPLE 16.2

What is the oxidation number of Mg?

Solution

Zero. (This is elemental magnesium.)

EXAMPLE 16.3

What is the oxidation number of nitrogen in the nitrite ion, NO_2^- ?

Solution

The oxidation number of oxygen in most of its compounds is -2 (rule 7). The oxidation numbers of the two oxygen atoms plus that of the nitrogen atom must total $1-$, the charge on the ion:

$$\begin{array}{cccc} & x + 2(-2) = -1 & & \\ \text{Oxidation} & & \text{Number of} & \text{Oxidation} & \text{Charge} \\ \text{number of} & & \text{oxygen} & \text{number of} & \text{on the} \\ \text{nitrogen} & & \text{atoms} & \text{each oxygen atom} & \text{nitrite ion} \\ & & & & \\ & x = +3 & & & \end{array}$$

Practice Problem 16.3 What is the oxidation number of sulfur in the sulfite ion, SO_3^{2-} ?

EXAMPLE 16.4

Calculate the oxidation number of sulfur in the thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$.

Solution

$$\begin{array}{c} 2x + 3(-2) = -2 \\ \swarrow \quad \searrow \quad \swarrow \quad \searrow \quad \swarrow \\ \text{Number of} \quad \text{Oxidation} \quad \text{Number of} \quad \text{Oxidation} \quad \text{Charge} \\ \text{sulfur} \quad \text{number of} \quad \text{oxygen} \quad \text{number of} \quad \text{on the} \\ \text{atoms} \quad \text{each sulfur} \quad \text{atoms} \quad \text{each oxygen} \quad \text{thiosulfate} \\ \text{atom} \end{array}$$
$$x = +2$$

Practice Problem 16.4 Calculate the oxidation number of chromium in the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$.

EXAMPLE 16.5

What is the oxidation number of hydrogen in (a) HF and (b) NaH?

Solution

- Fluorine has an oxidation number of -1 in all of its compounds (rule 8), so that of hydrogen in HF must be positive; it is $+1$ (rule 6).
- The oxidation number of sodium in its compounds is always $+1$ (rule 4), so that of hydrogen in NaH must be negative; it is -1 (rule 6).

Practice Problem 16.5 What is the oxidation number of hydrogen in (a) H_2SO_4 , (b) MgH_2 , and (c) H_2O_2 ?

Occasionally, oxidation numbers are fractional. For example, the oxidation number of iron in Fe_3O_4 is $+2\frac{2}{3}$. This does *not* mean that electrons have been split; the oxidation number simply gives the average of the numbers of electrons still controlled by the three iron atoms.

EXAMPLE 16.6

Calculate the oxidation number of nitrogen in (a) hydrazoic acid, HN_3 , (b) ammonia, NH_3 , and (c) hydrazine, N_2H_4 .

Solution

The hydrogen atoms in each compound have the oxidation number $+1$. Nitrogen must have an oxidation number such that the overall sum of oxidation numbers for each compound is zero:

- (a) $-\frac{1}{3}$ (b) -3 (c) -2

16.3 ■ Periodic Variation of Oxidation Numbers**437** **Snapshot Review**ChemSkill Builder
10.1, 10.2

- Oxidation numbers are used for covalently bonded atoms like charges are used for monatomic ions.
 - The sum of the oxidation numbers of all the *atoms* in a species is equal to the charge on the species.
- A. Calculate the oxidation number of nitrogen in each of the following:
 (a) NH₂OH, (b) N₂O, (c) N₂O₄, and (d) NaN₃.
- B. Write the formula of a covalent compound of element X with element Y if X has an oxidation number +6 and Y has an oxidation number -2.

16.2 Using Oxidation Numbers in Naming Compounds

In Chapter 6, we learned how to name cations. In the **Stock system**, the charges on monatomic ions were used to distinguish between different ions of the same element. For example, Cu⁺ and Cu²⁺ are named copper(I) ion and copper(II) ion, respectively. The Roman numeral actually represents the oxidation number, not the charge on the ion. Of course, for monatomic ions, the charge is equal to the oxidation number, and thus we used the charge to determine which Roman numeral to use. By using oxidation numbers, however, we can extend our compound-naming ability to include compounds other than those of monatomic ions. For example, Hg₂²⁺ is called the mercury(I) ion because the *oxidation number of each* mercury atom is +1.

The prefixes and suffixes used in Chapter 6 can also be interpreted in terms of oxidation numbers, rather than numbers of oxygen atoms. For example, the ending *-ous* corresponds to the oxoacid in which the central atom has the lower oxidation state in each case, and the ending *-ic* corresponds to the higher oxidation state. For example phosphorous acid has phosphorus in the +3 oxidation state; phosphoric acid has phosphorus in the +5 oxidation state. Phosphorus in hypophosphorous acid has an oxidation number +1.

**Snapshot Review**

- Oxidation numbers are represented by Roman numerals in naming ions of metals with ions of more than one possible charge.

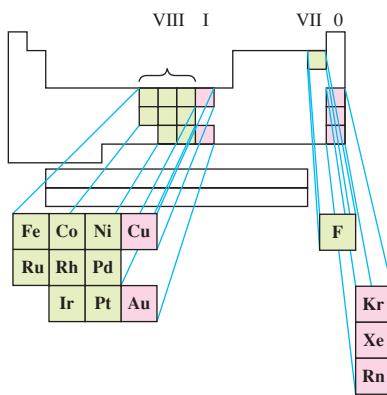
- A. Name (a) VCl₂, (b) MnO₂, and (c) Fe₂O₃.
- B. Write formulas for (a) copper(I) oxide and (b) copper(II) oxide.

16.3 Periodic Variation of Oxidation Numbers

In Section 16.1, we learned how to determine oxidation numbers of atoms of elements from the formulas of their ions or molecules. This section shows the opposite—how to write formulas for compounds based on knowledge of the possible oxidation numbers of the atoms of the elements. Predicting possible oxidation numbers is straightforward, but learning which are the most important oxidation numbers of even some of the most familiar elements takes a good deal of experience.

Predicting Oxidation Numbers

The maximum oxidation number for most elements is equal to the classical group number of the element.



- Elements with oxidation numbers that exceed the group number.
- Elements that do not have oxidation numbers as high as the group number.

Figure 16.1 Exceptions to the Maximum Oxidation Number Rule

For most of the elements, the *maximum* oxidation number is equal to the classical group number of the element. That is, the maximum oxidation number of lithium is +1 because lithium is in group IA, and the maximum oxidation number of iodine is +7 because iodine is in group VIIA. Exceptions to this rule are shown in Figure 16.1. Several elements, such as fluorine and most elements in group VIII, have maximum oxidation numbers less than their group numbers. Several of the elements of two groups—the coinage metals and the noble gases—have maximum oxidation numbers greater than their classical group numbers. Copper and gold have maximum oxidation numbers of +2 and +3, respectively, which are greater than the group number (IB). (Each of these elements also has an oxidation number of +1, but that is not the *maximum*.) Atoms of the noble gases that form compounds have positive oxidation numbers, all of which are greater than their group number, 0. Despite these exceptions, this simple rule allows us to predict at least one oxidation number for more than 90 elements.

Every element has an oxidation number of zero when it is uncombined (rule 2, Section 16.1). This second simple rule allows us to predict about 100 more oxidation numbers. (Some *compounds* have atoms with oxidation numbers of zero. For example, the carbon atom in formaldehyde CH₂O has an oxidation number of zero.)

The *minimum* oxidation number of the metallic elements and the noble gases is generally zero and that for hydrogen is -1. The minimum oxidation number of other nonmetallic elements is equal to the classical group number of the element minus 8.

EXAMPLE 16.7

What is the minimum oxidation number of nitrogen in any of its compounds?

Solution

$$\text{Minimum oxidation number} = \text{group number} - 8 = 5 - 8 = -3$$

Practice Problem 16.7 What is the minimum oxidation number of silver?

For metals and noble gases:
Minimum oxidation number
 $= 0$

For hydrogen:
Minimum oxidation number
 $= -1$

For other nonmetals:
Minimum oxidation number
 $= \text{group number} - 8$

EXAMPLE 16.8

What are three possible oxidation states of sulfur?

Solution

The maximum oxidation number of sulfur is +6, equal to its group number. Sulfur also has the oxidation state 0 when it is not combined and a minimum oxidation state of $6 - 8 = -2$. (Sulfur can also have oxidation states +4 and +2, not covered by the rules given so far.)

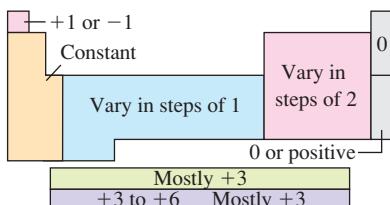
16.3 ■ Periodic Variation of Oxidation Numbers**439**

Figure 16.2 Periodic Variation of Oxidation Number

Practice Problem 16.8 What are three possible oxidation states of copper?

The rules given previously do not predict all of the oxidation numbers of the elements in their compounds, and there is no certainty that the oxidation numbers predicted by these rules will be those of the element in its most stable or most important compounds. Other oxidation states can be deduced by the location of the element in the periodic table. In their compounds, the alkali metals, alkaline earth metals, and group IIIB metals have constant oxidation states. The main group elements to the right of the transition group elements have oxidation numbers that usually vary in steps of 2. The transition group elements have oxidation numbers that may vary in steps of 1, and only a few of these elements have oxidation numbers equal to +1. The oxidation numbers of the lanthanides are mostly +3. The elements in the first half of the actinide series have oxidation numbers that increase from +3 to +6, but the elements of the last half of that series have oxidation numbers equal to +3. These generalizations are illustrated in Figure 16.2.

EXAMPLE 16.9

What are the possible positive oxidation numbers of sulfur?

Solution

The maximum oxidation number of sulfur, equal to its group number, is +6. Because the oxidation numbers vary mostly in steps of 2 in this portion of the periodic table, we can deduce (correctly) that sulfur also has +4 and +2 as oxidation numbers. Examples of compounds in which sulfur has these three oxidation numbers are SF₆, SF₄, and SF₂.

Practice Problem 16.9 What are four positive oxidation numbers of bromine?



ENRICHMENT

Metals with high oxidation numbers tend to act somewhat like nonmetals. For example, many transition metals form oxoanions, such as permanganate ion, chromate ion, and dichromate ion, in which the metal is covalently bonded to oxygen. The ability to form covalent bonds to oxygen is evidence of these metals' more covalent nature. (In their low oxidation states, most metals typically exist in ionic compounds as monatomic cations.) Titanium(IV) chloride is an example of a compound in which the

metal has a high oxidation number. It is a liquid at room temperature, and the liquid does not conduct electricity well. These characteristics are typical of covalent compounds. Because this is a binary covalent compound, it may be named titanium tetrachloride, using the prefix in Table 6.1, but modern practice prefers the Stock system name. It is easy enough to write the formula for the compound from either name, and either name is acceptable.

The rules in this section allow “educated guesses.”

The rules discussed so far allow us to make “educated guesses” about possible compounds formed by elements. However, not all compounds deduced by application of the rules actually exist. Moreover, some elements have more oxidation numbers than the rules identify. Nitrogen, for example, exhibits every integral oxidation number from -3 to $+5$, as well as a fractional oxidation number, $-\frac{1}{3}$, in HN_3 and its salts. Except for fluorine, the halogens also exhibit most of the integral oxidation numbers from -1 to $+7$. Detailed study of the chemistry of the elements and their compounds is necessary to know which compounds actually exist.

Writing Formulas for Covalent Compounds

Knowledge of possible oxidation numbers for the elements enables us to deduce formulas for covalent compounds, just as we did for ionic compounds in Chapter 5. Atoms of elements with positive oxidation numbers and atoms of elements with negative oxidation numbers are combined in a formula so that the total of the oxidation numbers of all the atoms equals zero. The resulting formula may be a compound of these elements.

EXAMPLE 16.10

Determine the formula of a compound of carbon and chlorine.

Solution

Chlorine in its compounds with elements other than oxygen and fluorine, exhibits a negative oxidation number, -1 (rule 8, Section 16.1). Thus, the oxidation number of carbon in this compound must be positive. The maximum oxidation number of carbon in its compounds is $+4$ because it is in group IV. Thus, the formula is CCl_4 . The sum of the four (-1) oxidation numbers for the chlorine atoms and the one ($+4$) oxidation number for the carbon atom is zero, the charge on the compound.



Snapshot Review

- Oxidation number is a periodic property. For example, for most elements the maximum oxidation number is equal to the classical group number, and the minimum oxidation number for nonmetals other than hydrogen is the group number minus 8.

- A. What is the maximum oxidation number of (a) S? (b) P? (c) Mg?
- B. What is the minimum oxidation number of (a) Kr? (b) Cr? (c) As?

16.4 Balancing Oxidation-Reduction Equations

When an atom increases its oxidation number during a reaction, it is said to have been oxidized. When an atom decreases its oxidation number during a reaction, it is said to have been reduced. **Oxidation** is an increase in oxidation number as a result of the loss of electrons or of “control” of electrons. **Reduction** is

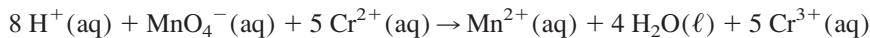
16.4 ■ Balancing Oxidation-Reduction Equations**441**

A memory device:

Loss of Electrons is**Oxidation.****Gain of Electrons is****Reduction****LEO the lion says GER.**

a decrease in oxidation number due to the gain of electrons or of “control” of electrons. A chemical species serves as an **oxidizing agent** by causing the oxidation of another species. When it acts as an oxidizing agent, one (or more) of its elements is reduced. A chemical species serves as a **reducing agent** by causing the reduction of another species. When it acts as a reducing agent, one (or more) of its elements is oxidized.

A reaction in which an oxidation and a reduction occur is called an **oxidation-reduction reaction**, or **redox reaction** for short. Every redox reaction must have an oxidation and a reduction. There can never be one of these processes without the other [although they may occur at different places (Chapter 17)]. A gain of electrons is not possible without a loss of electrons, and vice versa. For example, the reaction of MnO_4^- with Cr^{2+} is an oxidation-reduction reaction:



The chromium is oxidized, and the manganese is reduced. The chromium(II) ion is the reducing agent, and the permanganate ion is the oxidizing agent.

EXAMPLE 16.11

A towel used to dry hands can be classified as a drying agent, and the hands can be classified as wetting agents.

- What happens to the drying agent in the process of drying the hands? What happens to the wetting agent? What happens to the water?
- When an oxidation-reduction reaction occurs, what happens to the reducing agent, the oxidizing agent, and the electrons?

Solution

- The towel is the drying agent; it gets wet. The hands are the wetting agents; they get dry. The water is transferred from the wetting agent to the drying agent.
- The electrons in an oxidation-reduction reaction act like the water in part (a): They are transferred from the reducing agent to the oxidizing agent. The reducing agent is oxidized; the oxidizing agent is reduced.

The active metals listed in Table 8.2 are good reducing agents; the more active, the better the reducing agent. Similarly, F_2 is a very powerful oxidizing agent, and O_2 and Cl_2 are slightly lower in oxidizing ability. Quantitative measures of oxidizing and reducing power will be presented in Chapter 17.

EXAMPLE 16.12

With the knowledge that good oxidizing agents react with good reducing agents, explain why each of the following compounds does not exist: (a) FeCrO_4 . (b) CoI_3 .

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CHAPTER 16 ■ Oxidation Numbers

Solution

- (a) Fe^{2+} is easily oxidized to Fe^{3+} , and CrO_4^{2-} is a good oxidizing agent. The ions would react with each other to produce other substances.
- (b) Co^{3+} is a very good oxidizing agent, and I^- is a good reducing agent. These ions would also react with each other.

Practice Problem 16.12 Explain why CuI_2 cannot be made, but CuCl_2 is a stable compound.

We have already balanced a number of simple oxidation-reduction equations, starting in Chapter 8. Most combination and decomposition reactions and all single substitution and combustion reactions are oxidation-reduction reactions. However, many oxidation-reduction reactions are much more complicated than the ones we have already considered, and we must use a systematic method for balancing equations for them. Unfortunately, many different systematic methods are used, and each chemistry instructor seems to have his or her own favorite method. Most instructors will accept any valid method that a student understands, however. The method outlined here is a standard method that should be acceptable.

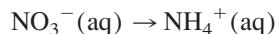
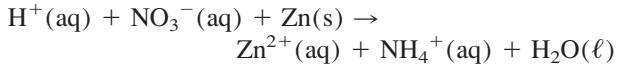
All methods of balancing oxidation-reduction equations are based on the overall gain of oxidation numbers in a reaction being the same as the overall loss of oxidation numbers in the reaction (because the same number of electrons must be gained as lost).

The first step in any method of balancing oxidation-reduction equations is to identify the element that is oxidized and the one that is reduced. Because the change in oxidation number is equal to a change in the number of electrons “controlled,” and the electrons must be “controlled” by some atom, the total gain in oxidation number is equal to the total loss in oxidation number. The oxidation half of a reaction may be written in one equation, and the reduction half in another. Neither **half-reaction** can be carried out without the other, but they can be done in different locations if they are connected in such a way that a complete electrical circuit is made (Chapter 17). The **half-reaction method** is illustrated by balancing the equation for the reaction of zinc metal with dilute nitric acid to produce ammonium ion, zinc ion, and water:

Steps

First, we consider the reduction half-reaction:

Step 1: Determine the oxidation number of each element in the reaction. Identify the element that is reduced, and balance the number of atoms of that element, if necessary. In this example, the nitrogen atom is reduced from an oxidation state of +5 to -3. After the element whose oxidation number changes has been balanced, no element will change oxidation number in steps 2 through 4.

Example

16.4 ■ Balancing Oxidation-Reduction Equations**443**

Step 2: Balance any other element present other than oxygen, hydrogen, or the element whose oxidation number changed.

Step 3: Balance the oxygen atoms by adding water to the side deficient in oxygen:

Step 4: Balance the hydrogen atoms by adding hydrogen ions (H^+) to the side deficient in hydrogen:

Step 5: Balance the charge by adding electrons (e^-) to the more positive, or less negative, side:

Step 6: Check to see that

- The net charge on the two sides of the equation is the same.
- The atoms of each element are balanced.
- The number of electrons is equal to the *total* change in oxidation state.

Repeat steps 1 through 6 to balance the oxidation half-reaction.

Step 1: Balance the atoms of the element that is oxidized:

Steps 2–4:

Step 5: Balance the charge:

Step 6: Check.

Adjust the coefficients in the balanced oxidation half-reaction and balanced reduction half-reaction equations to make each have the same number of electrons, and then combine them.

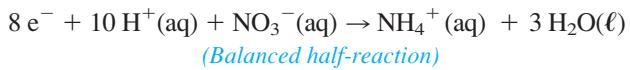
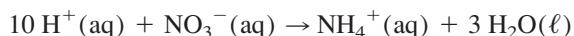
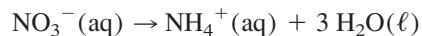
Step 7: The oxidation half-reaction for this example has two electrons involved, and the reduction half-reaction has 8 electrons involved. To make the numbers of electrons equal, we multiply the former by 4.

Adding the two half-reactions gives

Step 8: Eliminate any substances that appear unchanged on both sides of the combined equation.

Step 9: Check the numbers of atoms and the net charge of the complete equation.

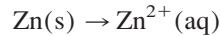
This example has no other elements besides those listed.



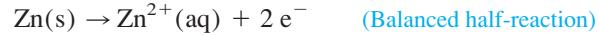
(a) The net charge on each side is 1+.

(b) 10 H, 1 N, 3 O on each side

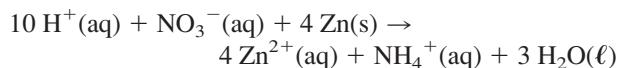
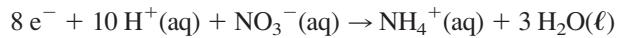
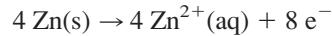
(c) Nitrogen in the +5 oxidation state going to the -3 oxidation state is a change of 8 oxidation numbers, equal to the number of electrons.



No other elements need to be balanced.



The net charge, numbers of atoms, and change in oxidation number are all correct.

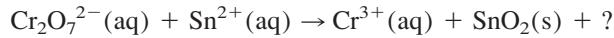


No duplication appears in this example.

9+ net charge on each side of the equation, 10 H, 1 N, 3 O, 4 Zn.

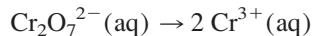
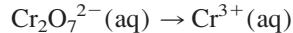
EXAMPLE 16.13

Balance the equation for the reaction of dichromate ion with tin(II) ion to produce chromium(III) ion, $SnO_2(s)$, and other products.

Solution

The reduction half-reaction is presented first:

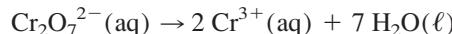
Step 1:



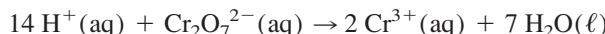
(The chromium is balanced first.)

Step 2: No change.

Step 3:



Step 4:



Step 5:



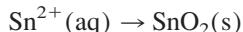
Step 6: (a) Net charge 6+ on each side

(b) 14 H, 7 O, 2 Cr on each side

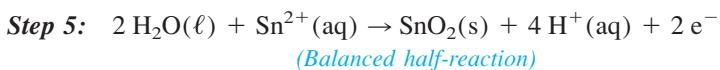
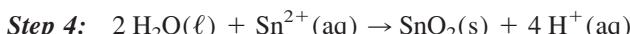
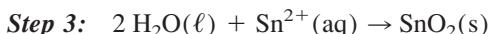
(c) Oxidation number change for *two atoms* from +6 to +3 is equal to the number of electrons.

The oxidation half-reaction is then worked out:

Step 1:

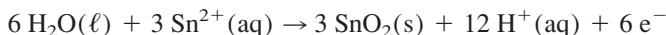


Step 2: No change.

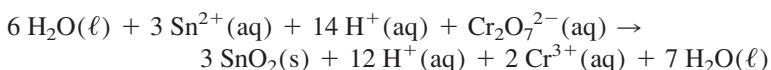


Step 6: Everything checks.

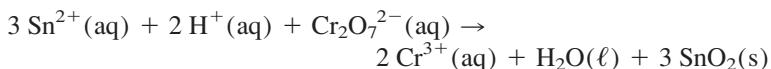
Step 7: Make the number of electrons in each the same by multiplying the oxidation half-reaction by 3:



Combine the two half-reactions,



Step 8: Eliminating 12 H⁺ and 6 H₂O from both sides yields the complete balanced equation:



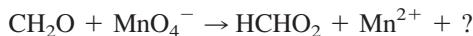
Step 9: 6+ net charge on each side, 3 Sn, 2 H, 2 Cr, 7 O

Practice Problem 16.13 Complete and balance the equation for the reaction of the permanganate ion with chloride ion in acid solution to give manganese(II) ion and perchlorate ion, as well as other products:



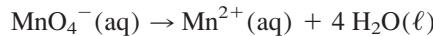
16.4 ■ Balancing Oxidation-Reduction Equations**445****EXAMPLE 16.14**

Complete and balance the equation for the oxidation of formaldehyde to formic acid by MnO_4^- in acid solution to give manganese(II) ion (Mn^{2+}):

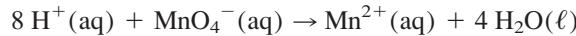
**Solution**

Step 2: No change

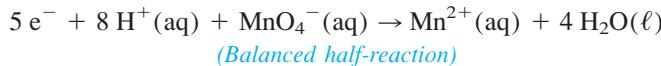
Step 3: Balance the oxygen atoms:



Step 4: Balance the hydrogen atoms:



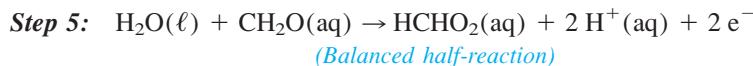
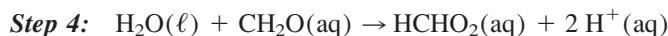
Step 5: Balance the charge:



Step 6: Everything checks.



Step 2: No change.



Step 6: Everything checks.

Step 7: Multiply the oxidation half-reaction by 5 to get 10 electrons:



Multiply the reduction half-reaction by 2 to get 10 electrons:



Combine the two equations, ignoring the electrons, which must cancel:



Step 8: Eliminating 10 of the hydrogen ions and five water molecules from each side yields

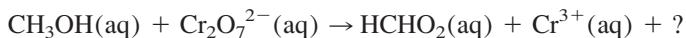


Step 9: Everything checks.

Practice Problem 16.14 Complete and balance the equation for the reaction of methyl alcohol (CH_3OH) with dichromate ion in acid solution

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to give formic acid (HCHO_2) and chromium(III) ion, as well as other products.



Sometimes, a single reactant can act as both oxidizing agent and reducing agent in the same reaction. Such a reactant is said to undergo autooxidation-reduction, or **disproportionation**.

EXAMPLE 16.15

When Cl_2 gas disproportionates in concentrated NaOH solution, NaClO_3 is produced. What other chlorine-containing compound is produced? Write a balanced chemical equation for the reaction.

Solution

Because the chlorine is oxidized to +5 in the sodium chlorate, it must be reduced to produce the other compound. The only oxidation number lower than zero for chlorine in Cl_2 is -1, and the compound is NaCl. The balanced equation is



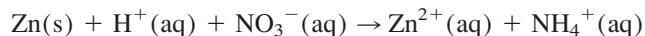
Practice Problem 16.15 If exposed to heat or light, or even left standing, H_2O_2 decomposes. What is the oxidizing agent, and what is the reducing agent? Write a balanced equation for the reaction.

**Snapshot Review**

ChemSkill Builder
10.4, 10.5, 10.6

- Be sure to balance the number of atoms of element oxidized or reduced (in step 1) and balance any “other” elements (step 2) in the few cases where necessary.
- Do not add any species that changes the oxidation state of any element after step 1.

- A. Calculate the change in oxidation number in a species that goes from (a) -1 to +5, (b) -1 to +1.
- B. Complete and balance the following equation:

**Key Terms**

Key terms are defined in the Glossary.

“control” of shared electrons (16.1)
disproportionation (16.4)
half-reaction (16.4)
half-reaction method (16.4)
oxidation (16.4)

oxidation number (16.1)
oxidation-reduction reaction (16.4)
oxidation state (16.1)
oxidizing agent (16.4)

redox reaction (16.4)
reducing agent (16.4)
reduction (16.4)
Stock system (16.2)

■ Answers to Snapshot Reviews

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Symbols/Abbreviations e^- (electron) (16.4)**Summary**

Oxidation numbers (also called oxidation states) are used as a sort of bookkeeping method for keeping track of the electrons in polyatomic ions or compounds that have covalent bonds. (For monatomic ions, the charge on the ions works just as well.) Oxidation number is defined as the number of electrons in a free atom minus the number “controlled” by that atom in the compound. The “control” of electrons in a covalent bond is assigned to the more electronegative atom of the bond. Eight simple rules can be used to determine the oxidation number of an element from the formula of its compound or ion (Section 16.1).

Oxidation numbers are used in the Stock system for naming compounds. Positive oxidation numbers are denoted as Roman numerals in parentheses in the *names* of the compounds; the numbers of atoms or ions can be deduced from the oxidation numbers. (In contrast, the subscripts in formulas give the numbers of atoms or ions, from which the oxidation numbers may be deduced.) (Section 16.2).

The oxidation numbers of the elements are periodic properties, and common oxidation numbers can often be

deduced from the classical periodic group number of an element. The possible oxidation numbers can be used to write possible formulas for compounds (Section 16.3).

Oxidation is defined as a gain in oxidation number, caused by a loss of electrons or of “control” of electrons. Reduction is defined as a loss in oxidation number, caused by a gain of electrons or of “control” of electrons. Complicated oxidation-reduction equations must be balanced according to some systematic method because they are too complex to be balanced by inspection. Although neither can take place alone, the oxidation and the reduction can occur in different locations if suitable electrical connections are provided. (Chapter 17) In the half-reaction method, the equation for the half-reaction involving oxidation and that for the half-reaction involving reduction are balanced separately; then the two are combined. Each may be multiplied by a small integer if necessary to balance the numbers of electrons involved.

Some reactants can be both oxidized and reduced in the same reaction. They are said to undergo disproportionation (Section 16.4).

Items for Special Attention

- Shared electrons are counted for each of the bonded atoms when writing electron dot diagrams, but only for the more electronegative atom when determining oxidation numbers.
- Oxidation numbers are usually but not always integral.
- The oxidation numbers predicted by Figure 16.2 will not be correct for all elements in all compounds.
- Be sure to start the half-reaction method by balancing the number of atoms of the element oxidized or reduced (before proceeding to step 2). The other elements involved cannot change oxidation number after the element oxidized or reduced has been balanced (in step 1). For example, do not add H₂ to balance hydrogen atoms in step 4.
- Do not confuse oxidation numbers with charges when balancing oxidation-reduction equations. Use Roman numerals for positive oxidation numbers and Arabic numbers for charges. (To denote negative oxidation numbers, use Arabic numerals below the formula and circle them; do not get them mixed up with charges. The Romans did not have negative numbers.)
- Balanced equations for half-reactions always include electrons; balanced equations for overall reactions never include electrons.
- Always check a completed equation for either a half-reaction or an overall reaction to make sure that each element is balanced and also that the net charge is balanced.

Answers to Snapshot Reviews16.1 A. (a) -1 (b) +1 (c) +4 (d) $-\frac{1}{3}$ B. XY₃16.2 A. (a) Vanadium(II) chloride (b) Manganese(IV) oxide
(c) Iron(III) oxideB. (a) Cu₂O (b) CuO

16.3 A. (a) +6 (b) +5 (c) +2

B. (a) 0 (b) 0 (c) -3

16.4 A. (a) $+5 - (-1) = +6$ (b) $+1 - (-1) = +2$
B. 4 Zn(s) + 10 H⁺(aq) + NO₃⁻(aq) \rightarrow
4 Zn²⁺(aq) + NH₄⁺(aq) + 3 H₂O(l)

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CHAPTER 16 ■ Oxidation Numbers

Self-Tutorial Problems

- 16.1** Write the formula for:
- An ionic compound whose cation (M) has a 3+ charge and whose anion (A) has a 1- charge
 - A compound with element Y in a +3 oxidation state and element Z in a -1 oxidation state
- 16.2** Explain why equations for half-reactions *must* include at least one ionic species.
- 16.3** What is the *sum* of the oxidation numbers of all the atoms in each of the following?
- $\text{Si}_6\text{O}_{18}^{12-}$
 - UO_2^{2+}
 - $\text{P}_2\text{O}_7^{4-}$
- 16.4** What is the oxidation number of the element in each of the following ions? (a) Co^{3+} (b) O_2^{2-} (c) Fe^{2+}
- 16.5** Determine the oxidation number of each atom in (a) CuS and (b) Cu_2S . (c) Name each compound.
- 16.6** What is the oxidation number of silver on each side of the following equation?
- $$4 \text{Ag(s)} + \text{O}_2\text{(g)} \xrightarrow{\text{Heat}} 2 \text{Ag}_2\text{O(s)}$$
- 16.7** Determine the oxidation number of each atom in (a) NH_4Cl and (b) SF_4 .
- 16.8** What is the *sum* of the oxidation numbers of all the atoms in each of the following?
- CNO^-
 - NH_3OH^+
 - Mn_3O_4
 - HPO_4^{2-}

Problems**16.1 Assigning Oxidation Numbers**

- 16.15** Draw an electron dot diagram for PSCl_3 , in which the phosphorus is the central atom. Determine the oxidation number of each element, and compare with the oxidation numbers in POCl_3 .
- 16.16** Draw an electron dot diagram for NCS^- . Determine the oxidation number of each element, and compare with the oxidation numbers of carbon and oxygen in carbon dioxide.
- 16.17** Determine the oxidation number of sulfur in each of the following:
- Na_2SO_3
 - SO_3
 - SO_3^{2-}
 - $\text{S}_2\text{O}_3^{2-}$
 - H_2SO_3
- 16.18** Determine the oxidation number of chlorine in each of the following compounds:
- ClO_2
 - Cl_2O
 - ClO
 - Cl_2O_7
 - Cl_2O_5
 - ClO_3
 - ICl_3

- 16.9** On which side of the equation for an oxidation half-reaction do the electrons appear?
- 16.10** Substance A is reduced two oxidation numbers and substance B is oxidized six oxidation numbers in their redox reaction.
- How many electrons are involved in the reduction?
 - How many electrons are involved in the oxidation?
 - What is the mole ratio of A to B in the overall equation?
- 16.11** Why isn't O_2 used instead of H_2O to balance oxygen atoms in step 3 of the half-reaction method?
- 16.12** How many electrons should be added to an equation for a half-reaction in which the left side has a net charge of 4+ and the right side has a net charge of 2-? To which side should they be added?
- 16.13** Determine the oxidation number of chlorine in each of the following ions:
- ClO^-
 - ClO_2^-
 - ClO_3^-
 - ClO_4^-
- 16.14** (a) Which of the types of reactions discussed in Chapter 8 is generally *not* an oxidation-reduction equation?
 (b) Do *all* oxidation-reduction equations have to be balanced by a systematic method?

- 16.19** Determine the oxidation number of bromine in each of the following:
- BrO_2^-
 - BrO^-
 - HBrO_2
 - NaBrO_3
 - NaBr
 - BrO_3^-
- 16.20** Determine the oxidation number of carbon in each of the following:
- CO_2
 - CH_2O
 - CO
 - CH_3OH
 - CO_3^{2-}
 - HCHO_2
- 16.21** What is the oxidation number of chromium in (a) CrO_4^{2-} and (b) $\text{Cr}_2\text{O}_7^{2-}$?
- 16.22** What is the oxidation number of manganese in (a) MnO_4^- , (b) MnO_4^{2-} , (c) Mn_2O_3 , and (d) Mn_3O_4 ?
- 16.23** Find the oxidation number of hydrogen in each of the following compounds:
- LiH
 - HCl
 - BeH_2
 - LiAlH_4

■ Problems

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- 16.24** Determine the oxidation number of carbon in each of the following compounds:

(a) CCl_4 (b) CHCl_3 (c) CH_2Cl_2
 (d) CH_3Cl (e) CH_4

- 16.25** What is the oxidation number of nitrogen in each of the following substances?

(a) NO (b) N_2O_3 (c) NH_2OH
 (d) N_2O_4 (e) N_2O_5 (f) NO_2
 (g) NH_3 (h) N_2H_4 (i) N_2O
 (j) HN_3 (k) N_2

- 16.26** What is the oxidation number of iron in each of the following compounds?

(a) FeO (b) Fe_2O_3 (c) Fe_3O_4

- 16.27** Which familiar metal forms a metal-metal bond in one of its oxidation states?

- 16.28** Determine the oxidation number of silicon in (a) SiCl_4 , (b) SiO_2 , (c) $\text{Ca}_6\text{Si}_6\text{O}_{18}$, and (d) $\text{Si}_4\text{O}_9^{2-}$.

- 16.29** What is the oxidation number of phosphorus in (a) hypophosphorous acid, (b) phosphoric acid, and (c) phosphorous acid?

- 16.30** Carbon in the +2 oxidation state is not too common, but it does exist in some familiar species. In which ones of the following species does carbon exist in the +2 oxidation state?

(a) CN^- (b) CO (c) CHCl_3
 (d) CH_2O (e) CH_3OH (f) CH_2Cl_2

- 16.31** In the reaction of SO_3^{2-} with an oxygen atom to form SO_4^{2-} , explain why the sulfur is oxidized. Does the sulfur atom actually lose any electrons?

- 16.32** Determine the oxidation number of each element in each substance in the following reactions:

(a) $2 \text{CrO}_4^{2-}(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\ell)$
 (b) $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$
 (c) $\text{MgO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{MgCO}_3(\text{s})$

- 16.33** What is the oxidation number of nitrogen in (a) nitrous acid and (b) the nitrite ion?

16.2 Using Oxidation Numbers in Naming Compounds

- 16.34** Name (a) PbO_2 , (b) BaO_2 , and (c) KO_2 .
16.35 Name (a) $\text{Al}_2(\text{HPO}_4)_3$, (b) $\text{Hg}_2(\text{NO}_3)_2$, and (c) $\text{Sn}(\text{NO}_3)_2$.
16.36 Write the formulas for (a) mercury(I) cyanide, (b) gold(III) oxide, and (c) gold(I) sulfide.
16.37 Explain the reason that we could use charges instead of oxidation numbers for naming monatomic cations in Chapter 6.

- 16.38** In naming metals with the classical system, does the *-ous* or the *-ic* suffix signify the higher oxidation state?

16.3 Periodic Variation of Oxidation Numbers

- 16.39** What are the maximum and minimum oxidation numbers of hydrogen?
- 16.40** In which oxoanions of Table 6.3 do elements have the highest oxidation numbers?
- 16.41** What is the maximum oxidation number of fluorine?
- 16.42** For each of the elements combined with oxygen in Table 6.3, in which ion does the element have the lowest oxidation number?
- 16.43** Consider the bromide ion and the oxoanions of bromine. Which suffix is used for the ion in which bromine has the lowest oxidation number, and which is used for the ion in which bromine has the highest?
- 16.44** Which suffix for an oxoacid (*-ous* or *-ic*) signifies the higher oxidation number for the central atom?
- 16.45** The maximum oxidation number for any element is +8, as for osmium in OsO_4 ; the maximum charge on a monatomic cation is 4+, as for Ce^{4+} . Explain the difference.
- 16.46** What are the maximum and minimum oxidation numbers in any of their compounds for (a) sulfur, (b) fluorine, (c) phosphorus, and (d) lead?
- 16.47** What are the maximum and minimum oxidation numbers in any of their compounds for (a) titanium, (b) cadmium, (c) silver, and (d) xenon?
- 16.48** What is the minimum oxidation number of (a) carbon, (b) neon, and (c) sodium?
- 16.49** What is the most probable positive oxidation number for arsenic other than +5? Write the formula for an arsenic-containing acid as an example.
- 16.50** What is (are) the most probable positive oxidation number(s) for tin?
- 16.51** What are the formulas for four compounds of fluorine and iodine?
- 16.52** What can be said about the oxidation numbers of the group VIA elements in oxoanions whose names have the suffix *-ate*?
- 16.53** In what ways are group IB elements and group VIII elements exceptions to the rule that the maximum oxidation number is usually equal to the group number?
- 16.54** In what ways are the noble gases and fluorine exceptions to the rule that the maximum oxidation number is usually equal to the group number?
- 16.55** Predict the formulas for three compounds of fluorine with sulfur.
- 16.56** What is the minimum oxidation number of (a) arsenic, (b) iron, and (c) hydrogen?

450**16.4 Balancing Oxidation-Reduction Equations**

16.57 What is the oxidizing agent, the reducing agent, the element oxidized, and the element reduced in each of the following equations? Which equation is easier to work with?

- $16 \text{ HCl(aq)} + 2 \text{ KMnO}_4(\text{aq}) \rightarrow 5 \text{ Cl}_2(\text{aq}) + 2 \text{ MnCl}_2(\text{aq}) + 2 \text{ KCl(aq)} + 8 \text{ H}_2\text{O}(\ell)$
- $16 \text{ H}^+(\text{aq}) + 2 \text{ MnO}_4^-(\text{aq}) + 10 \text{ Cl}^-(\text{aq}) \rightarrow 5 \text{ Cl}_2(\text{aq}) + 2 \text{ Mn}^{2+}(\text{aq}) + 8 \text{ H}_2\text{O}(\ell)$

16.58 In Problem 16.57, part (a), how many chlorine atoms are oxidized and how many retain their original oxidation state? In Problem 16.57, part (b)?

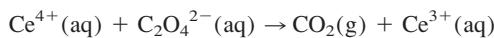
16.59 What is the oxidizing agent, the reducing agent, the element oxidized, and the element reduced in each of the following equations?

- $\text{Cu(s)} + \text{CuCl}_2(\text{aq}) \rightarrow 2 \text{ CuCl(s)}$
- $\text{Cd(s)} + \text{CuCl}_2(\text{s}) \xrightarrow{\text{Heat}} \text{CdCl}_2(\text{s}) + \text{Cu(s)}$
- $4 \text{ KI(aq)} + 2 \text{ CuCl}_2(\text{aq}) \rightarrow 2 \text{ CuI(s)} + \text{I}_2(\text{aq}) + 4 \text{ KCl(aq)}$
- $2 \text{ H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ H}_2\text{O}(\ell)$

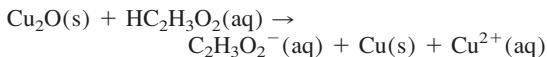
16.60 What is the oxidizing agent, the reducing agent, the element oxidized, and the element reduced in each of the following equations?

- $4 \text{ H}^+(\text{aq}) + 2 \text{ NO}_3^-(\text{aq}) + \text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{ NO}_2(\text{g}) + 2 \text{ H}_2\text{O}(\ell)$
- $\text{Cu}_2\text{O(s)} + 2 \text{ H}^+(\text{aq}) \rightarrow \text{Cu(s)} + \text{Cu}^{2+}(\text{aq}) + \text{H}_2\text{O}(\ell)$
- $\text{Zn(s)} + \text{CuCl}_2(\text{s}) \xrightarrow{\text{Heat}} \text{ZnCl}_2(\text{s}) + \text{Cu(s)}$

16.61 Balance the following oxidation-reduction equation:

**General Problems**

16.67 Complete and balance:

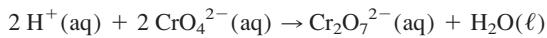


16.68 IF_7 is a well-known compound, but IBr_7 does not exist. Explain why not.

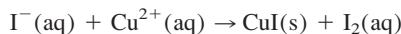
16.69 Consider the names of the oxoanions in Table 6.3. The ending *-ate* was used for ions with “more oxygen.” How could that rule be restated in terms of oxidation numbers?

16.70 What is the oxidation number of hydrogen in (a) hydrogen ion and (b) hydride ion?

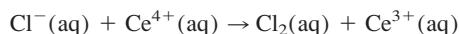
16.71 Calculate the change in oxidation state of chromium during the following reaction:

**CHAPTER 16 ■ Oxidation Numbers**

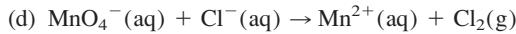
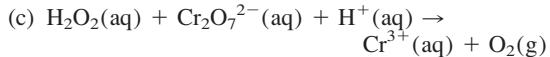
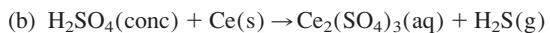
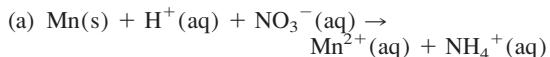
16.62 Balance the following oxidation-reduction equation:



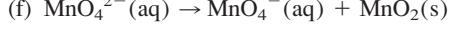
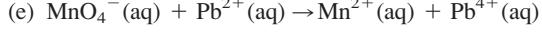
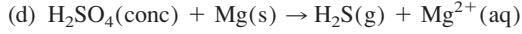
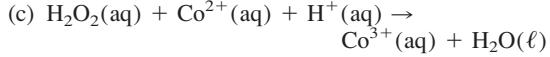
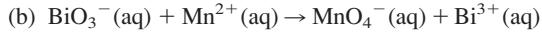
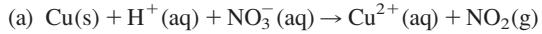
16.63 Balance the following oxidation-reduction equation:



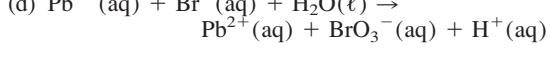
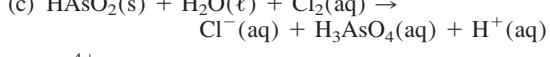
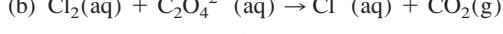
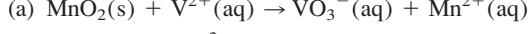
16.64 Complete and balance each of the following oxidation-reduction equations:



16.65 Complete and balance each of the following oxidation-reduction reactions:



16.66 Complete and balance each of the following equations:



16.72 Name the following compounds:



16.73 Explain why hydrogen peroxide can act sometimes as an oxidizing agent and sometimes as a reducing agent.

16.74 Draw an electron dot diagram for CN^- . Determine the oxidation number of each element, and compare with the oxidation numbers of carbon and oxygen in carbon monoxide, which has the same number of electrons. Why is there a difference?

16.75 Complete and balance an equation for the reaction in which cyanate ion (CNO^-) is oxidized to CO_2 and NO_3^- by MnO_4^- , in which two elements in the same chemical species are oxidized. (Hint: The carbon to nitrogen ratio is set by the formula of CNO^- .)

■ General Problems

16.76 Give an example of each type of compound referred to in Problem 16.1.

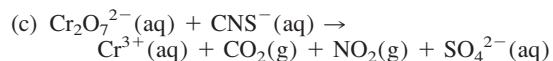
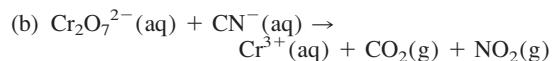
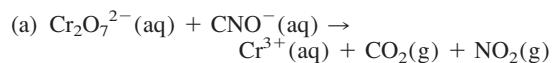
16.77 Based on equations in this chapter, select the good oxidizing agents and the good reducing agents from the following list:



16.78 Determine the oxidation number of the oxygen in each of the following compounds:

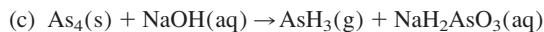
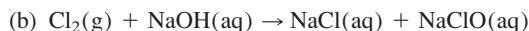
- (a) PbO_2 (b) CsO_2 (c) BaO_2

16.79 Complete and balance each of the following equations, in which more than one element is oxidized.

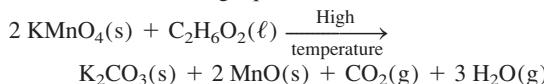


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16.80 Complete and balance each of the following equations:



16.81 Consider the following equation:



(a) What is the change in oxidation number for manganese?

(b) What is (are) the change(s) in oxidation number for carbon?

(c) Why wasn't a net ionic equation written for this reaction?

16.82 The compound TiCl_4 is mainly covalent. Name it in two ways.

17

Electrochemistry

- 17.1 Voltaic Cells
- 17.2 Standard Cell Potentials
- 17.3 The Nernst Equation
- 17.4 Electrolysis Cells
- 17.5 Electrolysis Calculations



Daniell cell

Review Clues

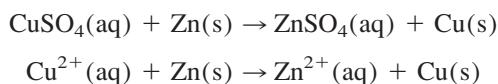
- Chapter 17** Section 16.4
Section 17.1 Section 5.2
Section 17.2 Table 8.2
Section 17.3 Appendix A1
Section 17.4 Sections 5.2, 8.3
Section 17.5 Sections 10.1, 10.3

Objectives

- 17.1** To use oxidation and reduction half-reactions at different places, suitably connected, to produce electricity from chemical reactions
- 17.2** To quantify the reaction tendencies of oxidizing and reducing agents
- 17.3** To determine the effect of concentration on potential
- 17.4** To use electricity to produce redox reactions
- 17.5** To calculate quantities of chemicals involved in electrolysis reactions from the quantity of charge that passes, or vice versa

Electrical energy can produce chemical reactions, and chemical reactions can produce electrical energy, depending on the experiment. The term **electrochemistry** includes both of these processes. Each occurs in a **cell**.

We learned in Chapter 16 that oxidation-reduction reactions involve the transfer of electrons from the reducing agent to the oxidizing agent. For example, zinc metal reacts with copper(II) ions to produce copper metal and zinc ions:

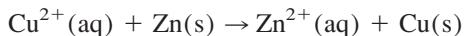


In voltaic cells, it is possible to carry out the oxidation and reduction half-reactions in different places when suitable provision is made for transporting the electrons over a wire from one half-reaction to the other and to transport ions from each half-reaction to the other in order to preserve electrical neutrality. The chemical reaction produces an electric current in the process. Voltaic cells, also called galvanic cells, are introduced in Section 17.1. The tendency for oxidizing agents and reducing agents to react with each other is measured by their standard cell potentials, presented in Section 17.2. In Section 17.3, the Nernst equation is introduced to allow calculation of potentials of cells that are not in their standard states.

In electrolysis cells, chemical reactions are produced by electric currents. (Section 17.4) Quantitative aspects of electrolysis reactions are presented in Section 17.5.

17.1 Voltaic Cells

What do we expect to happen if we place a bar of zinc metal in a solution of copper(II) sulfate? We get a reaction according to the net ionic equation (Chapter 9):

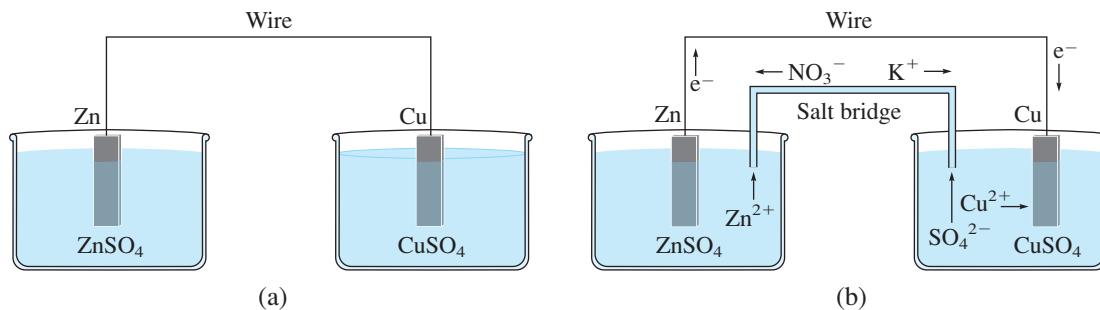


Now, suppose we put a zinc bar in a solution of zinc sulfate and a copper bar in a solution of copper(II) sulfate and connect the two metal bars with a wire for electrons to pass through. The bars serve as electrodes (see Section 5.2). (Figure 17.1a) Do we expect a reaction? Zinc atoms might lose electrons to become zinc ions in solution and the electrons could travel through the wire to add to copper(II) ions in the solution next to the copper bar. These ions would then become copper atoms deposited on the bar. Only one thing prevents this reaction from taking place: As soon as a relatively few electrons travel to the copper electrode, that solution becomes negatively charged and the zinc solution becomes positively charged. (There are fewer Cu^{2+} ions than SO_4^{2-} ions on one side, and more Zn^{2+} ions than SO_4^{2-} on the other side.) Because of the attraction of opposite charges and the repulsion of like charges, electrons will not flow from a positive environment to a negative one.

If we add a **salt bridge** containing a solution of ions to connect the two sides, the zinc ions and positive ions from the salt bridge can flow toward the copper side, and sulfate ions and negative ions from the salt bridge can flow toward the zinc side. We have completed an electric **circuit**. The buildup of charges in the two solutions is avoided, and the reaction can proceed (Figure 17.1b)

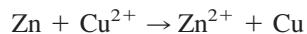
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CHAPTER 17 ■ Electrochemistry

**Figure 17.1** Construction of a Daniell Cell

(a) Despite a wire to transport electrons from the zinc electrode to the copper electrode, no reaction takes place. There isn't a complete circuit. (b) The addition of a salt bridge enables the ions to carry charge from one solution to the other, completing the circuit and producing an electric current.

Overall:



and electricity is produced. This system is an example of a **voltaic cell**, or **galvanic cell**. This particular cell is called a **Daniell cell** after its inventor, John Frederic Daniell (1790–1845). The flow of electrons through the wire can be made to do useful work, like lighting up a small bulb. Note several things about this system:

1. Both oxidation and reduction are taking place at the same time, though not at the same place.
2. The same overall reaction is taking place as if we had placed the zinc bar in the copper(II) ion solution.
3. The chemical energy of the reaction can be transformed into electric energy and then into light (or another form of energy).

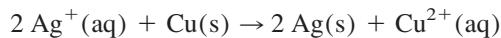
This is the principle of the voltaic cell, in which an oxidation-reduction reaction is used to produce electricity.

We are very familiar with cells, such as the dry cell and the alkaline cell (long-lasting substitute for the dry cell). Combinations of two or more cells are called **batteries**.

EXAMPLE 17.1

Write the net ionic equation for the reaction that will occur when a silver bar in a solution of AgNO_3 is suitably connected to a copper bar in a solution of CuSO_4 .

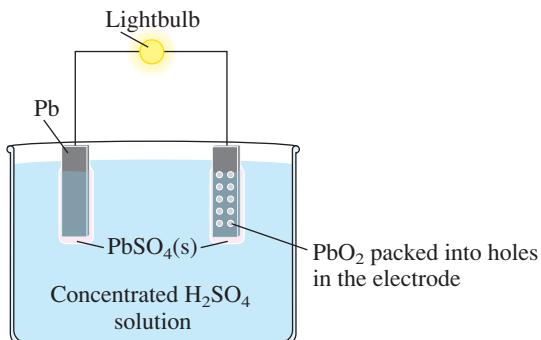
Solution



Practice Problem 17.1 Draw a figure like that of Figure 17.1b for the cell in Example 17.1, and put labeled arrows on the diagram showing the direction of spontaneous electron flow, positive ion flow, and negative ion flow.

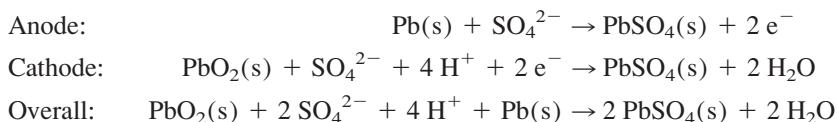
17.1 ■ Voltaic Cells**455****Figure 17.2** Lead Storage Cell

Electrons flow from the lead electrode to the lead(IV) oxide electrode.



Why do we use a salt bridge to connect the two solutions, instead of merely placing both electrodes into the same solution, containing both types of ions? If the copper(II) ions were in the solution with the zinc electrode, the two would simply react at the surface of that electrode; there would be no need for electrons to travel through the wire to get the redox reaction to proceed.

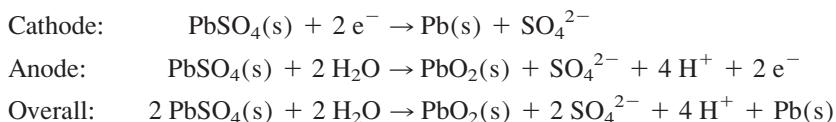
The **lead storage cell**, six of which constitute the lead storage battery, is familiar for its use in most automobiles. It will be described in some detail because it has several features that are different from those of the Daniell cell, described earlier. The lead storage cell (Figure 17.2) consists of a lead electrode coated with a paste of lead(II) sulfate and another electrode which has lead(IV) oxide as the active oxidizing agent, also coated with lead(II) sulfate. The electrolyte is concentrated sulfuric acid, in which PbSO₄ is insoluble. Both electrodes are situated in the same solution. The half-reactions are



The SO₄²⁻ ions and the H⁺ ions in these equations are in the concentrated sulfuric acid solution. As the discharge reaction proceeds, sulfuric acid (2 SO₄²⁻ + 4 H⁺) is used up and water is produced. The solution becomes diluted, and the state of the charge of the cell can be measured by measuring the density of the solution. (If the battery is not permanently sealed, a mechanic at a gas station can check the charge.)

It is possible to have both electrodes in the same solution because both the oxidizing agent (PbO₂) and the reducing agent (Pb), as well as their oxidation and reduction product (PbSO₄), are solids. They cannot migrate to the opposite electrode and cause a direct (as opposed to an electrochemical) reaction.

It is possible to recharge this cell by passing electricity from an external source through it in the opposite direction from the way the electricity flows when it is discharging. The auto battery is continually being recharged by electricity from the alternator, but every once in a while a more extensive recharge at the gas station may be required. Recharge proceeds as



The Daniell cell cannot be recharged in this manner. If we try it, copper(II) ions will migrate to the zinc electrode solution, where they will react directly with the zinc and produce a copper-plated electrode. Then, the cell will not function.



Snapshot Review



ChemSkill Builder 22.1,
22.2

- Reactants that react vigorously when in direct contact with each other also do so vigorously when suitably connected electrochemically, very often undergoing the same reaction.
- A complete circuit is necessary for a voltaic cell to operate.

- A. Write the equation for the reaction of Ni^{2+} with Ag^+ (a) directly and (b) in a voltaic cell.
- B. Explain the special usefulness of net ionic equations in this section.

17.2 Standard Cell Potentials

Learning a few electrical variables and their units will enable us to do electrochemical calculations, both for voltaic cells and for electrolysis cells. These are presented in Table 17.1. In this section, **potential**, also called **voltage**, is the important unit. Potential is the tendency for an electrochemical half-reaction or reaction to proceed. In this section, we will be using the **standard half-cell potential**, symbolized ϵ° . Standard half-cell potentials can be combined into **standard cell potentials**, also symbolized ϵ° . The superscript \circ denotes the **standard state of the system**, which means that the following conditions exist in the cell:

1. Any solids and liquids are pure substances.
2. Any solutes are 1.00 M.
3. Any gases are at 1.00 atm pressure.

Once we assign an ϵ° value to each half-cell, we can combine any two of them to calculate the potential of that cell. However, we cannot measure the potential of only half a cell because we cannot have either an oxidation or a

Table 17.1 Electrical Variables and Units*

Variable	Symbol	Unit	Abbreviation	Equivalencies and Relationship(s)
Potential	ϵ	Volt	V	
Charge	q	Coulomb	C	
		Charge on electron	e	$1 e = 1.60 \times 10^{-19} \text{ C}$
		Faraday	F	$1 \text{ F} = 1 \text{ mol } e^- = 96,500 \text{ C}$
Current	I	Ampere	A	$I = q/t$ (t = time)
Resistance	R	Ohm	Ω	$\epsilon = IR$ (Ohm's law)
Power	P	Watt	W	$P = \epsilon I$
Energy	E	Joule	J	$E = Pt$ (power \times time)

*The first three entries (ϵ , q , and I) are the important ones for this course.

17.2 ■ Standard Cell Potentials**457****Table 17.2** Standard Reduction Potentials (25°C)

	ε° (V)		ε° (V)
$\text{F}_2 + 2 \text{e}^- \rightarrow 2 \text{F}^-$	2.87	$\text{Sn}^{4+} + 2 \text{e}^- \rightarrow \text{Sn}^{2+}$	0.13
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$	0.000
$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow$ $\text{Mn}^{2+} + 4 \text{H}_2\text{O}$	1.51	$\text{Sn}^{2+} + 2 \text{e}^- \rightarrow \text{Sn}$	-0.13
$\text{Cl}_2 + 2 \text{e}^- \rightarrow 2 \text{Cl}^-$	1.36	$\text{Pb}^{2+} + 2 \text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow$ $2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	1.33	$\text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni}$	-0.25
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.74
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.53	$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$	0.34	$2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow$ $\text{H}_2 + 2 \text{OH}^-$	-0.828
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.15	$\text{Al}^{3+} + 3 \text{e}^- \rightarrow \text{Al}$	-1.66
		$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71

reduction without the other. We can measure the standard cell potential of any cell. How can we determine the half-cell potential of each half-reaction? We *define* the half-cell potential of the hydrogen/hydrogen ion standard half-cell as 0.000 V, then measure the potential of another half-cell, such as the copper half-cell, with that half-cell. The entire potential of this cell can then be assigned to the other (copper) half-cell, because the potential of the hydrogen half-cell is zero. Of course, we can do the same thing for every other half-cell, but we need not do so, since the hydrogen/hydrogen ion half-cell is hard to work with because it involves a gas. We can get an unknown half-cell potential from its cell potential with any half-cell of known potential. For example, once we get the copper half-cell potential, we can use it to calculate the unknown zinc half-cell potential from the Daniell cell potential. A collection of half-cell potentials, all written as reductions, is presented as Table 17.2.

The following principles allow calculation of cell potentials from reduction potentials:

1. The two half-cell potentials (one for the oxidation and the other for the reduction) add up to the cell potential for a complete cell.
2. Writing the chemical equation in the reverse direction requires changing the sign of the cell or half-cell potential. Note that all the equations in Table 17.2 refer to reduction half-reactions, but each complete cell requires one oxidation and one reduction. Thus one of the half-cell equations must be reversed (and the sign of its potential changed) to add to the other to make a complete cell equation.
3. Multiplying the coefficients of either type of equation (half-cell or cell) *does not change* the associated potential.
4. If the sign of a cell potential is positive, the reaction will go as written; if it is negative, the opposite reaction will proceed.

When an equation is reversed, the sign of the potential is changed.

Multiplying the coefficients of either type of equation (half-cell or cell) *does not change* the associated potential.

EXAMPLE 17.2

Given the half-cell potentials in Table 17.2, calculate the cell potential of (a) the Daniell cell. (b) the copper/silver cell.

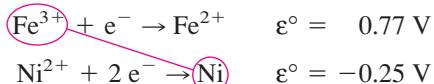
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CHAPTER 17 ■ Electrochemistry

Solution

(a) $\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}$	$\epsilon^\circ = -0.76 \text{ V}$	(From the table)
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^-$	$\epsilon^\circ = +0.76 \text{ V}$	(Reversing that equation and changing the sign)
$\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$	$\epsilon^\circ = +0.34 \text{ V}$	(From the table)
$\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$	$\epsilon^\circ = +1.10 \text{ V}$	(Adding the last two equations and their potentials)
(b) $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$\epsilon^\circ = +0.80 \text{ V}$	(From the table)
$2 \text{Ag}^+ + 2 \text{e}^- \rightarrow 2 \text{Ag}$	$\epsilon^\circ = +0.80 \text{ V}$	(Note: No change)
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2 \text{e}^-$	$\epsilon^\circ = -0.34 \text{ V}$	(Reversing the equation from part a)
$\text{Cu} + 2 \text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2 \text{Ag}$	$\epsilon^\circ = +0.46 \text{ V}$	(Adding the last two equations and their potentials)

Note that any reactant (or set of reactants) on the left side of an equation in Table 17.2 will react spontaneously with any product (or set of products) on the right side of an equation *below* it in the table. When the lower equation is reversed to make an oxidation half-reaction, and the sign of its potential is changed, the sum of the two potentials will be positive. For example, Fe^{3+} will react with Ni to produce Fe^{2+} and Ni^{2+} , with a standard potential of $0.77 \text{ V} + (+0.25 \text{ V}) = +1.02 \text{ V}$:



The *reactants* near the top of the table are very powerful oxidizing agents, and the *products* near the bottom of the table are powerful reducing agents.

**Snapshot Review**ChemSkill Builder 22.1,
22.2

- Standard potentials may be used to determine the tendencies of redox reactions to proceed.

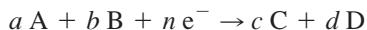
- A. Calculate the standard potential of the cell comprised of $\text{Sn}^{4+}/\text{Sn}^{2+}$ and Pb^{2+}/Pb .

17.3 The Nernst Equation

A standard cell (Section 17.2) has all solid and liquid reagents pure, all solutes 1.000 M, and all gases at 1.000 atm. However, in practice it is unlikely that we will want to get these conditions every time we determine a potential. To

17.3 ■ The Nernst Equation**459**

determine the potential of half-cells or cells where these conditions do not exist, we use the Nernst equation. For a general half-reaction,



a mathematical equation known as the **Nernst equation** gives the actual potential (ε) from the standard potential (ε°) and the molarities (or pressures in atmospheres):

Note that the argument of the log is a ratio of concentrations multiplied together, not a sum, and that the concentrations of the products are in the numerator.

$$\varepsilon = \varepsilon^\circ - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where n is the number of moles of electrons involved in the half-reaction or in *each* half-reaction. The square brackets enclosing the chemical species denote their molarities, and the exponents are the coefficients from the balanced equation. For example, $[A]^a$ is the molarity of A raised to the a power. The concentration of a pure solid or liquid is taken as exactly 1. Water in dilute aqueous solutions is also regarded as having a concentration of 1.

Significant digits in logarithms are treated in Appendix A1.

EXAMPLE 17.3

Calculate the potential of a zinc/zinc ion half-cell in which the pure zinc electrode is immersed in a 0.100 M zinc ion solution.

Solution

$$\varepsilon = \varepsilon^\circ - \left(\frac{0.0592}{n} \right) \log \left(\frac{1}{[Zn^{2+}]^1} \right) = -0.76 \text{ V} - \left(\frac{0.0592}{2} \right) \log \left(\frac{1}{0.100} \right) = -0.79 \text{ V}$$

Hint: Solve the molarity ratio first, take its logarithm, multiply by 0.0592, divide by the number of moles of electrons, then subtract that value algebraically from ε° .

Practice Problem 17.3 Calculate the potential of a silver/silver ion half-cell in which the silver electrode is immersed in a 0.100 M silver nitrate.

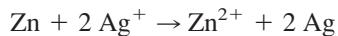
The Nernst equation can be used for complete cell reactions also. The number of moles of electrons (not shown in the equation for the cell reaction because the electrons cancel when the half-cell equations are combined) is the number in *each* half-cell just before those equations are combined.

EXAMPLE 17.4

Calculate the potential of a zinc/silver cell in which the zinc electrode is immersed in a 0.0100 M zinc nitrate and the silver electrode is in 0.500 M silver nitrate. Determine which metal is reduced spontaneously.

Solution

Silver ion is above zinc ion in Table 17.2, so the zinc half-reaction is reversed:



$$\varepsilon^\circ = +0.80 \text{ V} + (+0.76 \text{ V}) = 1.56 \text{ V}$$

$$\varepsilon = \varepsilon^\circ - \left(\frac{0.0592}{n} \right) \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right) = +1.56 \text{ V} - \left(\frac{0.0592}{2} \right) \log \left[\frac{0.0100}{(0.500)^2} \right] = +1.60 \text{ V}$$

Two moles of electrons were transferred from zinc to silver ions. The positive sign for the potential means that the reaction goes as written. The zinc is oxidized and the silver ion is reduced.

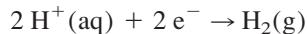
Practice Problem 17.4 Calculate the potential of a lead/copper cell in which the lead electrode is immersed in a 0.100 M lead(II) nitrate and the copper electrode is immersed in 0.200 M copper(II) sulfate. Determine which metal is reduced spontaneously.

**Snapshot Review**

ChemSkill Builder 22.5

□ Note that the argument of the log in the Nernst equation is a ratio of concentrations multiplied together, not a sum; that the concentrations of the products are in the numerator and those of the reactants are in the denominator.

- A. Calculate the potential of the following half-cell with H₂ gas at 1.000 atm and hydrogen ion at 0.100 M:



17.4 Electrolysis Cells

In Chapter 8, we found that certain decomposition reactions were carried out by use of electricity. The production of a chemical reaction by means of electric current is called **electrolysis**. The very most reactive metals and fluorine are usually produced in their elemental forms in **electrolysis cells**. The production of aluminum is a prime example.

The requirements for an electrolysis reaction are

1. Ions capable of movement—that is, in the liquid state or in a liquid solution—so that they can carry the charge.
2. An external source of electric energy with sufficient voltage to cause the desired reaction to occur.

The conditions under which an electrolysis reaction is carried out are extremely important. If a solution is used, the most easily oxidized substance will be oxidized and the most easily reduced substance will be reduced. We can

17.4 ■ Electrolysis Cells**461**

use our knowledge of redox potentials to deduce which of the substances in a system will undergo electrolysis. For example, if an aqueous sodium chloride solution is electrolyzed, hydrogen will be produced by reduction of the water rather than sodium from the NaCl. (We can tell that sodium will not be produced because it is too active. Even if it were produced, it would react immediately with the water to produce hydrogen gas and sodium ions.)

EXAMPLE 17.5

What would be the reduction product of the electrolysis of an aqueous solution of an aluminum salt?

Solution

Hydrogen. Aluminum is a very active metal. Al^{3+} (aq) cannot be reduced to aluminum metal ($\epsilon^\circ = -1.66 \text{ V}$); the water is much more easily reduced to hydrogen ($\epsilon^\circ = -0.828 \text{ V}$). (See Table 17.2) (Aluminum oxide melts at too high a temperature to use its molten state, and aluminum chloride sublimes rather than melting, so aluminum metal is produced from a solution of aluminum oxide in a molten compound called cryolite, Na_3AlF_6 . Carbon is used as the anode, and CO gas is produced rather than oxygen gas.) This process is called the Hall process.

Practice Problem 17.5 Write a balanced chemical equation for the commercial electrolysis of aluminum oxide to produce aluminum.



Snapshot Review



ChemSkill Builder 22.3

- An electrolysis reaction depends strongly on the conditions under which it is carried out.
- A. Which of the following ions could be reduced to the element from aqueous solution?
- (a) Cu^{2+}
 - (b) H^+
 - (c) Na^+
 - (d) Ni^{2+}

ITEM OF INTEREST

Impure copper metal is purified by making it the anode of an electrolytic cell, with a pure copper cathode. When a specific potential is applied to the cell, both the copper and more active impurities go into solution, but only the copper deposits on the cathode. The more active metals stay in solution. The less active impurities do not go into solution, but fall to the bottom of the vessel holding the cell. These impurities include gold and silver (also in group IB), and their recovery more than pays for the purification process.

17.5 Electrolysis Calculations

The second two variables in Table 17.1 are used in the calculation of the quantity of chemical reaction that will accompany the passage of a measured quantity of **charge**. In electrolysis cells, the passage of charge causes chemical reaction. Charge can flow by electrons passing through a conductor (such as copper wire) or by the motion of ions in a solution or a molten salt. The passage of charge is an electric current, and the quantity of charge that passes per second is the current. The variables and their units are presented in Table 17.1. Note that $q = It$ and $1 \text{ C} = (1 \text{ A})(1 \text{ s})$. The charge on the electron is $1.60 \times 10^{-19} \text{ C}$, and a mole of electrons has a total charge of 96,500 C, called a **faraday** in honor of Michael Faraday (1791–1867) who first discovered the relationships between the quantity of charge that passes and the quantity of chemical reaction that the current generates.

With only this little background as a minimum, we are ready to calculate the quantity of reaction that will be caused by passage of a specified electric charge as well as other quantities.

EXAMPLE 17.6

Calculate the mass of copper metal that will be deposited by passage of a 10.0-A current through a solution of copper(II) sulfate for 3.00 h.

Solution

The chemical reaction of interest is



Two moles of electrons produce 1 mol of copper metal.

$$3.00 \text{ h} \left(\frac{60.0 \text{ min}}{1 \text{ h}} \right) \left(\frac{60.0 \text{ s}}{1 \text{ min}} \right) \left(\frac{10.0 \text{ C}}{1 \text{ s}} \right) \left(\frac{1 \text{ mole e}^-}{96,500 \text{ C}} \right) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \right) \left(\frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 35.5 \text{ g Cu}$$

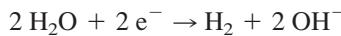
The current Definition of a faraday From the equation

Practice Problem 17.6 Calculate the mass of silver metal that will be deposited by passage of a 10.0-A current through a solution of silver nitrate for 3.00 h.

EXAMPLE 17.7

Calculate the time required to produce 2.50 g of hydrogen by the electrolysis of water (containing sodium sulfate to carry the charge) with a current of 5.00 A.

Solution



$$2.50 \text{ g H}_2 \left(\frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol H}_2} \right) \left(\frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1 \text{ s}}{5.00 \text{ C}} \right) = 4.78 \times 10^4 \text{ s} = 13.3 \text{ h}$$

■ Key Terms

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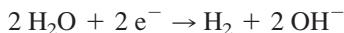
ITEM OF INTEREST

Galvanic cell reactions, such as those involving the everyday use of batteries, follow the same equations as electrolysis cells do. When we measure cell potentials, however, we do not allow the reactions to proceed, because if they did, their potentials would change as the concentrations changed. The potentials are measured without a complete circuit.

Practice Problem 17.7 Calculate the time required to produce 1.00×10^6 g of aluminum metal by the Hall process (See Practice Problem 17.5) with a current of 500 A.

EXAMPLE 17.8

Calculate the current required to produce 2.50 g of hydrogen by the electrolysis of water (containing sodium sulfate to carry the charge) in 3.00 h.

Solution

$$2.50 \text{ g H}_2 \left(\frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol H}_2} \right) \left(\frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 2.39 \times 10^5 \text{ C}$$

$$3.00 \text{ h} \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) = 10,800 \text{ s}$$

$$\frac{2.39 \times 10^5 \text{ C}}{10,800 \text{ s}} = 22.1 \text{ A}$$

**Snapshot Review**

ChemSkill Builder 22.4

□ The quantity of chemical reaction in an electrolysis cell can be calculated from the quantity of charge that passes plus the information presented in Chapters 10 and 11.

- A. Calculate the time required to deposit 6.00 g of silver metal from $\text{AgNO}_3(\text{aq})$ with a current of 2.50 A.

Key Terms

Key terms are defined in the Glossary.

battery (17.1)
cell (intro)
charge (17.5)
circuit (17.1)
Daniell cell (17.1)
electrochemistry (intro)
electrolysis (17.4)

electrolysis cell (17.4)
faraday (17.5)
galvanic cell (17.1)
lead storage cell (17.1)
Nernst equation (17.3)
potential (17.2)
salt bridge (17.1)

standard cell potential (17.2)
standard half-cell potential (17.2)
standard state of the system (17.2)
voltage (17.2)
voltaic cell (17.1)

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CHAPTER 17 ■ Electrochemistry

Symbols

e (charge on the electron) (17.2) ϵ (potential) (17.3)

ϵ° (standard potential) (17.2)

e^- (electron) (17.1)

Summary

Voltaic cells produce electric current by means of oxidation and reduction reactions occurring at different locations. A complete circuit is necessary, including a wire to transport the electrons and a path for ions to migrate to maintain charge neutrality at each electrode. To allow for ion mobility, the reactants must be in a solution or a molten salt. (Section 17.1)

The inherent tendencies of redox half-reactions to proceed are measured with standard half-cell potentials. The larger the (positive) potential, the greater the tendency for a reduction to occur. When combining half-cells into a complete cell, reversing an equation requires changing the sign of the potential, but altering the coefficients in an equation does not affect the potential. (Section 17.2)

The potential of a half-cell or cell is dependent on the concentrations of the reagents involved. The

potential can be calculated using the Nernst equation. (Section 17.3)

Electrolysis reactions use direct current to produce redox reactions. Production of very active elemental metals and very active elemental nonmetals is often done using electrolysis. The conditions under which an electrolysis is carried out often make a great deal of difference as to which products are obtained. (Section 17.4)

Calculation of the quantity of reaction from the quantity of charge that passes, or vice versa, can be done using the techniques of Sections 10.1 and 10.3, as long as we know how to measure the quantity of charge. Current in amperes times time in seconds gives the charge in coulombs, and coulombs can easily be converted to faradays (moles of electrons). (Section 17.5)

Items for Special Attention

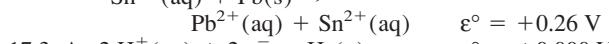
- If ϵ° for a cell is positive, it is an *indication* that the cell reaction is spontaneous as written. If ϵ for a cell is positive, it is *certain* that the cell reaction is spontaneous as written.
- In the Nernst equation, the concentration terms of the *products* are in the numerator and those of the *reactants* are

in the denominator. The exponents are the corresponding coefficients from the balanced equation. The terms are multiplied and/or divided, not added or subtracted.

Answers to Snapshot Reviews

- 17.1 A. (a) and (b) $\text{Ni(s)} + 2 \text{Ag}^+(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2 \text{Ag(s)}$
 B. Because electrons *must* be in every half-reaction equation, there must be at least one ionic species included in every equation to balance the charge.

17.2 A. $\text{Sn}^{4+}(\text{aq}) + 2 e^- \rightarrow \text{Sn}^{2+}(\text{aq}) \quad \epsilon^\circ = +0.13 \text{ V}$
 $\text{Pb(s)} \rightarrow \text{Pb}^{2+}(\text{aq}) + 2 e^- \quad \epsilon^\circ = +0.13 \text{ V}$



17.3 A. $2 \text{H}^+(\text{aq}) + 2 e^- \rightarrow \text{H}_2(\text{g}) \quad \epsilon^\circ = +0.000 \text{ V}$

$$\epsilon = \epsilon^\circ - \frac{0.0592}{2} \log \frac{\text{P}_{\text{H}_2}}{[\text{H}^+]^2}$$

$$= 0.000 - 0.0296 \log \frac{1}{(0.100)^2} = -0.592 \text{ V}$$

- 17.4 A. Cu^{2+} B. H^+ C. Ni^{2+}
 17.5 A. $\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)}$
 $6.00 \text{ g Ag} \left(\frac{1 \text{ mol Ag}}{108 \text{ g Ag}} \right) \left(\frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \right) \left(\frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1 \text{ s}}{2.50 \text{ C}} \right) = 2140 \text{ s} = 35.7 \text{ min}$

■ Problems

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Self-Tutorial Problems

- 17.1** Explain why a salt bridge is required in a Daniell cell, but not in a lead storage cell.
- 17.2** In Chapter 8 it was stated that more active metals (Table 8.2) displace less active metals from their compounds. Is the same true in voltaic cells?
- 17.3** Explain why equations for half-reactions *must* include at least one ionic species.
- 17.4** Consider the equation, with standard potential -0.828 V :



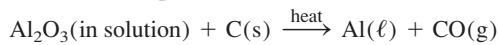
Which of the following sets of conditions corresponds to that standard potential?

- (a) 1 M OH^- and 1 atm H_2 (b) 2 M OH^- and 1 atm H_2
 (c) 1 M OH^- and 1 atm air (d) 2 M OH^- and 1 atm air
- 17.5** The reaction $\text{X} + 2\text{e}^- \rightarrow \text{X}^{2-}$ has a standard potential of 0.90 V . What is the potential for each of the following reactions?
- (a) $2\text{X} + 4\text{e}^- \rightarrow 2\text{X}^{2-}$
 (b) $2\text{X}^{2-} \rightarrow 2\text{X} + 4\text{e}^-$
- 17.6** Does a positive potential signify that a half-cell reaction will proceed spontaneously in the direction written?
- 17.7** What unit is equivalent to the each of the following combinations of units? (a) ampere-second,
 (b) coulomb/second.

- 17.8** Calculate the charge on the electron from the knowledge that a faraday (the charge on a mole of electrons) is $96,500\text{ C}$.

- 17.9** How many moles of electrons is represented by each of the following: (a) 5.00 C (b) reduction of 1.00 mol of water?
 (c) $2.00 \times 10^{11}\text{ e}^-$? (d) reduction of 1.00 mol of PbO_2 to Pb^{2+} ? (e) oxidation of 1.00 mol of Ce^{3+} to Ce^{4+} ?

- 17.10** How many moles of electrons does it take to reduce 2.50 mol of Al_2O_3 (dissolved in Na_3AlF_6) to aluminum? The unbalanced equation is



- 17.11** Consider the reaction



Reverse the equation and amend the potential accordingly. According to the original equation, will X or Z react spontaneously with the other ion? According to the reversed equation, which one will react with the other ion?

- 17.12** A mixture of copper and nickel metal, with a mass of 10.69 g , was treated with nitric acid to make an aqueous solution. The solution was electrolyzed with a voltage that was sufficient to reduce the copper only. The electrode weighed 20.171 g before the electrolysis, and 25.782 g afterward. Calculate the percentage of copper in the original sample.

Problems**17.1 Voltaic Cells**

- 17.13** Diagram the apparatus for the electrochemical reaction of copper metal in aqueous copper(II) ion with lead metal in aqueous lead(II) ion. Using Table 8.2, predict which metal will be oxidized. Draw arrows to indicate the direction of electron flow, positive ion flow, and negative ion flow.
- 17.14** The half-reaction of two ions such as Ce^{4+} and Ce^{3+} , neither of which can serve as an electrode, is done with an inert electrode such as a platinum bar. Diagram the apparatus for the electrochemical reaction of aqueous cerium(IV) ion and cerium(III) ion with MnO_4^- and Mn^{2+} . (Cerium(IV) ion is a better oxidizing agent than is permanganate ion.)

- 17.15** In each part, choose which ion, if either, is easier to reduce:
 (a) MnO_4^- or $\text{Cr}_2\text{O}_7^{2-}$ (b) Sn^{2+} or Pb^{2+} (c) Fe^{3+} or Fe^{2+}
- 17.16** In each part, choose the substance, if either, that is easier to oxidize:
 (a) Zn or Fe^{2+} (b) H_2 or Fe^{2+} (c) H_2 or Fe
- 17.17** Which potential listed in Table 17.2 represents the reduction of hydrogen in (a) acid solution? (b) neutral or basic solution?

- 17.18** Since the reaction in the Daniell cell and the direct reaction of zinc metal and copper(II) ion are the same, and the Daniell cell produces electrical energy, what happens to the chemical energy when the elements react directly?

17.2 Standard Cell Potentials

- 17.19** Calculate the standard potential of each of the following cells:
- (a) $\text{Cu} + \text{Fe}^{2+} \rightarrow \text{Cu}^{2+} + \text{Fe}$
 (b) $2\text{Ag} + \text{Fe}^{2+} \rightarrow 2\text{Ag}^+ + \text{Fe}$
 (c) $\text{Cu} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+}$
 (d) $\text{Cu} + \text{Pb}^{2+} \rightarrow \text{Cu}^{2+} + \text{Pb}$
- 17.20** Calculate the standard potential of each of the following cells. State which one(s), if any, will proceed spontaneously as written.
- (a) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$
 (b) $2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow \text{H}_2 + 2\text{Fe}^{3+}$
 (c) $\text{Sn} + \text{Pb}^{2+} \rightarrow \text{Sn}^{2+} + \text{Pb}$
 (d) $\text{Zn} + \text{Pb}^{2+} \rightarrow \text{Zn}^{2+} + \text{Pb}$

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- 17.21** (a) The potential of the reduction of X^{2+} to X is 0.55 V. Will X react with 1 M H^+ ? (b) The potential of the reduction of Z^+ to Z is -0.55 V. Will Z react with 1 M H^+ ? (c) Which metal, X or Z, will reduce the ion of the other metal spontaneously?

- 17.22** Using data from Table 17.2, explain why Cu^+ is not stable in aqueous solution.
- 17.23** Using the answer from the prior problem, determine what products would be expected from the reaction of Cu_2O and dilute sulfuric acid.

17.3 The Nernst Equation

- 17.24** Calculate the potential of each of the following:

- $Fe^{2+}(0.100\text{ M}) + 2 e^- \rightarrow Fe(s)$
- $Fe^{3+}(0.100\text{ M}) + e^- \rightarrow Fe^{2+}(0.100\text{ M})$
- $Pb^{2+}(0.500\text{ M}) + 2 e^- \rightarrow Pb(s)$
- $MnO_4^-(2.00\text{ M}) + 8 H^+(1.00\text{ M}) + 5 e^- \rightarrow Mn^{2+}(0.500\text{ M}) + 4 H_2O(\ell)$

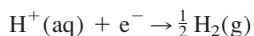
- 17.25** Calculate the potential of each of the following:

- $Cu \rightarrow Cu^{2+}(0.100\text{ M}) + 2 e^-$
- $Ag(s) \rightarrow Ag^+(0.100\text{ M}) + e^-$

- 17.26** Calculate the potential of each of the following:

- $Cu + Fe^{2+}(0.100\text{ M}) \rightarrow Cu^{2+}(0.100\text{ M}) + Fe$
- $2 Ag(s) + Fe^{2+}(0.100\text{ M}) \rightarrow 2 Ag^+(0.100\text{ M}) + Fe(s)$
- $Cu(s) + 2 Fe^{3+}(0.100\text{ M}) \rightarrow Cu^{2+}(0.100\text{ M}) + 2 Fe^{2+}(0.100\text{ M})$
- $Cu(s) + Pb^{2+}(0.100\text{ M}) \rightarrow Cu^{2+}(2.00\text{ M}) + Pb(s)$
- $MnO_4^-(2.00\text{ M}) + 8 H^+(1.00\text{ M}) + 5 Fe^{2+}(0.100\text{ M}) \rightarrow Mn^{2+}(0.500\text{ M}) + 5 Fe^{3+}(0.100\text{ M}) + 4 H_2O(\ell)$

- 17.27** Using the following equation, calculate the potential of the half-cell consisting of hydrogen gas at 1.000 atm and hydrogen ion at 0.100 M. Compare the result with that for Snapshot Review problem 17.3 A and explain the results.



- 17.28** Calculate the potential for each of the following reactions under the conditions given, and state whether the reaction will proceed as written or in the opposite direction.

- $MnO_4^-(0.125\text{ M}) + 8 H^+(1.00\text{ M}) + 5 Fe^{2+}(0.600\text{ M}) \rightarrow Mn^{2+}(0.500\text{ M}) + 5 Fe^{3+}(0.900\text{ M}) + 4 H_2O(\ell)$
- $Sn(NO_3)_2(3.00\text{ M}) + Pb(NO_3)_2(2.00\text{ M}) \rightarrow Pb(s) + Sn(NO_3)_4(0.500\text{ M})$
- $2 AgNO_3(1.50\text{ M}) + Zn(s) \rightarrow Zn(NO_3)_2(0.400\text{ M}) + 2 Ag(s)$

- 17.29** Calculate the potential for each of the following reactions under the conditions given, and state whether the

CHAPTER 17 ■ Electrochemistry

reaction will proceed as written or in the opposite direction.

- $Cu(s) + Fe^{2+}(0.200\text{ M}) \rightarrow Cu^{2+}(0.0100\text{ M}) + Fe(s)$
- $2 Ag(s) + Fe^{2+}(0.500\text{ M}) \rightarrow 2 Ag^+(1.25\text{ M}) + Fe(s)$
- $Cu(s) + 2 Fe^{3+}(2.00\text{ M}) \rightarrow Cu^{2+}(0.800\text{ M}) + 2 Fe^{2+}(0.00100\text{ M})$
- $Cu(s) + Pb^{2+}(0.750\text{ M}) \rightarrow Cu^{2+}(0.250\text{ M}) + Pb$

17.4 Electrolysis Cells

- 17.30** What products are formed if aqueous aluminum sulfate is electrolyzed between aluminum electrodes?

- 17.31** What product would be produced first by the electrolytic reduction of iron(III) sulfate?

- 17.32** What product, if any, would be formed by the reaction of iron(III) chloride and iron metal?

- 17.33** What product, if any, would be formed by the reaction of copper(II) sulfate and copper metal?

- 17.34** Diagram a cell for the electrolysis of water. Make the apparatus in a U-tube so that the gases will not mix. Be sure to include all reagents necessary for the experiment to work.

- 17.35** Match the overall equations for electrolysis reactions, on the left, with the conditions for the reactions, on the right.

- | | |
|--|-------------------|
| (a) $2 NaCl \rightarrow 2 Na + Cl_2$ | (i) dilute |
| (b) $2 H_2O \rightarrow 2 H_2 + O_2$ | (ii) concentrated |
| (c) $2 NaCl + 2 H_2O \rightarrow 2 Na^+ + H_2 + Cl_2 + 2 OH^-$ | (iii) molten NaCl |

- 17.36** State whether each of the following equations would describe the overall reaction in a voltaic cell or an electrolysis cell:

- $Ni(s) + Cl_2(g) \rightarrow Ni^{2+}(\text{aq}) + 2 Cl^-(\text{aq})$
- $NiCl_2(\text{aq}) \rightarrow Ni(s) + Cl_2(g)$
- $Zn(s) + 2 AgNO_3(\text{aq}) \rightarrow 2 Ag(s) + Zn(NO_3)_2(\text{aq})$
- $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(\ell)$
- $Al_2O_3(Na_3AlF_6) + 3 C(s) \rightarrow 2 Al(\ell) + 3 CO(g)$

17.5 Electrolysis Calculations

- 17.37** Three cells are connected in series, so the same current passes through each one. The first cell contains silver electrodes in silver nitrate solution, the second copper electrodes in copper(II) sulfate solution, and the third gallium electrodes in gallium(III) chloride solution. In one experiment, 1.500 g of silver is deposited in the first cell. What masses of copper and gallium are deposited in the other cells?

■ General Problems

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- 17.38** Calculate the mass of mercury deposited by passage of 19,200 C through $\text{Hg}_2(\text{NO}_3)_2(\text{aq})$.
- 17.39** Calculate the mass of mercury deposited by a 10.0-A current passing for 3.00 h through $\text{Hg}_2(\text{NO}_3)_2(\text{aq})$.
- 17.40** Calculate the hydroxide ion concentration produced by passage of a 0.400-A current through 25.00 mL of 5.000 M NaCl solution for 500.0 s. Assume that there is no change in volume and that only hydrogen is produced at the cathode and only chlorine at the anode.

General Problems

- 17.42** Since a positive cell potential means that a reaction will proceed spontaneously as written, and a negative potential means that it will proceed spontaneously in the opposite direction, what could a zero potential mean?
- 17.43** To electrolyze NaCl to yield Na and Cl_2 , molten NaCl is required. Sometimes an impurity such as LiCl is added to the solid NaCl before heating.
- What happens to the freezing point (melting point) of a solution when a solute is added?
 - Explain why the impurity is added.
 - Should the impurity have any ions that are more easily reduced than sodium?
- 17.44** In a cell composed of a $\text{Co}^{3+}/\text{Co}^{2+}$ half-cell suitably connected to a $\text{Cr}^{3+}/\text{Cr}^{2+}$ half-cell, each of the ions is 1.00 M. Write the equation for the spontaneous reaction.
- 17.45** In the cell of Problem 17.44, write the equation for the spontaneous reaction if each ion were initially 2.00 M.
- 17.46** What is the product of passage of a current of 3.00 A for 2.00 h through 1.00 L of a solution of 1.50 M Fe^{3+} ?

- 17.41** Two pure copper electrodes are immersed in a CuSO_4 solution. One is connected to a battery and the other to a cell with two pure silver electrodes immersed in silver nitrate solution. The second silver electrode is also connected to the battery. If sufficient charge passes to deposit 1.00 g of copper on the cathode of the first cell, (a) what mass of copper is “dissolved” from the anode of that cell? (b) What mass of silver is deposited on the cathode of the second cell?

- 17.47** What is the product of passage of a current of 3.00 A for 2.00 h through 1.00 L of a solution of 1.50 M Cu^{2+} ?
- 17.48** What would happen if Cu^+ were present in aqueous solution with nothing else around to react with?
- 17.49** State whether each of the following equations would describe the overall reaction in a voltaic cell or an electrolysis cell:
- $2 \text{Fe}^{2+}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{Fe}^{3+}(\text{aq}) + 2 \text{Cl}^-(\text{aq})$
 - $14 \text{H}^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3 \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 6 \text{CO}_2(\text{g}) + 7 \text{H}_2\text{O}(\ell)$
 - $\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{Ag}(\text{s}) \rightarrow 5 \text{Ag}^+(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\ell)$
- 17.50** The electrolytic reduction of $\text{Cu}(\text{CN})_2^-$ to Cu (plus cyanide ion) requires vigorous stirring to be most effective. (a) How many moles of electrons are required per mole of Cu? (b) Explain why the stirring is so important.

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Chemical Equilibrium

- 18.1 Rates of Reaction
- 18.2 The Condition of Equilibrium
- 18.3 LeChâtelier's Principle
- 18.4 Equilibrium Constants



Cobalt(II) chloride equilibrium

Review Clues

- Section 18.1** Sections 8.3, 12.5
Section 18.3 Sections 12.5, 12.6, 15.2
Section 18.4 Sections 10.1, 10.4, 11.1

Objectives

- 18.1** To predict how changes in the conditions affect the rate of a chemical reaction
18.2 To predict the behavior of an equilibrium system once it has been formed
18.3 To predict the effect of a change of conditions on a system initially at equilibrium
18.4 To use equilibrium constants to determine the concentrations of reactants and products in a system at equilibrium

18.1 ■ Rates of Reaction**469**

We know that (pure) liquid water at 0°C will freeze if heat is removed from it and that ice at 0°C will melt if heat is added to it. However, if no heat is added or removed from a mixture of ice and liquid water at 0°C, both the melting and freezing processes still continue. In this case, the rate of melting and the rate of freezing are the same, so the mass of the ice and the mass of the liquid water do not change. (The shape of the ice might change, however, as some melting and freezing take place.) When exactly opposite physical processes or chemical reactions occur together at the *same rate*, a condition of *equilibrium* is said to be established. When two opposite processes occur at equal rates, nothing may *appear* to be happening. However, both processes continue at the rates dictated by the conditions. If the conditions change, a change in the system may be observed.

Because chemical equilibrium involves rates of reactions, this chapter first investigates the factors that affect the rate of a reaction (Section 18.1). The molecular basis of chemical equilibrium and some of its terminology are then presented in Section 18.2. LeChâtelier's principle, discussed in Section 18.3, explains qualitatively how to predict what happens to a system at equilibrium when a change is imposed on the system. Section 18.4 presents the equilibrium constant, which allows us to obtain quantitative results for systems at equilibrium.

18.1 Rates of Reaction

The **rate** of a chemical reaction is defined as the change in the concentration of a reactant or product per unit time. For example, the rate may be described as the disappearance of 0.300 mol/L of a certain reactant per hour or the appearance of 0.00100 mol/L of a certain product per second.

Any of six factors can affect the rate: (1) the nature of the reactants, (2) the temperature, (3) the presence of a catalyst, (4) the concentration of reactants in solution, (5) the pressure of gaseous reactants, and (6) the state of subdivision of solid reactants. For a reaction to occur, the atoms, molecules, or ions must come into contact with one another with enough energy to rearrange chemical bonds in some way. Increased concentration, gas pressure, or surface area of a solid tends to get the particles to collide more frequently, and increased temperature tends to get them to collide more frequently and with greater energy to accomplish more effective collisions. Catalysts work in very many different ways.

Some reactions, such as an explosion of nitroglycerine, inherently tend to proceed rapidly. Others, such as the reaction of solid limestone with carbon dioxide in water to form soluble calcium hydrogen carbonate, tend to proceed slowly. It may take centuries for underground streams to form caverns by reaction with limestone (see Figure 8.9). For a given reaction, chemists have no control over the nature of the reactants.

Raising the temperature generally increases the rate of a chemical reaction. A general approximation is that a 10°C rise in temperature doubles the rate of a reaction. The actual increase for any given reaction will not follow this rule exactly, of course, but a great many reactions follow it approximately.

A **catalyst** increases the rate of a chemical reaction (Section 8.3). The thousands of different catalysts work in many different ways. For example, SO₂ and

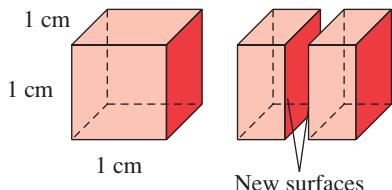
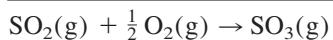
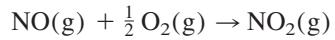
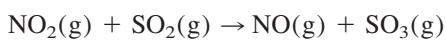
470**CHAPTER 18 ■ Chemical Equilibrium**

Figure 18.1 State of Subdivision of a Solid

When a 1-cm³ cube is cut in half, its surface area increases by one-third, and the solid reacts with liquids or gases at its surface. This is one example of how decreasing the particle size increases the surface area.

O₂ react rather slowly to produce SO₃, but NO₂ reacts with SO₂ rapidly to produce SO₃ and NO. The NO reacts rapidly with O₂ to re-form NO₂, and this two-step process can be repeated many, many times.



The overall effect is to increase the rate of oxidation of SO₂ to SO₃ and have the NO₂ still present.

Enzymes are catalysts that accelerate reactions in living things. A given reaction may proceed at the same rate without the enzyme but only at a much higher temperature. For example, glucose, C₆H₁₂O₆, reacts with oxygen to form carbon dioxide and water. At body temperature without any enzymes, glucose does not react with oxygen at all. In the body, many enzymes cause rapid conversion of glucose. In the absence of such enzymes, the system has to be heated to get glucose to react with oxygen at any reasonable rate.

In general, the higher the concentration of a reactant in a solution, the higher the rate of reaction. Increases in the concentration of a reactant involved in one reaction will cause rate increases different from those increases in concentration of a reactant involved in another reaction. In general, however, an increase in concentration causes an increase in rate. Conversely, a decrease in concentration generally causes a decrease in rate.

The pressure of a gaseous reactant is a measure of its concentration. At a given temperature, pressure is proportional to the number of moles per liter, as given by the ideal gas law (Section 12.5):

$$P = \left(\frac{n}{V} \right) RT$$

Thus, this effect is a corollary of the concentration effect. In general, the higher the pressure, the higher the rate of reaction.

The state of subdivision of a solid is important to the rate of its reaction. When a solid reacts with a liquid or a gas, contact between the two reactants occurs only at the surface of the solid. The more surface area per unit mass, the faster the reaction can occur (Figure 18.1). Thus, finely divided solids tend to react more rapidly than the same solids in particles of larger sizes. An alarming illustration of this effect is a coal dust explosion in a mine. The finely divided coal, set off by a spark, can react almost instantaneously with oxygen. Coal in lump form burns slowly and quietly and may have to be ignited with kindling to get it started in the first place.

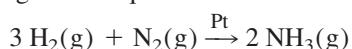
**Snapshot Review**

- The rate of a given reaction increases with (a) increasing temperature, (b) increasing concentration, (c) increasing pressure of a gas, (d) increasing surface area of a solid, or (e) the presence of a catalyst.

- A. Would a wet piece of iron rust faster in air or pure oxygen? Explain.

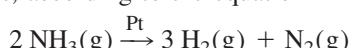
18.2 The Condition of Equilibrium

Suppose we introduce some nitrogen and hydrogen plus a catalyst (such as finely divided platinum) into a vessel and increase the temperature of the system to 500°C (Figure 18.2). The nitrogen begins to react with the hydrogen to form ammonia, according to the equation



The rate of the reaction is rapid at first but slows down as some reactants are used up. Because the pressures of the nitrogen and the hydrogen both decrease, the rate at which the combination occurs also decreases (Section 18.1).

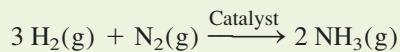
Suppose we introduce some ammonia into a similar vessel with the same catalyst and increase the temperature of the system to 500°C (see Figure 18.2). A decomposition occurs, according to the equation



The initial rate of this reaction is lowered as some of the ammonia is used up. However, as hydrogen and nitrogen are produced, they begin to react to form ammonia. They react slowly at first because little of either is present to react. As their pressures increase as a result of the ammonia decomposition, their rate of combination increases. So in this vessel, we have a decreasing rate of decomposition of ammonia and an increasing rate of combination of hydrogen and

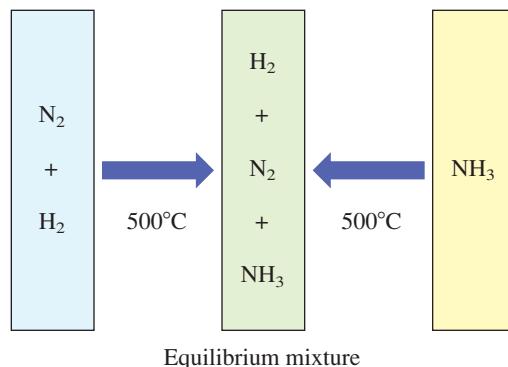
ITEM OF INTEREST

The equilibrium system for the combination of hydrogen and nitrogen is economically very important:



It is very difficult to get nitrogen gas to react to form compounds, yet compounds of nitrogen are necessary for preparing fertilizers and explosives, among many other useful products. The German chemist Fritz Haber (1868–1934) devised the *Haber process* to “fix” nitrogen (convert it to a compound). The process was first used to produce explosives during World War I, when Germany was cut off from imports of natural nitrates by a shipping blockade. The process is now extremely important for agriculture to enable growth of enough food for an exploding world population.

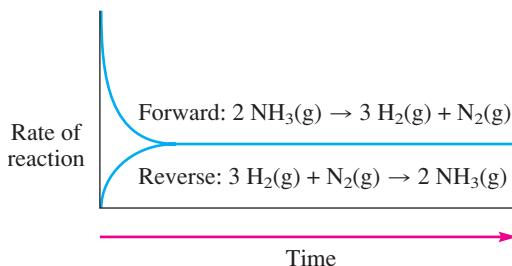
Figure 18.2 Approaching Equilibrium from Both Directions



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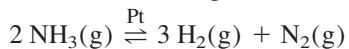
CHAPTER 18 ■ Chemical Equilibrium

Figure 18.3 Rates of Forward and Reverse Reactions in the Experiment Starting with NH₃



nitrogen. When these two rates become equal (Figure 18.3), a state of **equilibrium** will exist. Equilibrium is a **dynamic state**; both reactions continue to occur. Because the rate of combination equals the rate of decomposition, no *net* reaction occurs. The decomposition reaction does not go to completion (Section 10.5). Neither reaction stops, but the effect of the two opposing reactions will make the decomposition reaction *appear* to stop. No matter how long this system exists, as long as we do not change the conditions on the system, none of the pressures of any of the gases will change. (A similar situation is reached in the vessel in which the hydrogen and nitrogen were placed.)

For efficiency, we can write both the forward and reverse reactions of an equilibrium system in one equation, using a double arrow to denote that the reaction goes in both directions. For example:



If we start with the substance on the left, we produce the substances on the right. If we start with the substances on the right, we produce the substance on the left. Because either set of substances produces the other, either set can be placed on the left. The substances written on the left side are conventionally called the reactants, and those written on the right side are called the products. When the substances on the left undergo reaction to produce those on the right, a reaction called the **forward reaction**, the reaction is said to **proceed to the right**. When the substances on the right undergo reaction to produce those on the left, called the **reverse reaction**, the reaction is said to **proceed to the left**.

All chemical reactions, at least in theory, are equilibrium reactions. Even the reactions of a strong acid with a strong base to produce water and a salt (Chapter 8), which we considered to proceed until the limiting reactant was used up (Section 10.4), will be shown (Section 19.3) to have a very tiny concentration of H⁺ or OH⁻ (or both) remaining at the end of the process.



Snapshot Review



ChemSkill Builder 17.1

- Two exactly opposite reactions can occur in a system at the same time. If they occur at the same rate, the system is in a state of chemical equilibrium.
- All reactions, at least theoretically, are equilibrium reactions.

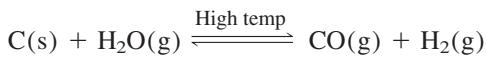
- A. A researcher, studying the reaction A + B ⇌ C + D, started with 1.000 mol of A and 1.000 mol of B in a 1.00-L flask, and got 0.175 mol of C after 40 h. To determine whether the reaction was at equilibrium or was just very slow, she started another experiment with 1.00 mol each of C and D in a 1.00-L flask. If both experiments achieve equilibrium, how much A should she expect after an adequate time?

18.3 LeChâtelier's Principle

When the conditions that affect the rate of a chemical reaction are changed in a system at equilibrium, the rates of the forward and the reverse reaction may be affected differently. If these rates become different, more reactants or products are produced. The direction of the shift of an equilibrium can be predicted qualitatively using LeChâtelier's principle. **LeChâtelier's principle** states that if a *stress* is applied to a system *at equilibrium*, the equilibrium will tend to *shift* in a direction to relieve that stress.

A **stress** is a change of conditions imposed on the system, such as a change in the concentration or pressure of one or more of the reactants or products or a change in the system's temperature. A **shift** is a net reaction of reactants to form products or of products to form reactants. If no further stress is applied, a new equilibrium will be established, with different concentrations of reactants and products from those in the original system. Some stresses cause no shift. The addition of a catalyst affects the rates of both forward and reverse reactions equally and thus does not cause any shift in the equilibrium.

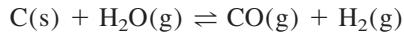
The following equilibrium is used to convert water and coal (impure carbon) to a (more convenient) gaseous fuel, called "water gas."



The addition of a catalyst affects the rates of both forward and reverse reactions equally and thus does not cause any shift in an equilibrium.

EXAMPLE 18.1

What will be the effect of adding carbon monoxide to the water gas system at equilibrium?



Solution

The addition of CO is a stress, causing an increase in the CO pressure. The equilibrium can shift to the left to use up some of the added CO, tending to relieve the stress. After the shift, more carbon and H₂O and less H₂ are present. Also, less CO is present than there would have been if no shift had occurred, but more than was present in the original equilibrium mixture. The system reaches a new equilibrium.

Practice Problem 18.1 What will be the effect of adding H₂O(g) to the water gas system at equilibrium?

EXAMPLE 18.2

Explain in terms of reaction rates why the addition of CO causes the equilibrium of Example 18.1 to shift to the left.

Solution

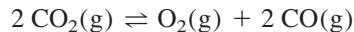
Before the additional CO is added, the system is at equilibrium, which means that the rate of CO formation and the rate of CO decomposition are equal. The

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addition of CO increases the CO pressure, which increases the rate of CO combination with H₂. At the instant when the CO is added, the rate of combination of C and H₂O has not yet been affected. Thus, for some period of time, the reverse rate is greater than the forward rate. The result is a shift to the left until the rate of combination of C and H₂O catches up to the rate of combination of CO and H₂. As the H₂O builds up and the products decrease in pressure, the two reaction rates approach each other until a new equilibrium is established.

EXAMPLE 18.3

What will be the effect of the addition of oxygen to the following system at equilibrium?



Solution

The stress is the addition of oxygen, causing an increase in the O₂ pressure. The equilibrium will shift to the left to use up some of the O₂, tending to relieve the stress. After the shift, less CO and more CO₂ are present. Also, less O₂ is present than there would have been if no shift had occurred, but more than was present in the original equilibrium mixture. The system reaches a new equilibrium.

Practice Problem 18.3 What will be the effect of the addition of nitrogen to the following system at equilibrium at high temperature?



EXAMPLE 18.4

In a certain vessel, 1.0 mol of H₂ is at equilibrium with NH₃ and N₂. After 0.3 mol of H₂ is removed, a new equilibrium is established. In what range is the number of moles of H₂ in the new equilibrium?

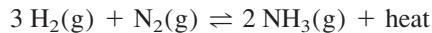
Solution

There will be less than 1.0 mol but more than 0.7 mol of H₂. Some but not all of the removed H₂ is replaced by the equilibrium shift.

Addition (or removal) of heat to a system at equilibrium causes a shift just like addition (or removal) of a reactant or product.

EXAMPLE 18.5

What will be the effect of adding heat to the following system at equilibrium?



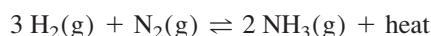
Solution

The stress is the addition of heat, causing an increase in temperature. The equilibrium can shift to the left to use up some of the added heat, tending to relieve

the stress. After the shift, more nitrogen and hydrogen but less ammonia are present. The system reaches a new equilibrium at a higher temperature.

EXAMPLE 18.6

What will be the effect of a temperature increase on the following system at equilibrium?

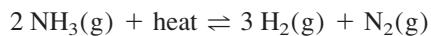


Solution

The temperature is increased by adding energy, usually in the form of heat. Some of the added heat can be removed by a shift of the equilibrium to the left, so more nitrogen and hydrogen are produced and some ammonia is used up. (This problem is merely a rewording of that presented in Example 18.5.)

EXAMPLE 18.7

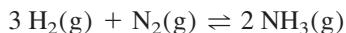
What effect will lowering the temperature have on the following equilibrium system?



Solution

The temperature will be lowered by removal of heat. The equilibrium will shift to the left to replace some of the heat removed. Note that this equation is the reverse of the equation in Example 18.6. The effect here is opposite to that caused by increasing the temperature in that example, even though both equilibria shifted to the left. Because the reactions are written differently, a shift to the left in that case produced more hydrogen and nitrogen and in this case produces more ammonia.

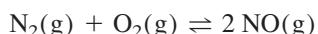
A change in the partial pressure of a gaseous reactant or product will cause a shift in an equilibrium system. Note that a change in the *total pressure*, for example by addition of an inert gas, does not necessarily shift the equilibrium, but a change in all the partial pressures may do so. If all the partial pressures are changed at once—for example, by a change in the volume of the container—the equilibrium will shift to reduce the stress if possible. For example, consider the reaction of nitrogen and hydrogen to produce ammonia:



If this system is at equilibrium in a container of a certain volume, and the volume of the container is decreased, all the partial pressures are increased. The equilibrium will shift to decrease the total pressure by making fewer moles; that is, it will shift to the right. (Reaction of every 4 mol of the elements produces only 2 mol of ammonia.) Making fewer moles reduces the stress of the increased pressure due to reduction of the volume.

EXAMPLE 18.8

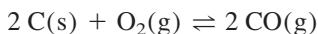
Predict how increasing the volume of the container will affect the equilibrium state at high temperature of the reaction of nitrogen and oxygen to make nitrogen monoxide, NO:

**Solution**

Because there are 2 mol of gas on each side of this equation, neither a shift to the left nor a shift to the right will change the total pressure. The increase in volume causes a reduction in pressure but it will not shift the equilibrium.

EXAMPLE 18.9

Predict how increasing the volume of the container will affect the equilibrium state of the reaction of solid carbon and oxygen gas to make carbon monoxide gas:

**Solution**

The increase in volume causes a decrease in partial pressure of each of the *gases*. The carbon is a solid and has no partial pressure. Therefore, the equilibrium will shift to the right to increase the number of moles of gas at equilibrium.

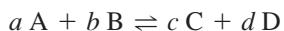
**Snapshot Review**

ChemSkill Builder 17.5

- If a stress is placed on a system at equilibrium, the equilibrium will shift to reduce the stress. (If the system is not at equilibrium to begin with, LeChâtelier's principle does not apply.)
- A. (a) If ammonia is added to a system of ammonia and its elements at equilibrium, which way will the equilibrium shift? (b) What will happen to the temperature of the system because of this shift?

18.4 Equilibrium Constants

LeChâtelier's principle (Section 18.3) allows us to make qualitative predictions about the effects of changes of conditions on an equilibrium system but does not allow quantitative calculations. However, at equilibrium at a given temperature, a certain ratio of concentration terms is very nearly constant for all solutes and gases involved in any given reaction. (Solids and pure liquids are not included in the ratio.) Because it is not exactly constant, we will use two or at most three significant digits in equilibrium constant calculations. For the general reaction



18.4 ■ Equilibrium Constants**477**

the following ratio is a constant at equilibrium at a given temperature:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The equilibrium constant expression is in the same form as the ratio in the Nernst equation (Chapter 17). The square brackets mean “the molarity of” the substance they enclose, and the constant K is called the **equilibrium constant**. The entire equation is known as the **equilibrium constant expression**. No matter what the *initial* concentrations of reactants or products, the ratio of the concentrations *at equilibrium* will be equal to the constant K . The value of K depends only on the specific chemical equation and on the temperature. It does not depend on any of the other factors that can affect the rate of a reaction. For example, if different quantities of the same reactants and products are introduced into different reaction vessels, they will react with one another until, at equilibrium, the same ratio of concentrations, each raised to the appropriate power, is established.

The value of K for a reaction gives quantitative information about the extent of the reaction. That is, a large value of K (usually about 10^4 or larger) means that, at equilibrium, the reaction proceeds almost completely to the right; a small value of K (usually less than 10^{-4} or so) means that, at equilibrium, the reactants have not reacted much at all (or the “products” have reacted almost completely). If concentrations of the reactants and products at equilibrium are known, a value for K can be calculated. If a value for K and some initial concentration data are known, concentrations at equilibrium can be calculated.

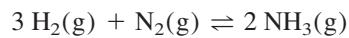
Several points concerning the equilibrium constant expression must be emphasized:

1. *Equilibrium* concentrations are used.
2. The concentrations (raised to the appropriate powers) are multiplied and divided, not added or subtracted.
3. The exponents of the concentration terms are equal to the respective coefficients in the balanced chemical equation.
4. The concentrations of the substances on the right side of the equation appear in the numerator of the equilibrium constant expression, and those of the substances on the left side appear in the denominator.
5. No terms related to solids or pure liquids, including water in dilute aqueous solutions, are included in the equilibrium constant expression.

EXAMPLE 18.10

Write an equilibrium constant expression for the reaction of nitrogen and hydrogen to form ammonia at 500°C.

Solution

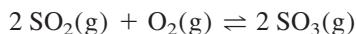


$$K = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

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CHAPTER 18 ■ Chemical Equilibrium

Practice Problem 18.10 Write an equilibrium constant expression for the following reaction at 500°C:



EXAMPLE 18.11

Write an equilibrium constant expression for the reaction of ammonia to form nitrogen and hydrogen at 500°C.

Solution



$$K = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2}$$

This expression is the reciprocal of that obtained in Example 18.10 because the chemical reaction is written in the reverse direction.

Practice Problem 18.11 Write an equilibrium constant expression for the following reactions, and explain how they are related:

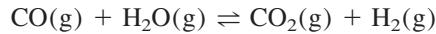
- (a) $2 \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2\text{O}(\text{g})$
(b) $\text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g})$

Finding Values of Equilibrium Constants

The values used in the equilibrium constant expression are *concentrations*, not numbers of moles. Moreover, they are concentrations of the reactants and products *at equilibrium*.

EXAMPLE 18.12

For the following reaction at a certain high temperature,



the concentrations in a particular equilibrium mixture are $\text{CO}(\text{g})$, 0.0600 mol/L; $\text{H}_2\text{O}(\text{g})$, 0.120 mol/L; $\text{CO}_2(\text{g})$, 0.150 mol/L; and $\text{H}_2(\text{g})$, 0.300 mol/L. Calculate the value of the equilibrium constant at this temperature.

Solution

The equilibrium constant expression for this reaction is

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

18.4 ■ Equilibrium Constants**479**

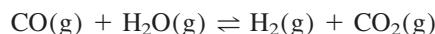
Substituting the equilibrium concentrations yields the value of the equilibrium constant:

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.150 \text{ mol/L})(0.300 \text{ mol/L})}{(0.0600 \text{ mol/L})(0.120 \text{ mol/L})} = 6.25$$

If the equilibrium concentrations are not given in the problem, perhaps they can be calculated from data given in the problem. Note that in an equilibrium system, concentration ratios are equal to mole ratios because all the substances are in the same solution or mixture of gases. (See Problem 18.3)

EXAMPLE 18.13

Consider the reaction



- When 0.0190 mol of carbon monoxide gas and 0.0400 mol of water vapor are placed in a 1.00-L flask and allowed to come to equilibrium at a high temperature, the concentration of carbon dioxide is found to be 0.0165 mol/L. Calculate the value of the equilibrium constant.
- If 0.00950 mol of CO and 0.0200 mol of H₂O are placed in a 0.500-L flask and allowed to come to equilibrium at the same temperature, and the same concentration of CO₂ is formed, what is the value of the equilibrium constant?

Solution

- Two initial concentrations and one equilibrium concentration are given in this problem. We can tabulate the values given and then work out all the equilibrium concentrations. The units are all moles per liter.

CO(g)	+	H ₂ O(g)	\rightleftharpoons	H ₂ (g)	+	CO ₂ (g)
<i>Initial concentrations</i>		0.0190		0.0400		0.0000
<i>Change due to reaction</i>						
<i>Equilibrium concentrations</i>						0.0165

We see immediately that the 0.0165 mol/L of carbon dioxide must have been produced by the reaction, and we deduce from the balanced equation that 0.0165 mol/L of hydrogen has also been produced and that 0.0165 mol/L of each reactant has been used up.

CO(g)	+	H ₂ O(g)	\rightleftharpoons	H ₂ (g)	+	CO ₂ (g)
<i>Initial concentrations</i>		0.0190		0.0400		0.0000
<i>Change due to reaction</i>		-0.0165		-0.0165		+0.0165
<i>Equilibrium concentrations</i>						0.0165

With the initial concentrations and the changes brought about by the reaction, we can calculate the rest of the equilibrium concentrations:

CO(g)	+	H ₂ O(g)	\rightleftharpoons	H ₂ (g)	+	CO ₂ (g)
<i>Initial concentrations</i>		0.0190		0.0400		0.0000
<i>Change due to reaction</i>		-0.0165		-0.0165		+0.0165
<i>Equilibrium concentrations</i>		0.0025		0.0235		0.0165

Finally, we put these *equilibrium* concentrations in the equilibrium constant expression and solve:

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0165 \text{ mol/L})^2}{(0.0025 \text{ mol/L})(0.0235 \text{ mol/L})} = 4.6$$

- (b) Because the *concentrations* are all the same as in part (a), the value of K is the same.

EXAMPLE 18.14

If 0.0150 mol of SO_3 is placed in a 1.00-L vessel and allowed to come to equilibrium at a high temperature, 0.00760 mol of SO_3 remains. Calculate the value of the equilibrium constant for the reaction



Solution

Tabulate the concentrations given, the changes in concentration, and the concentrations that can be deduced from them:

Extra Help

$$\begin{aligned} 0.0074 \text{ mol } \text{SO}_3 &\left(\frac{2 \text{ mol } \text{SO}_2}{2 \text{ mol } \text{SO}_3} \right) \\ &= 0.0074 \text{ mol } \text{SO}_2 \\ 0.0074 \text{ mol } \text{SO}_3 &\left(\frac{1 \text{ mol } \text{O}_2}{2 \text{ mol } \text{SO}_3} \right) \\ &= 0.0037 \text{ mol } \text{O}_2 \end{aligned}$$

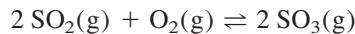
	$2 \text{SO}_3(\text{g})$	\rightleftharpoons	$2 \text{SO}_2(\text{g})$	$+$	$\text{O}_2(\text{g})$
Initial concentrations	0.0150		0.0000		0.0000
Change due to reaction	-0.0074		+0.0074		+0.0037
Equilibrium concentrations	0.0076		0.0074		0.0037

Solve for K :

$$K = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{(0.0074)^2(0.0037)}{(0.0076)^2} = 3.5 \times 10^{-3}$$

Note that the *changes in concentration* are in the same ratio as the coefficients in the balanced chemical equation but that neither the initial concentrations nor the equilibrium concentrations are in that ratio.

Practice Problem 18.14 If 0.0150 mol of SO_2 and 0.00750 mol of O_2 are placed in a 1.00-L vessel at high temperature, 0.00370 mol of O_2 remains at equilibrium. Calculate the value of the equilibrium constant for the reaction



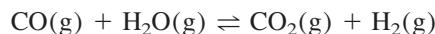
Compare this value to that found in Example 18.14, and also compare the equilibrium concentrations.

Calculations Using the Values of Equilibrium Constants

If the value of the equilibrium constant is given, we may solve for the equilibrium concentrations in terms of initial concentrations. Algebraic variables, such as x , are used in the equilibrium concentration terms.

EXAMPLE 18.15

Calculate the concentration of CO₂ at equilibrium if 0.0125 mol of CO and 0.0125 mol of H₂O gas are introduced into a 1.00-L flask at high temperature and allowed to come to equilibrium. The value of the equilibrium constant is 0.63.

**Solution**

The equilibrium constant expression is

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 0.63$$

Let x equal the equilibrium concentration of CO₂. Then,

	CO(g)	+	H ₂ O(g)	\rightleftharpoons	CO ₂ (g)	+	H ₂ (g)
<i>Initial concentrations</i>	0.0125		0.0125		0.00		0.00
<i>Change due to reaction</i>	$-x$		$-x$		x		x
<i>Equilibrium concentrations</i>	0.0125 - x		0.0125 - x		x		x

Substituting these values into the equilibrium constant expression yields

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{x^2}{(0.0125 - x)^2} = 0.63$$

Taking the square root of both sides yields

$$\frac{x}{(0.0125 - x)} = 0.794$$

$$x = 5.53 \times 10^{-3}$$

The concentration of each product is thus 5.53×10^{-3} mol/L, and that of each reactant is

$$0.0125 \text{ mol/L} - 0.00553 \text{ mol/L} = 0.00697 \text{ mol/L}$$

To check, put these values into the equilibrium constant expression, and solve for K :

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.00553)^2}{(0.00697)^2} = 0.63$$

The value checks.

Note that the square root of a number between 0 and 1 is larger than the number.

Extra Help

$$\begin{aligned} x &= 0.794(0.0125 - x) \\ &= 0.009925 - 0.794x \\ x + 0.794x &= 1.794x \\ &= 0.009925 \end{aligned}$$

EXAMPLE 18.16

At 525°C, $K = 3.35 \times 10^{-3}$ mol/L for the reaction



Calculate the concentration of carbon dioxide at equilibrium.

Solution

Because substances that are solids do not have terms in the equilibrium constant expression,

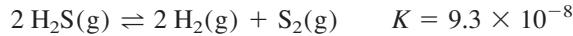
$$K = [\text{CO}_2] = 3.35 \times 10^{-3} \text{ mol/L}$$

Thus, the concentration of CO_2 is 3.35×10^{-3} mol/L.

If the equilibrium constant is very large, we expect very little of at least one of the reactants to remain unreacted. In contrast, if the equilibrium constant is very small, we expect very little of the products to be produced. We can use these facts to approximate some solutions to problems involving equilibrium constants because a small value *added to* or *subtracted from* a larger quantity has a negligible effect. In this book, approximations that cause an error of no greater than 5–10% are acceptable.

EXAMPLE 18.17

If 0.200 mol of H_2S is placed in a 1.00-L vessel at 700°C and allowed to come to equilibrium, what will the concentrations of H_2 and S_2 be?

**Solution**

	2 $\text{H}_2\text{S(g)}$	\rightleftharpoons	2 $\text{H}_2(\text{g})$	+	$\text{S}_2(\text{g})$
<i>Initial concentrations</i>	0.200		0.000		0.000
<i>Change due to reaction</i>	$-2x$		$+2x$		$+x$
<i>Equilibrium concentrations</i>	$0.200 - 2x$		$2x$		x

$$K = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2(x)}{(0.200 - 2x)^2} = 9.3 \times 10^{-8}$$

Because the value of K is so low, we expect x to have a very small value. We can thus ignore $2x$ when subtracted from the larger value, 0.200, which gives

$$K = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{4x^3}{(0.200)^2} = 9.3 \times 10^{-8}$$
$$x^3 = 9.3 \times 10^{-10}$$

$$[\text{S}_2] = x = 9.76 \times 10^{-4} = 9.8 \times 10^{-4} \text{ M}$$

$$[\text{H}_2] = 2x = 1.95 \times 10^{-3} = 2.0 \times 10^{-3} \text{ M}$$

This small value of $2x$ is insignificant when subtracted from 0.200.

Substitute the final concentration values into the equilibrium constant expression to check the approximation:

$$K = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(1.95 \times 10^{-3})^2(9.76 \times 10^{-4})}{(0.200)^2} = 9.3 \times 10^{-8}$$

Because this value of K is equal (within two significant digits) to the value given in the statement of the problem, the approximation is allowable.

18.4 ■ Equilibrium Constants**483**

Practice Problem 18.17 Consider the equilibrium given in Example 18.17. If 0.200 mol of H₂S and 0.200 mol of H₂ are placed in a 1.00-L vessel and allowed to come to equilibrium, what will the equilibrium concentration of S₂ be? Explain why this value is so different from that found in Example 18.17.

EXAMPLE 18.18

The following reaction occurs at 400°C:



If 0.0125 mol of H₂ and 0.0125 mol of I₂ are placed in a 1.00-L vessel and allowed to come to equilibrium, can an approximation be used in the calculation of the concentration of each substance at equilibrium? What is the concentration of gaseous iodine at equilibrium?

Solution

	H ₂ (g)	+	I ₂ (g)	⇒	2 HI(g)
<i>Initial concentrations</i>	0.0125		0.0125		0.00
<i>Change due to reaction</i>	-x		-x		+2x
<i>Equilibrium concentrations</i>	0.0125 - x		0.0125 - x		2x

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(0.0125 - x)^2} = 50.0$$

If we approximate by assuming that x is insignificant when subtracted from 0.0125:

$$K = \frac{(2x)^2}{(0.0125)^2} = 50.0$$

$$x^2 = 0.00195$$

$$x = 0.0442$$

This value of x is certainly *not* insignificant relative to 0.0125. It exceeds 0.0125, and it certainly cannot be ignored. A more exact solution method is required. Begin by taking the square root of each side of the original equilibrium constant expression:

$$\frac{2x}{0.0125 - x} = 7.071$$

$$x = 0.00974$$

$$[\text{HI}] = 2x = 0.0195 \text{ mol/L}$$

$$[\text{I}_2] = 0.0125 - 0.00974 = 0.00276 \text{ mol/L}$$

Checking:

$$\frac{(0.0195)^2}{(0.00276)^2} = 50$$

This method is sufficiently accurate.

Extra Help

$$\begin{aligned} 2x &= (0.0125 - x)7.071 \\ &= 0.08839 - 7.071x \\ 9.071x &= 0.08839 \end{aligned}$$

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CHAPTER 18 ■ Chemical Equilibrium



Snapshot Review



ChemSkill Builder 17.4

- An equilibrium constant is equal to a ratio of concentrations multiplied and divided, not added or subtracted. Each term is a numeric value, not a chemical.

- A. Write the equilibrium constant expression for the high-temperature reaction



- B. Calculate the value of the equilibrium constant for this reaction if 0.0400 mol of each reactant is placed in a 1.00-L flask and allowed to come to equilibrium, at which point there is 0.0325 mol of SO_2Cl_2 present.

Key Terms

Key terms are defined in the Glossary.

catalyst (18.1)
dynamic state (18.2)
enzyme (18.1)
equilibrium (18.2)
equilibrium constant (18.4)

equilibrium constant expression (18.4)
forward reaction (18.2)
LeChâtelier's principle (18.3)
proceed to the left (18.2)
proceed to the right (18.2)

rate (18.1)
reverse reaction (18.2)
shift (18.3)
state of subdivision (18.1)
stress (18.3)

Symbols

\rightleftharpoons (equilibrium) (18.2)

[A] (molarity of A) (18.4)

K (equilibrium constant) (18.4)

Summary

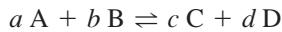
Six factors affect the rate of a chemical reaction: (1) the nature of the reactants, (2) the temperature, (3) the presence of a catalyst, (4) the concentration of a solute, (5) the pressure of a gas, and (6) the state of subdivision of a solid. The last two of these may be considered as effects of concentration (Section 18.1).

Two exactly opposite processes occurring in the same place at the same time at the same rate constitute a state called equilibrium. Although no reaction appears to be occurring in a mixture at equilibrium because the effects of the opposite processes cancel each other, each process continues. We say that equilibrium is a dynamic state. Both reactions can be represented in one chemical equation, using a double arrow to indicate an equilibrium (Section 18.2).

LeChâtelier's principle governs the response of a system initially at equilibrium to a stress (an external

change) placed on it. The equilibrium tends to reduce the stress. For example, an equilibrium will shift to reduce the concentration of a substance that has just been added to the system, to use up heat in a system whose temperature has just been raised (heat has been added), or to produce more moles of gas (thus raising the pressure) because of a decrease in all the partial pressures. However, addition of a catalyst causes no shift in an equilibrium. LeChâtelier's principle is qualitative; it indicates the direction of an equilibrium shift but not the extent (Section 18.3).

Quantitative calculations can be made for systems at equilibrium using the equilibrium constant expression. For the general reaction



■ Self-Tutorial Problems**485**

the following ratio is a constant:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The equilibrium concentrations of the substances on the right side of the chemical equation are placed in the numerator and divided by the equilibrium concentrations of the substances on the left side, all raised to their appropriate powers (equal to the coefficients in the balanced equation).

Given equilibrium concentrations, the value of K can be calculated by simply substituting those concentrations in the equilibrium constant expression. A somewhat more difficult problem gives initial concentrations of some reactants and one equilibrium concentration and requires

determination of the equilibrium concentrations of the other substances followed by substitution into the equilibrium constant expression to solve for K . We can apply the concepts used to solve problems involving limiting quantities (Section 10.4) to find the equilibrium concentrations and use a tabulation method to make the solution process easier. The balanced chemical equation governs the *changes* in concentrations. If initial concentrations of some reactants and the value of K are given, algebraic variables (such as x) are used for the equilibrium concentrations. We substitute these quantities in the equilibrium constant expression and solve for x , the unknown equilibrium concentration. Approximations that involve ignoring small concentrations only when they are added to or subtracted from larger ones are often helpful (Section 18.4).

Items for Special Attention

- The equilibrium concentrations, not numbers of moles, are the factors in equilibrium constant expressions.
- In equilibrium constant expressions, the concentration terms are multiplied and divided, not added or subtracted. The concentrations in the numerator are those of the substances on the right side of the chemical equation, and those in the denominator are for the substances on the left side. The exponents in the equilibrium constant expression

correspond to the coefficients in the balanced chemical equation.

- The balanced chemical equation governs the concentrations produced and used up by the reaction (the second row of a tabulation such as those used in the examples in Section 18.4). We can treat concentrations in this way because the concentration ratio of the substances in a given solution or gas mixture is the same as the mole ratio.

Answers to Snapshot Reviews

- 18.1 A. In pure oxygen, because the oxygen pressure is much higher.
 18.2 A. If equilibrium is achieved in both experiments, she should get 0.825 mol of A, just as she had remaining in the forward reaction.
 18.3 A. (a) Toward the elements. (b) Heat is used up, so the temperature will drop.
 18.4 A. $K = \frac{[\text{SO}_2\text{Cl}_2][\text{POCl}_3]}{[\text{SO}_3][\text{PCl}_5]}$

- B. All in moles per liter:

	$\text{PCl}_5(\text{g})$	$+\text{SO}_3(\text{g})$	\rightleftharpoons	$\text{SO}_2\text{Cl}_2(\text{g})$	$+\text{POCl}_3(\text{g})$
<i>Initial</i>	0.0400	0.0400		0.0000	0.0000
<i>Change</i>	-0.0325	-0.0325		+0.0325	+0.0325
<i>Final</i>	0.0075	0.0075		0.0325	0.0325

$$K = \frac{(0.0325)^2}{(0.0075)^2} = 19$$
Self-Tutorial Problems

- 18.1 If an equilibrium shifts to the right in response to a stress, is that shift another stress?
 18.2 Which of the following statements is a correct interpretation of this balanced chemical equation?

$$4 \text{Cl}_2(\text{g}) + \text{CH}_4(\text{g}) \xrightarrow{\text{High temp}} 4 \text{HCl}(\text{g}) + \text{CCl}_4(\text{g})$$
 (a) Only 4 mol of Cl_2 and 1 mol of CH_4 can be put into a vessel.
 (b) Only 4 mol of Cl_2 for every 1 mol of CH_4 can be put into a vessel.
 (c) No matter how much of each reactant is added to a vessel, only 4 mol of Cl_2 and 1 mol of CH_4 will react.
 (d) When 4 mol of Cl_2 and 1 mol of CH_4 are placed in a vessel, they will react to give 4 mol of HCl .
 (e) Cl_2 and CH_4 react in a 4 : 1 mole ratio.

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- 18.3 Explain why the concentration ratios in addition to mole ratios are governed by the balanced chemical equation for an equilibrium system in a solution.
- 18.4 (a) What is the rate of decomposition of ammonia at the point where hydrogen and nitrogen are first introduced into an empty reaction vessel at 500°C?
(b) What happens to this rate as time passes?
- 18.5 Write an equilibrium constant expression for the following reaction:
- $$\text{CH}_3\text{OH}(\ell) + \text{HCHO}_2(\ell) \rightleftharpoons \text{CH}_3\text{OCHO}(\ell) + \text{H}_2\text{O}(\ell)$$
- 18.6 Write an equilibrium constant expression for each of the following reactions:
- (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons \text{HI}(\text{g}) + \text{HI}(\text{g})$
(b) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$
(c) $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2 \text{HI}(\text{g})$
- 18.7 Write an equilibrium constant expression for each of the following reactions:
- (a) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$
(b) Heat + $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$

Problems**18.1 Rates of Reaction**

- 18.11 Calculate the number of moles per liter of a gas at 25°C and (a) 0.800 atm pressure and (b) 2.00 atm pressure.
(c) Show that, all other conditions remaining the same, the pressure of a gas and its concentration in moles per liter are directly proportional.
- 18.12 How can scouts on a camping trip get a log to burn faster?
- 18.13 A certain industrial process produces 10.5 mol/L of product per minute at 25°C. How could that same reaction be speeded up to produce 21.0 mol/L of product per minute without changing the nature or concentrations of the reactants or the temperature?
- 18.14 A certain reaction produces 1.50 mol/L of product per minute at 25°C. How could that same reaction be speeded up to produce 6.00 mol/L of product per minute without change in the contents of the reaction vessel?
- 18.15 (a) At which of the following temperatures will the decomposition reaction of the Haber process go fastest?

$$0^\circ\text{C} \quad 200^\circ\text{C} \quad 500^\circ\text{C}$$

- (b) At which of these temperatures will the combination reaction go fastest?
- 18.16 (a) Calculate the surface area of a cube that is 1.00 cm on each edge (see Figure 18.1).
(b) How much will the surface area increase if the cube is cut in half, as shown in the figure?

CHAPTER 18 ■ Chemical Equilibrium

- 18.8 Write an equilibrium constant expression for each of the following reactions:
- (a) $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
(b) $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{heat}$
- 18.9 What is the relationship between the equilibrium constant values for the two equations in each of the following sets?
- (a) $\text{N}_2\text{O}_4(\ell) \rightleftharpoons 2 \text{NO}_2(\text{g})$
$$2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\ell)$$

(b) $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g})$
$$\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$$
- 18.10 Write an equilibrium constant expression for each of the following reactions:
- (a) $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g})$
(b) $2 \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}(\text{g})$
(c) $2 \text{NaHCO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$

- (c) How much will the surface area be if the cube is cut nine times in each direction—vertically front to back, vertically side to side, and horizontally (to make 20 surfaces in each direction)?

18.2 The Condition of Equilibrium

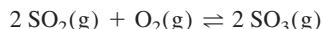
- 18.17 (a) At a certain point in a reaction leading to the equilibrium system
- $$2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g})$$
- the rate of decomposition of CO_2 is 2.28×10^{-5} mol/L·s. What is the rate of combination of CO with O_2 if this point is at the start of this experiment?
- (b) What is the rate of combination of CO with O_2 if at this point the system is at equilibrium?
- 18.18 At a certain point in a reaction leading to the equilibrium system
- $$2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g})$$
- the rate of combination of O_2 with CO is 6.14×10^{-5} mol/L·s. What is the rate of combination of CO at this point?
- 18.19 At a certain point in a reaction leading to the equilibrium system
- $$2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g})$$

■ Problems

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the rate of reaction of O_2 is 2.55×10^{-3} mol/L·s and the rate of reaction of CO_2 is 4.05×10^{-3} mol/L·s. At what point is the system toward achieving equilibrium?

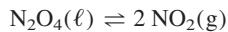
- 18.20 (a) At a certain point in a reaction leading to the equilibrium system



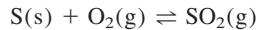
the rate of decomposition of SO_3 is 9.50×10^{-3} mol/L·s, and the rate of reaction of O_2 is 5.50×10^{-3} mol/L·s. When the reaction gets to equilibrium, will there be more or less SO_3 present than there is at this point?

- (b) Was SO_3 or SO_2 plus O_2 the starting material in this experiment?

- 18.21 If N_2O_4 is decomposing at 0.929 mol/h and NO_2 is combining at 0.929 mol/h, is the system at equilibrium?

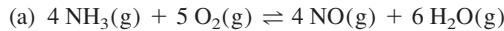


- 18.22 What change in concentration of sulfur occurs as the following equilibrium shifts left?

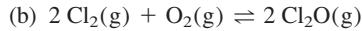


18.3 LeChâtelier's Principle

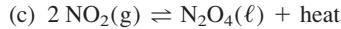
- 18.23 State the direction of the shift of equilibrium (if any) in each of the following systems that will be caused by the indicated change:



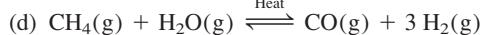
Removing NH_3



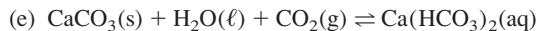
Adding Cl_2O



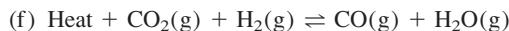
Increasing the total volume



Adding a catalyst



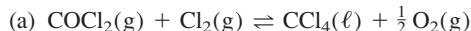
Adding CO_2



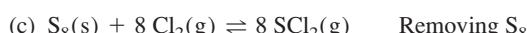
Raising the temperature



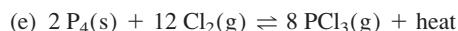
- 18.24 State the direction of the shift of equilibrium (if any) in each of the following systems that will be caused by the indicated change:



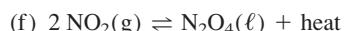
Removing Cl_2



Increasing the volume

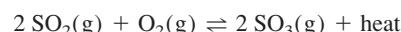


Raising the temperature

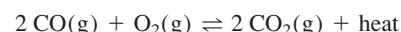


Cooling the system

- 18.25 What is the effect of raising the temperature on the total pressure of the following system at equilibrium?



- 18.26 What shift, if any, will occur in the following system at equilibrium as a result of each change?



- (a) Adding CO_2

- (b) Increasing the volume

- (c) Adding CO

- (d) Removing O_2

- (e) Adding O_2

- (f) Increasing the temperature

- (g) Adding a catalyst

- 18.27 What shift, if any, will occur in the following system at equilibrium as a result of each change?



- (a) Adding NO

- (b) Adding NH_3

- (c) Removing $H_2O(g)$

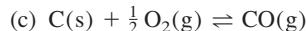
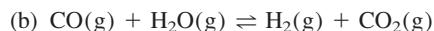
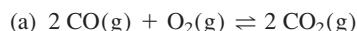
- (d) Adding O_2

- (e) Decreasing the temperature

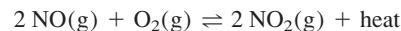
- (f) Increasing the volume

- (g) Adding a catalyst

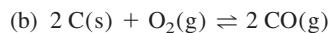
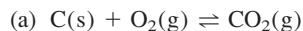
- 18.28 What is the effect, if any, of increasing the total volume on each of the following systems at equilibrium?



- 18.29 What is the effect of lowering the temperature on the following system at equilibrium?

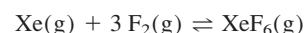


- 18.30 What effect on each of the following systems at equilibrium will the removal of half of the carbon have on the concentration of O_2 ?



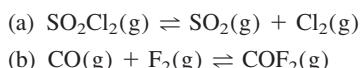
18.4 Equilibrium Constants

- 18.31 Write an equilibrium constant expression for the following reaction:

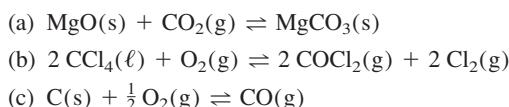


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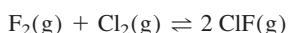
- 18.32** Write an equilibrium constant expression for each of the following reactions:



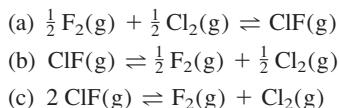
- 18.33** Write an equilibrium constant expression for each of the following reactions:



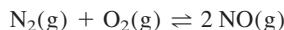
- 18.34** At a certain temperature, the value of the equilibrium constant for the following reaction is 6.4×10^9 :



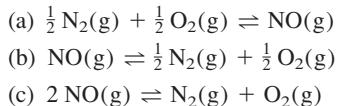
Calculate the value of the equilibrium constant for each of the following reactions:



- 18.35** At a certain temperature, the value of the equilibrium constant for the following reaction is 6.7×10^{-31} :



Calculate the value of the equilibrium constant for each of the following reactions:



- 18.36** Calculate the value of the equilibrium constant for the reaction $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ if 2.62 mol of COCl_2 is introduced into a 2.00-L reaction vessel and allowed to come to equilibrium, at which point 0.010 mol/L of COCl_2 remains.

- 18.37** Calculate the value of the equilibrium constant for the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$ if 0.100 mol of NO_2 is introduced into a 1.00-L reaction vessel and allowed to come to equilibrium, at which point 8.8×10^{-6} mol/L of NO_2 remains.

- 18.38** For the following equilibrium at 725°C , $K = 3.8 \times 10^{-5}$:

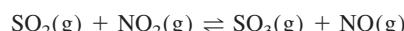
**CHAPTER 18 ■ Chemical Equilibrium**

Calculate the concentration of iodine atoms after 0.0100 mol of I_2 is introduced into a 1.00-L vessel and allowed to come to equilibrium.

- 18.39** Calculate the equilibrium concentration of C for the following reaction if 0.0600 mol of A and 0.0600 mol of B are introduced into a 2.00-L reaction vessel and allowed to come to equilibrium:

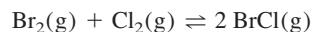


- 18.40** At 700°C , $K = 9.00$ for the following reaction, which is one of the reactions in the commercial production of sulfuric acid:



If $[\text{NO}] = 0.0515 \text{ mol/L}$, $[\text{NO}_2] = 0.00418 \text{ mol/L}$, and $[\text{SO}_2] = 0.0675 \text{ mol/L}$ at equilibrium, what is the concentration of SO_3 ?

- 18.41** Calculate the value of K for the following equilibrium at high temperature (where all the substances involved are gases) if 0.0333 mol of Br_2 and 0.0366 mol of Cl_2 are placed in a 1.00-L vessel, and at equilibrium there is 0.0133 mol/L of Br_2 remaining:

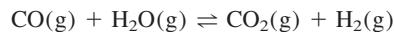


- 18.42** For the following equilibrium at 680°C , $K = 0.520$:



Calculate the CO concentration at equilibrium after 0.0200 mol each of CO_2 and H_2 are placed in a 2.00-L vessel and allowed to come to equilibrium.

- 18.43** For the following reaction at 600°C , $K = 2.44$:



Calculate the concentration at equilibrium of CO_2 if 0.400 mol of CO and 0.400 mol of H_2O are placed in a 2.00-L container and allowed to come to equilibrium at 600°C .

- 18.44** If 0.150 mol of T is placed in a 1.00-L vessel and allowed to come to equilibrium, what will be the equilibrium concentration of R? Solve this problem with each of the following equations, and compare the answers:

**General Problems**

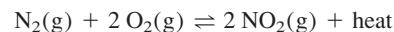
- 18.45** What effect, if any, is predicted by LeChâtelier's principle if the temperature is increased for a mixture of nitrogen and oxygen only?



- 18.46** A 1.00-L mixture of SO_2 , O_2 , and SO_3 at 100°C is heated to 500°C at constant pressure. Explain why Charles' law

(Section 12.3) cannot be used to calculate the new volume of the mixture.

- 18.47** At a certain point in a reaction leading to the equilibrium system

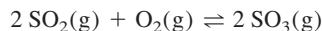


■ General Problems

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the rate of decomposition of NO_2 is 4.00×10^{-3} mol/L·s, and the rate of reaction of N_2 is 2.50×10^{-3} mol/L·s. In which direction is the reaction proceeding?

- 18.48 (a) At a certain point in a reaction leading to the equilibrium system



the rate of decomposition of SO_3 is 1.92×10^{-3} mol/L·s, and the rate of reaction of O_2 is 8.83×10^{-4} mol/L·s. When the reaction gets to equilibrium, will there be more or less SO_3 present than there is at this point?

- (b) Was SO_3 or SO_2 plus O_2 the starting material in this experiment?

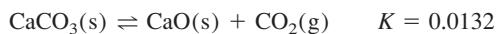
- 18.49 At a certain point in a reaction leading to the equilibrium system



the rate of decomposition of NH_3 is 3.00×10^{-3} mol/L·s, and the rate of reaction of H_2 is 4.50×10^{-3} mol/L·s. In which direction, if either, is the reaction proceeding?

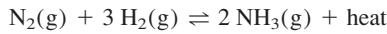
- 18.50 Calculate the total surface area after a cube 1.00 cm on each edge has been divided into cubes 1.00 mm on each edge. Compare this surface area to that of the 1-cm³ cube of Problem 18.16(a).

- 18.51 (a) Calculate the concentration of $\text{CO}_2(\text{g})$ after 0.100 mol of CaCO_3 is placed in a 1.00-L vessel and allowed to come to equilibrium at 800°C.



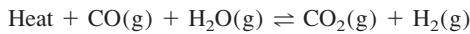
- (b) What would the concentration be if 0.0100 mol had been used?

- 18.52 (a) Will the following equilibrium proceed to the right most completely at a temperature of 0°C, 200°C, or 500°C?



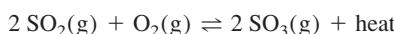
- (b) Explain why a temperature of 500°C is used in the industrial production of ammonia (the Haber process). (*Hint:* See Problem 18.15.)

- 18.53 Predict, if possible, the direction of the shift in the equilibrium of the following system as a result of each pair of changes:



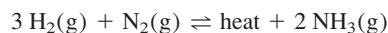
- (a) Adding a catalyst and CO
(b) Removing H_2 and H_2O
(c) Adding H_2O and increasing the temperature
(d) Adding CO and lowering the temperature

- 18.54 Predict, if possible, the direction of the shift in the equilibrium of the following system as a result of each pair of changes:

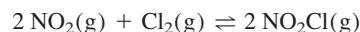


- (a) Adding O_2 and raising the temperature
(b) Adding SO_3 and decreasing the volume
(c) Adding SO_2 and SO_3
(d) Adding a catalyst and removing SO_3

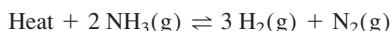
- 18.55 What is the effect on the temperature of adding nitrogen to the following system at equilibrium?



- 18.56 If 0.100 mol of Cl_2 and 0.190 mol of NO_2 are placed in a 750-mL vessel and allowed to come to equilibrium at a certain temperature, the equilibrium concentration of NO_2Cl is 0.076 mol/L. What is the value of K for the following equilibrium at that temperature?



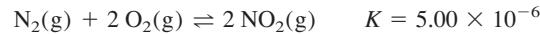
- 18.57 What is the effect on the temperature of increasing the volume of the following system at equilibrium?



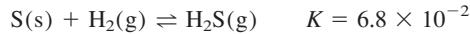
- 18.58 If 0.400 mol of Cl_2 and 0.800 mol of NO_2 are placed in a 2.00-L vessel and allowed to come to equilibrium at a certain temperature, the equilibrium concentration of NO_2Cl is 0.150 mol/L. What is the value of K for the following equilibrium at that temperature?



- 18.59 Calculate the equilibrium concentration of each species after 0.0500 mol of NO_2 is heated to a high temperature in a 1.000-L vessel, at which point it partially decomposes to its elements.

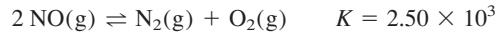


- 18.60 At 90°C, the following equilibrium is established:



If 0.150 mol of hydrogen and 0.500 mol of sulfur are heated to 90°C in a 1.00-L vessel, what will be the *pressure* of H_2S at equilibrium?

- 18.61 Calculate the equilibrium concentration of each species after 0.180 mol of NO is heated to 2000 K in a 1.000-L vessel, at which point it partially decomposes to its elements.



- 18.62 An equilibrium mixture of N_2 , H_2 , and NH_3 contains isotopically pure ^1H . That is, there is no deuterium (^2H , also denoted by D) in the system. A mixture of D_2 , N_2 , and ND_3 in the same ratio as the equilibrium mixture is added to that mixture. What hydrogen-containing substances will be found in the equilibrium mixture after the passage of sufficient time? Explain.

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Acid-Base Theory

- 19.1 The Brønsted Theory
- 19.2 Dissociation Constants
- 19.3 Autoionization of Water
- 19.4 Buffer Solutions
- 19.5 Polyprotic Acids



Phenolphthalein in acid and base

Review Clues

- Chapter 19** Chapters 8, 9, 10, 11, 18
Section 19.1 Section 8.4, Chapter 9
Section 19.2 Section 11.2, Chapters 9, 18
Section 19.3 Chapter 9
Section 19.4 Chapter 9
Section 19.5 Sections 6.3, 8.4, 10.4

Objectives

- 19.1** To extend the definitions of acids and bases to explain why the solutions of most salts are acidic or basic in water
19.2 To use equilibrium constants for acid-base reactions
19.3 To calculate the effects of the ionization of water
19.4 To understand buffer solutions and to calculate their resistance to changes in pH
19.5 To use equilibrium constants for acids with more than one ionizable hydrogen atom

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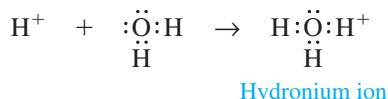
In Chapter 8, we learned the Arrhenius definition of acids and bases—that an acid is a substance that can increase the concentration of H^+ ions in water and a base is a substance that can increase the concentration of OH^- ions in water. In Chapter 18, we learned about equilibrium systems. This chapter extends both of these concepts in discussing acid-base equilibria in aqueous solutions, which are extremely important to biological as well as chemical processes.

Section 19.1 discusses the Brønsted theory of acids and bases, which extends the concepts of acid and base beyond aqueous solutions and also explains the acidic or basic nature of solutions of most salts. Dissociation constants, the equilibrium constants for the reactions of weak acids or bases with water, are introduced in Section 19.2. The concept of the ionization of covalent compounds is extended to water itself in Section 19.3, which also covers pH, a scale of acidity and basicity. Section 19.4 describes buffer solutions, which resist change in their acidity or basicity even when some strong acid or base is added. Both the preparation and the action of buffer solutions are explained. Section 19.5 discusses the equilibria of acids containing more than one ionizable hydrogen atom per molecule.

19.1 The Brønsted Theory

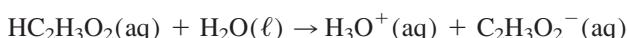
In 1923, Johannes N. Brønsted (1879–1947) and Thomas M. Lowry (1874–1936) independently defined acids and bases in a different way from the Arrhenius definitions. The resulting theory is sometimes called the Brønsted-Lowry theory, but more often is referred to as just the Brønsted theory. The **Brønsted theory** extends the definitions of acid and base in a way that explains more than the Arrhenius definitions can explain. According to this theory, a **Brønsted acid** is a **proton donor**, and a **Brønsted base** is a **proton acceptor**.

In this context, a **proton** is defined as the nucleus of a hydrogen atom. It has nothing to do with the protons in a chlorine nucleus, a sodium nucleus, or any other nucleus. The nucleus of a normal hydrogen atom (${}^1\text{H}$) consists of one proton, but the Brønsted definition of a proton also includes the nucleus of heavy hydrogen (${}^2\text{H}$). The proton is not a stable chemical species. Because it has no electrons and is an extremely tiny particle (even on the atomic scale), it has an extremely high density of positive charge. It is capable of sharing (negatively charged) electrons with any species that has a lone pair of electrons. In an aqueous solution, it shares a pair of electrons with a water molecule, forming the **hydronium ion** (H_3O^+):



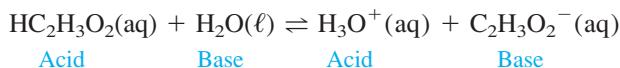
All the atoms in the hydronium ion have the required numbers of electrons to be stable (Section 5.5), and the ion is chemically stable (in the absence of bases and active metals).

Acids are proton donors. When acetic acid is dissolved in water, it reacts with the water, as follows:

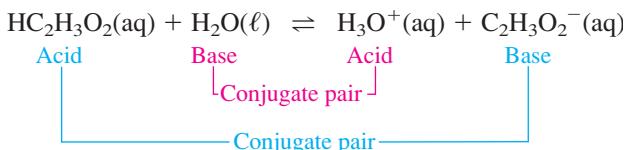


The $\text{HC}_2\text{H}_3\text{O}_2$ molecule donates its proton (H^+) to the H_2O molecule, so the acetic acid is acting as a Brønsted acid. However, the water molecule accepts

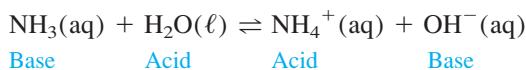
that proton, so in this reaction, the water molecule is acting as a Brønsted base. Moreover, the reaction is an equilibrium reaction because it proceeds to the left as well. In the reverse reaction, the hydronium ion donates the proton to the acetate ion, and these ions are thus an acid and a base, respectively:



The acid on the left ($\text{HC}_2\text{H}_3\text{O}_2$) and the base on the right ($\text{C}_2\text{H}_3\text{O}_2^-$) are related to each other; they differ by one proton (H^+). They are called a **conjugate acid-base pair**. Similarly, the base on the left (H_2O) and the acid on the right (H_3O^+) are related in the same way and are also a conjugate pair. Every Brønsted acid has a **conjugate base**, and every Brønsted base has a **conjugate acid**.



The reaction of ammonia with water extends these concepts:

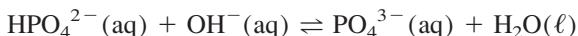
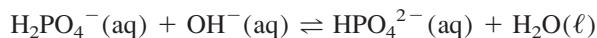
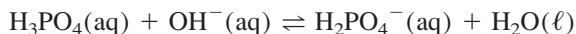


In the forward reaction, the ammonia molecule accepts a proton from the water molecule and thus is a base. The water molecule donates the proton, so in this reaction, water acts as an acid. In the reverse reaction, the ammonium ion acts as an acid, and the hydroxide ion acts as a base.

Thus, water can act as an acid, and it also can act as a base, even though we are not used to thinking of it as being either acidic or basic. It acts as an acid in the presence of a stronger base and as a base in the presence of a stronger acid. We say that water is **amphotropic**.

EXAMPLE 19.1

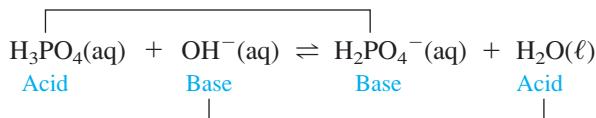
- (a) Classify each species in the following reactions as an acid or a base, and connect each conjugate pair:

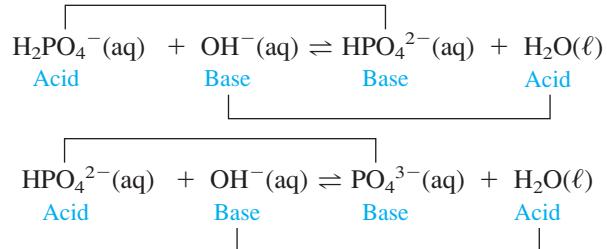


- (b) Identify the species in part (a) that are Brønsted acids in one reaction and Brønsted bases in another.

Solution

(a)



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- (b) The ion H_2PO_4^- is a base in the first reaction and an acid in the second.
 The ion HPO_4^{2-} is a base in the second reaction and an acid in the third.

Practice Problem 19.1 Rewrite the equations of Example 19.1 as total equations, using KOH as the base. Do all the acids have hydrogen written first?

$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	Acidic
$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	Neutral
$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	Basic

An aqueous solution is acidic if and only if the hydronium ion concentration is greater than the hydroxide ion concentration, and a solution is basic if and only if the hydroxide ion concentration is greater than the hydronium ion concentration. The solution is neutral if the concentrations of these two ions are equal.

Acid and Base Strength

Acid strength determines to what extent an acid reacts with water. All acids react extensively with Arrhenius bases.

We learned in Chapter 8 that some acids are strong and others are weak. Its **acid strength** determines to what extent any acid reacts with water to form hydronium ions. The equilibrium for the reaction of a strong acid with water proceeds far to the right. Essentially 100% of a strong molecular acid reacts with water to form hydronium ions. The equilibrium for ionization of a weak acid in water proceeds very little to the right. (Remember that both strong and weak acids react extensively with Arrhenius bases.) Because different acids ionize to different extents, it is not surprising that their conjugate bases also have different tendencies to react with hydronium ions or with water. That is, *the stronger the conjugate acid, the weaker is its conjugate base*.

Hydrogen chloride is a strong acid, meaning that it reacts with water essentially 100%. The chloride ion formed has virtually no attraction for hydronium ion at room temperature. Chloride ion can be said to be a **feeble base**. Less strong acids, such as acetic acid, ionize only a few percent. Their conjugate bases are stronger than those of strong acids. Some acids, such as boric acid, ionize to a very limited extent; an acid like this may be called a **feeble acid**. Its conjugate base reacts almost 100% with hydronium ion to form the molecular acid. In fact, conjugates of feeble acids react extensively even with water to form the acid. In short, the stronger the acid or base, the weaker is its conjugate. The relative strengths of conjugate acid-base pairs are summarized in Table 19.1.

Like acids, bases also can be strong, weak, or feeble. Most strong bases are ionic compounds when pure, and they dissociate completely into separate ions when dissolved in water. For example,

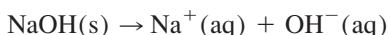
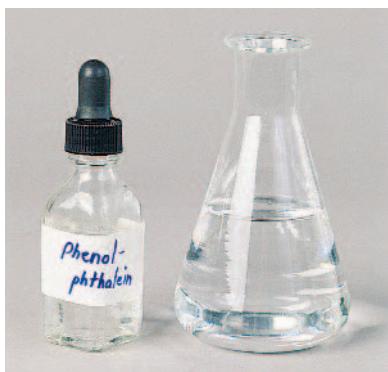


Table 19.1 Relative Strengths of Acids and Bases and Their Conjugates

Conjugate Acid	Conjugate Base
Strong	Feeble
Weak	Weak
Feeble	Strong

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CHAPTER 19 ■ Acid-Base Theory



This is more a solution process than a chemical reaction. In contrast, weak bases, like weak acids, *react* slightly with water to form ions. The reaction of ammonia with water, described earlier, is one example. Conjugate ions of molecular acids are also bases, as just described. **Base strength** determines the extent to which a base interacts with water to form ions. The stronger the base, the weaker its conjugate acid.

Because nitrate ion (NO_3^-) has no tendency to react with hydronium ion, how much should we expect it to react with water? (Hydronium ion is certainly a stronger acid than water; it produces water as its conjugate base when it reacts with another base.) Because nitrate ion does not react with hydronium ion, it certainly has no tendency to react with water; it is a feeble base.



EXAMPLE 19.2

Acetic acid is a weak acid. How strong is its conjugate base?

Solution

Table 19.1 shows that the conjugate of a weak acid is a weak base. The acetate ion is weakly basic.

Practice Problem 19.2 How strong a base is (a) the perchlorate ion? (b) the carbonate ion?

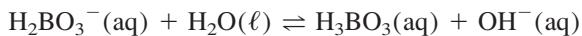


EXAMPLE 19.3

Boric acid is a feeble acid. (It is so weak that its solution is used to bathe infected eyes.) How strong a base is its conjugate—the dihydrogen borate ion, H_2BO_3^- ?

Solution

Because the acid is feeble, its conjugate base is strong. The H_2BO_3^- ion reacts extensively with water to form H_3BO_3 and OH^- (Figure 19.1):



Acidic or Basic Nature of Salt Solutions

Aqueous solutions of most salts test acidic or basic. We can explain this in terms of the strengths of Brønsted acids and bases. For example, an aqueous solution of sodium acetate tests basic to litmus paper. The solutes are the feeble acid Na^+ and the weak base $\text{C}_2\text{H}_3\text{O}_2^-$. Because the base present is a *stronger* base (not a strong base) than the acid present is an acid, the solution tests basic:

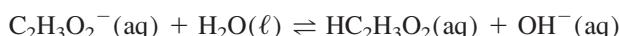


Figure 19.1 Basicity of Sodium Dihydrogen Borate Solution

A solution of NaH_2BO_3 in water turns phenolphthalein red because of the extensive reaction of H_2BO_3^- with water.

19.1 ■ The Brønsted Theory**495**

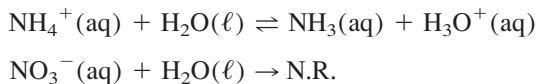
The presence of excess OH^- (relative to the quantity of H_3O^+) in the solution is what makes the solution basic.

EXAMPLE 19.4

A solution of ammonium nitrate tests acidic to litmus paper. Explain why such a solution is acidic.

Solution

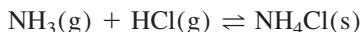
The solution contains a feeble base (nitrate ion) and a weak acid (ammonium ion). The acid is stronger than the base, so the solution is somewhat acidic:



The hydronium ion concentration is greater than the hydroxide ion concentration, so the solution is somewhat acidic.

Acids and Bases Without Water

The Brønsted theory extends the concepts of acid and base beyond reactions in aqueous solution. For example, it describes the reaction of ammonia gas with hydrogen chloride gas to form solid ammonium chloride:



Here, hydrogen chloride donates its proton to the lone pair of electrons on the ammonia molecule and is therefore a Brønsted acid. The ammonia molecule is a base because it accepts that proton. The same pair of substances act as a base and an acid in aqueous solution.



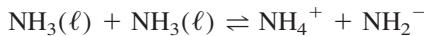
Snapshot Review



ChemSkill Builder 18.1

- The Brønsted theory expands the definitions of acids and bases to explain the acidity or basicity of solutions previously regarded as salts and to explain reactions in other than aqueous solutions.

- A. Label each substance in the equation for the autoionization of liquid ammonia as Brønsted acid or base:



- B. Which of the following equilibrium reactions is expected to proceed almost to completion?

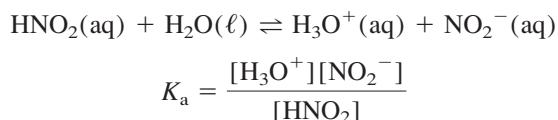
- (a) $\text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\ell)$
 (b) $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

- C. Write each of the equations of Problem B in the reverse direction. Which of *these* reactions is expected to proceed almost to completion?

- D. What is the conjugate base of H_3PO_3 ?

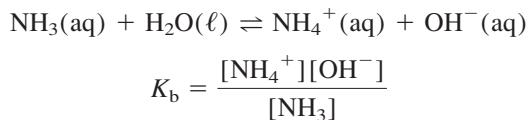
19.2 Dissociation Constants

Because the reactions of Brønsted acids and bases with water are equilibrium reactions, we can write equilibrium constant expressions for these **ionizations** or **dissociations**. For example, the dissociation of nitrous acid in water and its equilibrium constant expression are as follows:



The concentration of water is not included explicitly in this expression (it is incorporated into the value of K_a) because in dilute aqueous solution, the concentration of water is a constant, almost equal to the concentration of water when pure (55.6 M). The constant K_a is called the **acid dissociation constant**. The subscript “a” indicates that the constant is for the ionization of an *acid*.

Similarly, an equilibrium constant expression can be written for the reaction of a weak base with water:



The constant K_b is called the **base dissociation constant**. The subscript “b” indicates that the constant is for the ionization of a *base*.

Either K_a or K_b may sometimes be represented by K_i , called an **ionization constant** because ions are formed in these reactions.

Selected values of K_a and K_b are presented in Table 19.2. Although the reactions are equilibria and can be written with either set of species on the left, the equilibrium constant values in such tables represent the equations with the molecular acid or base on the *left* and the ions on the *right*.

EXAMPLE 19.5

Calculate the hydronium ion concentration of 1.77 M HNO_3 .

Table 19.2 Selected K_a and K_b Values

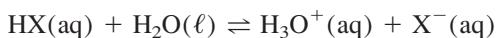
Acid	Formula	K_a	Base	Formula	K_b
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.76×10^{-5}	Ammonia	NH_3	1.77×10^{-5}
Boric acid	HBH_2O_3	7.3×10^{-10}	Methylamine	CH_3NH_2	4.4×10^{-4}
Formic acid	HCHO_2	1.7×10^{-4}	Pyridine	$\text{C}_5\text{H}_5\text{N}$	2.3×10^{-9}
Hydrofluoric acid	HF	6.7×10^{-4}			
Nitrous acid	HNO_2	4.5×10^{-4}			
Phenol	HOCH_2H_5	1.3×10^{-10}			

19.2 ■ Dissociation Constants**497****Solution**

Nitric acid is a strong acid and in aqueous solution is 100% ionized to H_3O^+ and NO_3^- . The hydronium ion concentration is therefore 1.77 M. (The nitrate ion concentration is also 1.77 M.)

EXAMPLE 19.6

When 0.1000 mol of an unknown acid, represented as HX, is dissolved in enough water to make 1.000 L of solution, the hydronium ion concentration is found to be 6.93×10^{-3} M. Calculate the value of K_a for HX.

**Solution**

The initial concentrations, changes in concentration, and equilibrium concentrations can be tabulated as in Chapter 18:

	HX(aq)	$+$	$\text{H}_2\text{O}(\ell)$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	$+$	$\text{X}^-(\text{aq})$
<i>Initial</i>	0.1000				0		0
<i>Change</i>	-0.00693				+0.00693		+0.00693
<i>Equilibrium</i>	0.09307				0.00693		0.00693

The value of K_a can then be calculated, using the equilibrium concentrations:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} = \frac{(0.00693)^2}{(0.09307)} = 5.16 \times 10^{-4}$$

EXAMPLE 19.7

Calculate the hydronium ion concentration and the acetate ion concentration that result when 0.160 mol of acetic acid is dissolved in enough water to make 1.00 L of solution.

Solution

The initial concentration of acetic acid (before ionization) is 0.160 M. After it ionizes, its concentration and those of its products can be tabulated:

	$\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$	$+$	$\text{H}_2\text{O}(\ell)$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	$+$	$\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$
<i>Initial</i>	0.160				0.00		0.00
<i>Change</i>	-x				+x		+x
<i>Equilibrium</i>	0.160 - x				x		x

The equilibrium constant expression and the value of K_a from Table 19.2 can be used to solve for x:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{(0.160 - x)} = 1.76 \times 10^{-5}$$

Ignoring x when it is subtracted from 0.160 yields

$$x^2 = 2.816 \times 10^{-6}$$

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CHAPTER 19 ■ Acid-Base Theory

Taking the square root of both sides of the equation yields

$$x = 1.68 \times 10^{-3}$$

Because x represents both the hydronium ion concentration and the acetate ion concentration, both of these are equal to 1.68×10^{-3} M. Finally, 1.68×10^{-3} M is about 1% of 0.160 M, so the approximation is acceptable.

Practice Problem 19.7 Calculate the hydroxide ion concentration that results when 0.160 mol of ammonia is dissolved in enough water to make 1.00 L of solution.



Snapshot Review



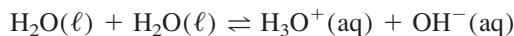
ChemSkill Builder
18.1, 18.5

- The ionization constant expression has no term for the concentration of water because it is used for dilute aqueous solutions only, in which the concentration of water is constant.

- A. Calculate the concentration of ammonium ion in 0.0165 M aqueous ammonia. $K_b = 1.77 \times 10^{-5}$

19.3 Autoionization of Water

We learned in Section 19.1 that water can act as either an acid or a base. In fact, water can act as both an acid and a base *in the same reaction*:



This reaction, which is an example of **autoionization**, proceeds to the right to only a very tiny extent because water is such a weak acid and base. To write an equilibrium constant expression for this reaction, we again consider the concentration of water itself to be a constant, which we incorporate into the value of K . We get another type of constant, called the **water ionization constant** and denoted K_w :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Note that this equilibrium constant expression has no denominator and also that the corresponding chemical equation is written with water as the reactant (on the left). The value of K_w for dilute aqueous solutions at 25°C is 1.00×10^{-14} . Because the product $[\text{H}_3\text{O}^+][\text{OH}^-]$ is a constant, the concentration of hydronium ion in any dilute aqueous solution can be calculated from the concentration of hydroxide ion, and vice versa.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

EXAMPLE 19.8

Calculate the hydronium ion concentration of a solution in which the hydroxide ion concentration is 6.15×10^{-2} M.

19.3 ■ Autoionization of Water**499****Table 19.3** Approximate pH Values for Some Common Items

Item	pH
Gastric juice	1–2
Soft drinks	3
Vinegar	3
Orange juice	3.5
Tomatoes	4
Rainwater	6
Pure water	7
Human blood	7.3
Seawater	8.5
Baking soda, aqueous	8.5
Ammonia, aqueous	11–12
Washing soda, aqueous	12

Solution

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+](6.15 \times 10^{-2}) = 1.00 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14}}{6.15 \times 10^{-2}} = 1.63 \times 10^{-13} \text{ M}$$

Note that both hydronium ions and hydroxide ions are present in every dilute aqueous solution. A solution is acidic if the hydronium ion concentration is greater than the hydroxide ion concentration, neutral if these two concentrations are equal, and basic if the hydroxide ion concentration is greater than the hydronium ion concentration:

$$[\text{H}_3\text{O}^+] > [\text{OH}^-] \quad \text{Acidic}$$

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] \quad \text{Neutral}$$

$$[\text{H}_3\text{O}^+] < [\text{OH}^-] \quad \text{Basic}$$

EXAMPLE 19.9

Calculate the hydronium ion concentration in (a) a 0.10 M HCl solution and (b) a 0.10 M NaOH solution.

Solution

(a) HCl is a strong acid, so 0.10 M HCl consists of 0.10 M H_3O^+ and 0.10 M Cl^- . The hydronium ion concentration is 0.10 M.

(b) NaOH is a strong, soluble base, so the hydroxide ion concentration is 0.10 M. To find the hydronium ion concentration, use the K_w expression:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (\text{H}_3\text{O}^+)[0.10 \text{ M}] = 1.00 \times 10^{-14}$$

Thus,

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-13} \text{ M}$$

Practice Problem 19.9 Calculate the hydroxide ion concentration of (a) 0.0050 M HCl and (b) 0.0050 M NaOH.

To enable scientists to express the acidity of a solution without using exponential notation, a biologist invented the pH scale. The **pH** of a solution is defined as the negative of the logarithm of the *hydronium ion* concentration:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Significant digits in logarithms are treated in Appendix 1, pages 591–93. The pH values for some common items are presented in Table 19.3.

A similar term, pOH, is defined as the negative of the logarithm of the hydroxide ion concentration:

$$\text{pOH} = -\log [\text{OH}^-]$$

pOH is used much less often than pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

EXAMPLE 19.10

Calculate the pH of a solution that has a hydronium ion concentration of 3.5×10^{-5} M.

Solution

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.5 \times 10^{-5}) = 4.46$$

Practice Problem 19.10 Calculate the hydronium ion concentration of a solution with a pH of 12.014.

EXAMPLE 19.11

Analogously to pH, pOH can be defined as

$$\text{pOH} = -\log [\text{OH}^-]$$

Show that $\text{pH} + \text{pOH} = 14.00$ in all dilute aqueous solutions.

Solution

All we need to do is take the logarithm of the equation for K_w . (The log of a product is the sum of the logs of the terms.)

$$\begin{aligned}K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \\ \log(1.0 \times 10^{-14}) &= (-\text{pH}) + (-\text{pOH}) = -14.00\end{aligned}$$

Multiplying this last equation by -1 yields

$$\text{pH} + \text{pOH} = 14.00$$

This equation is useful to calculate pH from pOH, and vice versa.

EXAMPLE 19.12

Calculate the hydronium ion concentration of a solution with pH = 6.429.

Solution

$$[\text{H}_3\text{O}^+] = 3.72 \times 10^{-7} \text{ M}$$

Use three significant digits because there are three digits after the decimal point in the value given for the pH.

Practice Problem 19.12 Calculate the hydronium ion concentration of a solution with pH = 9.44.

19.3 ■ Autoionization of Water**501**

The pH is less than 7 for acidic solutions, equal to 7 for neutral solutions, and greater than 7 for basic solutions.

$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	Acidic	$\text{pH} < 7$
$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	Neutral	$\text{pH} = 7$
$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	Basic	$\text{pH} > 7$

EXAMPLE 19.13

Calculate the pH of a solution that is 6.9×10^{-2} M in NaOH.

Solution

The pH is based on the *hydronium ion* concentration. The hydroxide ion concentration is 6.9×10^{-2} M, so first calculate the hydronium ion concentration, using the K_w expression:

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+](6.9 \times 10^{-2}) &= 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= 1.45 \times 10^{-13} \text{ M} \end{aligned}$$

Converting to a pH value gives

$$\text{pH} = 12.84$$

Practice Problem 19.13 Calculate the pH of a 6.92×10^{-1} M NaCl solution.

In aqueous solutions of weak acids or weak bases, two or more equilibrium systems exist at the same time, including the ionization of water. In such solutions, all equilibrium constant expressions must be satisfied in order for the system to be at equilibrium. Therefore, we can use any or all of the equilibrium constant expressions in these problems.

EXAMPLE 19.14

Calculate the pH of a solution that is 0.165 M in NH₃.

Solution

The pH is based on the *hydronium ion* concentration. Because we are given the ammonia concentration, we first use it to calculate the hydroxide ion concentration. The initial concentration of ammonia (before reaction) is 0.165 M. After it reacts with water, its concentration and those of its products are given in the following table:

	NH ₃ (aq)	+	H ₂ O(ℓ)	⇒	NH ₄ ⁺ (aq)	+	OH ⁻ (aq)
Initial	0.165				0.00		0.00
Change	-x				+x		+x
Equilibrium	0.165 - x				x		x

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CHAPTER 19 ■ Acid-Base Theory

The equilibrium constant expression and the value of K_b from Table 19.2 are used to solve for x :

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{x^2}{0.165 - x} = 1.77 \times 10^{-5}$$

Ignoring x when subtracted from 0.165 yields

$$x^2 = 2.921 \times 10^{-6}$$

Taking the square root of both sides of the equation yields

$$x = 1.709 \times 10^{-3}$$

The hydroxide ion concentration is 1.709×10^{-3} M. As a check, we can see that 1.709×10^{-3} M is 1% of 0.165 M, so the approximation is acceptable.

We can now use the K_w expression to calculate the hydronium ion concentration:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$
$$[\text{H}_3\text{O}^+](1.709 \times 10^{-3}) = 1.0 \times 10^{-14}$$

Thus,

$$[\text{H}_3\text{O}^+] = 5.851 \times 10^{-12} \text{ M}$$

and

$$\text{pH} = -\log(5.851 \times 10^{-12}) = 11.233$$

Practice Problem 19.14 Calculate the pH of a 0.180 M $\text{HC}_2\text{H}_3\text{O}_2$ solution.



Snapshot Review



ChemSkill Builder 18.2

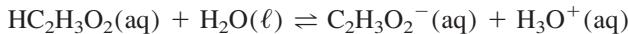
- There is *some* hydronium ion and *some* hydroxide ion in every dilute aqueous solution, whether acidic, basic, or neutral.
 - The pH is the negative logarithm of the *hydronium ion* concentration, not of the concentration of any other ion.
- A. Calculate the pH of (a) 1.00×10^{-3} M H_3O^+ and (b) 1.00×10^{-3} M OH^- .
 - B. Calculate the pH of the solution of Snapshot Review Problem A, Section 19.2.

19.4 Buffer Solutions

An aqueous solution of a weak acid or a weak base contains two substances that react with each other to some extent—the acid or base and the water. When another substance is added to this solution, it can affect the original pair of reactants without necessarily reacting directly with either. It may, as predicted by LeChâtelier's principle, suppress the reaction of the original two reactants. For example, if sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, is added to an aqueous solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, it does not react directly with the acid or with the water. Instead,

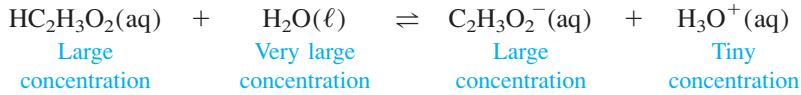
19.4 ■ Buffer Solutions**503**

the acetate ion represses the ionization of the acetic acid. The equilibrium for the acetic acid solution is



When $\text{NaC}_2\text{H}_3\text{O}_2$ is added to this solution, the Na^+ ion does not affect this equilibrium because it is a spectator ion. The acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, appears on the right side of the equation. Addition of a species that appears on the right shifts the equilibrium to the left.

Suppose we make a solution containing both a weak acid and its conjugate base (as a soluble salt). Such a solution is called a **buffer solution**. We can make a buffer solution by dissolving acetic acid and sodium acetate in water, for example. For acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, the conjugate base is the acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$. (Remember that soluble salts, strong acids, and soluble hydroxides are completely ionized in solution.) Thus, in the same solution both acetic acid and its conjugate base, the acetate ion, are present. The acidity of this solution is less than that of a solution of acetic acid alone because the acetate ion represses the ionization of the acetic acid. Furthermore, the buffer solution has the special property of resisting change in its pH even when some (reasonable quantity of) strong acid or strong base is added. Let us see how this property arises. The following equation gives the equilibrium of the acid and water, with the relative concentration of each species in the buffer solution written below it:



When H_3O^+ is added to this buffer solution, the equilibrium will shift to the left, using up most of the added H_3O^+ . The pH will not drop as much as it would have if the equilibrium were not present. If OH^- is added to the system instead of H_3O^+ , the OH^- reacts with the H_3O^+ present. However, in response to the stress of lowering the concentration of H_3O^+ , the equilibrium shifts to the right to produce more H_3O^+ . The pH is not increased as much as it would have if the equilibrium were not present.

An acidic buffer solution has an excess of all the reactants and products, except for H_3O^+ . Thus, when we try to change the concentration of H_3O^+ by adding strong acid or base, the equilibrium shifts, in accordance with LeChâtelier's principle, to resist that change. The pH changes very little. (We will do calculations to show quantitatively how little the pH changes in such systems later in this section.)

To summarize the important facts about buffer solutions:

- They are prepared by combining, in aqueous solution, a weak acid and its conjugate base or a weak base and its conjugate acid.
- They resist changes in their pH values, even if a limited quantity of strong acid or base is added.
- Buffer solutions of molecular acids and their conjugates accomplish that stability of pH by shifting their equilibria to use up added H_3O^+ or to replace H_3O^+ that has reacted with added OH^- .

Human blood is buffered at a pH of 7.3, and if the pH varies more than 0.2 units, dire results, even death, may occur. The principle of buffering is even used in a commercial pain reliever to reduce the acidity of plain aspirin (Figure 19.2).



Figure 19.2 A Product that Uses the Principles of Buffering
Buffered aspirin lessens the chance that the acid of plain aspirin will upset the stomach.

EXAMPLE 19.15

Explain how a weak base and its conjugate acid form a buffer solution.

Solution

The equilibrium of a weak base and water has OH^- as a product. If strong acid is added to the system, the strong acid reacts with the OH^- . However, more OH^- is produced as the equilibrium shifts in accordance with LeChâtelier's principle, so the pH does not change much. If a strong base is added to the system, the equilibrium shifts to use up some of the added OH^- , and again, the pH is fairly stable.

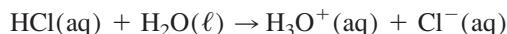
EXAMPLE 19.16

Explain why a solution of a strong acid and its conjugate base does not act as a buffer solution.

Solution

A strong acid in solution is completely ionized. The equilibrium cannot shift to replace H_3O^+ because the acid is already ionized 100%. Also, it cannot shift the other way because, by definition, a strong acid in solution is completely ionized.

Consider a solution of HCl and NaCl, for example:



Because HCl is a strong acid, this “equilibrium” proceeds completely to the right. If OH^- ions are added, no more HCl can react to replace the H_3O^+ ions used up because all of the HCl has already reacted. If H_3O^+ ions are added, the equilibrium will not shift to the left because HCl is a strong acid.

Practice Problem 19.16 Explain why a solution of a strong base and its conjugate acid do not form a buffer solution.

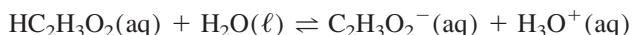
The same procedures we have used for calculations involving weak acid and weak base equilibria can be used for calculations concerning buffer solutions. The major difference is that *nonzero* concentrations of both the weak acid or base and its conjugate are initially present.

EXAMPLE 19.17

Calculate the pH of a solution of 0.150 mol of $\text{HC}_2\text{H}_3\text{O}_2$ and 0.195 mol of $\text{NaC}_2\text{H}_3\text{O}_2$ in 1.00 L of solution.

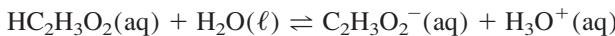
Solution

The acid ionizes according to the equation



19.4 ■ Buffer Solutions**505**

Sodium acetate is a salt, so initially, the concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ is 0.195 M. The acetate ion affects the position of the acid equilibrium.



<i>Initial</i>	0.150	0.195	0
<i>Change</i>	$-x$	$+x$	$+x$
<i>Equilibrium</i>	$0.150 - x$	$0.195 + x$	x
$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]}$			

Neglecting x when added to or subtracted from larger quantities and using the value of K_a in Table 19.2 yields:

$$K_a = \frac{(0.195)(x)}{0.150} = 1.76 \times 10^{-5}$$

$$x = 1.354 \times 10^{-5}$$

The approximations made by ignoring x when added to 0.195 M and subtracted from 0.150 M are valid. Because $[\text{H}_3\text{O}^+]$ is 1.354×10^{-5} M,

$$\text{pH} = 4.868$$

Practice Problem 19.17 Calculate the pH of a solution containing 0.120 M NH_3 and 0.160 M NH_4Cl .

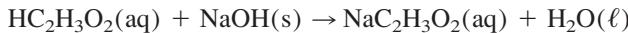
If strong acid or strong base is added to a buffer solution, a net reaction takes place. To calculate the pH of such solutions, we first assume that the strong acid or base reacts as completely as possible, given that some reactant is present in limiting quantity, as discussed in Section 10.4. Only then do we concentrate on the equilibrium calculation.

EXAMPLE 19.18

Calculate the pH after 0.0300 mol of solid NaOH is added to 1.000 L of a solution containing 0.150 mol of $\text{HC}_2\text{H}_3\text{O}_2$ and 0.195 mol of $\text{NaC}_2\text{H}_3\text{O}_2$. Assume that the volume of the solution does not change.

Solution

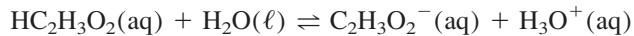
When a base is added to an acid, they react to form a salt (Chapter 8). Here, the base (NaOH) is in limiting quantity because a greater number of moles of the acid is present, and the acid and base react in a 1 : 1 ratio:



<i>Initial</i>	0.150	0.0300	0.195	Excess
<i>Changes due to acid-base reaction</i>	-0.0300	-0.0300	$+0.0300$	$+0.0300$
<i>Concentrations before equilibrium</i>	0.120	0.0000	0.225	Excess

506**CHAPTER 19 ■ Acid-Base Theory**

Right after the NaOH is added, 0.0300 mol of OH⁻ reacts with 0.0300 mol of HC₂H₃O₂, leaving 0.120 mol of HC₂H₃O₂ and 0.225 mol of C₂H₃O₂⁻ in the solution. Thus, these are the initial concentrations *for the equilibrium reaction*:



<i>Initial</i>	0.120	0.225	0
<i>Change</i>	-x	+x	+x
<i>Equilibrium</i>	0.120 - x	0.225 + x	x

$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(0.225)(x)}{0.120} = 1.76 \times 10^{-5}$$

$$x = 9.387 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 5.027$$

Comparing the pH of the solution in Example 19.17 to this pH, which is for the same solution after 0.0300 mol of strong base has been added to it, we can see that only a very small change has taken place—from 4.868 to 5.027. If 0.0300 mol of NaOH had been added to a solution of a strong acid with pH 4.868 (which was not buffered), the pH would have risen to 12.48.

EXAMPLE 19.19

Calculate the pH of 1.000 L of a solution originally containing 1.35×10^{-5} M HCl (which has the same hydronium ion concentration as the buffer solution of Example 19.17 and the original buffer solution of Example 19.18) after 0.0300 mol of LiOH has been added to it.

Solution

After neutralization of all the HCl present, there is essentially 0.0300 mol of LiOH left. In 1.000 L of solution, the hydroxide ion concentration is 0.0300 M, and the pH is 12.48. Note the difference between the effect of the base on this solution and its effect on the buffered solution of Example 19.19.

**Snapshot Review**ChemSkill Builder
19.2, 19.3

- A buffer solution can be prepared by adding a weak acid or base plus its conjugate to a solution or by preparing one of these from the other in the solution by reaction with strong acid or base, using the principles of limiting quantities reactions (Section 10.4).

- A. Explain how to make a nitrous acid–sodium nitrite buffer from sodium nitrite and hydrochloric acid, using the equation(s) of Snapshot Review Problem C, Section 19.1.

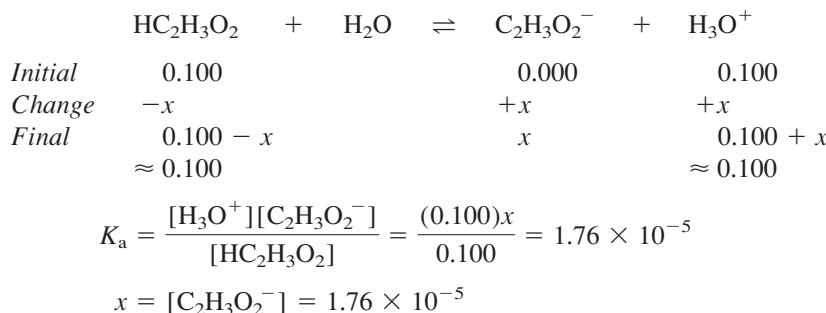
19.5 Polyprotic Acids

Before taking up polyprotic acids, let us review. Suppose we rework Example 19.17, but we will add HCl instead of sodium acetate and we will calculate the acetate ion concentration. The same principles apply.

EXAMPLE 19.20

Calculate the acetate ion concentration in a solution of 0.100 M acetic acid and 0.100 M HCl.

Solution



The presence of the strong acid represses the ionization of the weaker acid, just as predicted by LeChâtelier's principle. In fact, the presence of any stronger acid will repress the ionization of a weaker one, even if the stronger acid is not strong.

Acids that contain more than one ionizable hydrogen atom per molecule are called **polyprotic acids**. These acids ionize in steps. The second (or third) proton has a much lower dissociation constant than does the prior proton because it is harder to remove a hydrogen ion the more negatively charged the Brønsted acid (Table 19.4). Also, the prior ionization produces hydronium ions that repress the further ionization, in accord with LeChâtelier's principle. Any acid ionizes less in the presence of a stronger acid (see Example 19.20). Thus, the hydronium ion in a solution of a polyprotic acid comes mainly from the first step in the ionization.

Table 19.4 Selected Dissociation Constants of Polyprotic Acids

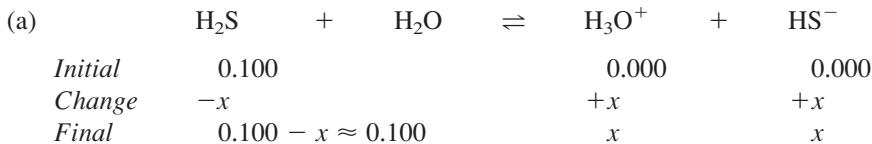
Name	Formula	K_1	K_2	K_3
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.94×10^{-5}	1.62×10^{-12}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.10×10^{-4}	1.68×10^{-5}	4.1×10^{-7}
Hydrosulfuric	H_2S	9.1×10^{-8}	1.1×10^{-12}	
Malic	$\text{H}_2\text{C}_4\text{H}_4\text{O}_5$	3.9×10^{-4}	7.8×10^{-6}	
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	5.90×10^{-2}	6.40×10^{-5}	
Phosphoric	H_3PO_4	7.52×10^{-3}	6.23×10^{-8}	2.2×10^{-13}

ITEM OF INTEREST

H₂S has been very useful in precipitating metal sulfides from their solutions. Controlling the acidity of the solution controls the sulfide ion concentration so that metal ions whose sulfides have sufficiently different solubilities can be separated. The fact that H₂S is a gas makes it easy to separate from other reagents. However, H₂S is more poisonous than hydrogen cyanide, HCN, and it must be handled with great care. (It is less dangerous than HCN because, unlike HCN, it is so easy to smell that everyone knows that it is present.)

EXAMPLE 19.21

- (a) Calculate the hydronium concentration of 0.100 M H₂S. (b) Calculate the sulfide ion concentration in that solution.

Solution

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{x^2}{0.100} = 9.1 \times 10^{-8}$$

$$x = 9.54 \times 10^{-5} = [\text{H}_3\text{O}^+] = [\text{HS}^-]$$



$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(9.54 \times 10^{-5})[\text{S}^{2-}]}{9.54 \times 10^{-5}} = 1.1 \times 10^{-12}$$

$$[\text{S}^{2-}] = 1.1 \times 10^{-12}$$

We conclude that the hydronium ion concentration provided by the second step of the ionization (also equal to 1.1×10^{-12} M) is totally insignificant compared with that provided by the first step. There are two reasons for that: (1) The value of the equilibrium constant is much smaller, and (2) the hydronium ion provided by the first step represses the ionization of the second.

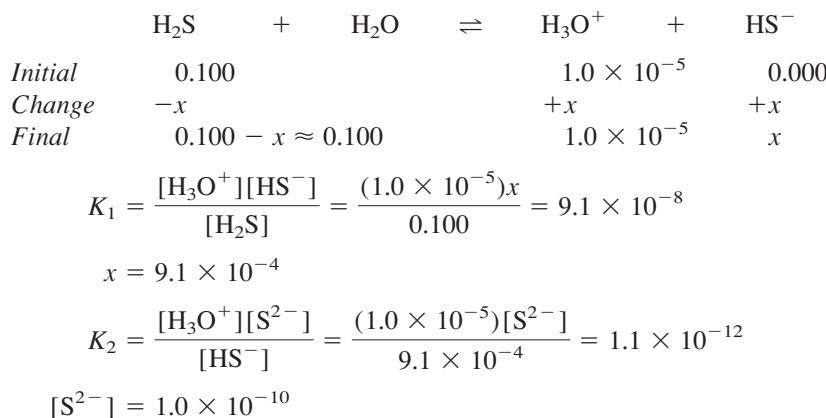
Practice Problem 19.21 We did not need the second ionization of H₂S to calculate the pH of a 0.100 M solution of the acid. Why did we need the second step for the sulfide ion concentration?

EXAMPLE 19.22

Calculate the sulfide concentration of a 0.100 M H₂S solution buffered at pH = 5.00.

19.5 ■ Polyprotic Acids**509****Solution**

Since the solution is buffered, the acidity does not change despite addition of hydronium ion from the ionization of the acid.

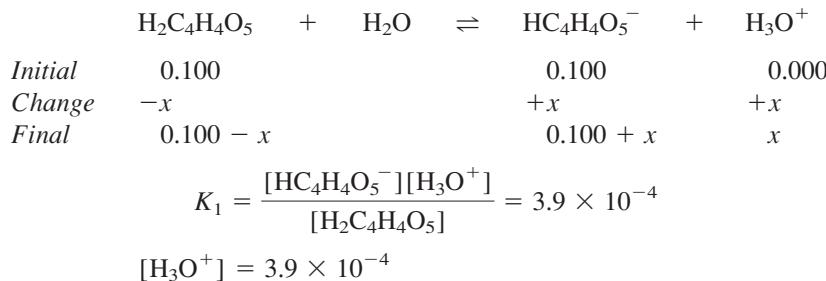


In the less acidic solution, both equilibria are shifted right, giving a greater sulfide ion concentration than the unbuffered H_2S solution (see Example 19.21).

Buffer solutions can be prepared with polyprotic acids, just as with monoprotic acids. If any acid and its conjugate, which differs by *one* proton, are together in the same solution, they form a buffer solution. Instead, if an acid and its salt are combined, they will react to produce one or more acid salt(s).

EXAMPLE 19.23

What is the hydronium ion concentration of a solution containing 0.100 M malic acid and 0.100 M sodium hydrogen malate?

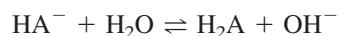
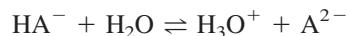
Solution

Practice Problem 19.23 What is the major product after equal volumes of 0.100 M H_2SO_3 and 0.100 M Na_2SO_3 are combined?

It must be noted that we cannot calculate the pH of an acid salt alone in solution by the methods that we have been using. The problem is that the anion

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can react with water in two ways, making the calculation more difficult than is appropriate even for the general chemistry course.



The hydronium ion produced by this first reaction reacts with the hydroxide ion produced by the second, further driving each reaction to the right and complicating the calculations even more.



Snapshot Review

- Polyprotic acids ionize in steps, each having its own value for the dissociation constant.
 - Since the successive constants are lower than the preceding ones, the second (or third) ionization does not contribute appreciably to the hydronium ion concentration of the solution of acid in water, but is the only source of the doubly (or triply) charged ion.
- A. Calculate the pH of 1.00 M H_3PO_4 .
B. Calculate the pH of a solution of 0.100 M NaH_2PO_4 and 0.100 M Na_2HPO_4 .

Key Terms

Key terms are defined in the Glossary.

acid dissociation constant (19.2)
acid strength (19.1)
amphiprotic (19.1)
autoionization (19.3)
base dissociation constant (19.2)
base strength (19.1)
Brønsted acid (19.1)
Brønsted base (19.1)
Brønsted theory (19.1)

buffer solution (19.4)
conjugate acid (19.1)
conjugate acid-base pair (19.1)
conjugate base (19.1)
dissociation (19.2)
feeble acid (19.1)
feeble base (19.1)
hydronium ion (19.1)
ionization (19.2)

ionization constant (19.2)
pH (19.3)
polyprotic acid (19.5)
proton (19.1)
proton acceptor (19.1)
proton donor (19.1)
water ionization constant (19.3)

Symbols

K_a (acid dissociation constant) (19.2)

K_i (ionization constant) (19.2)

K_1 (first dissociation constant) 19.5

K_b (base dissociation constant) (19.2)

K_w (water ionization constant) (19.3)

Summary

The Brønsted theory of acids and bases extends the definition of acids and bases, which allows an explanation of why most salts dissolved in water do not form

neutral solutions. Acids are defined as proton donors, and bases are proton acceptors. An excess of H_3O^+ ions over OH^- ions makes an aqueous solution acidic, and

■ Items for Special Attention

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an excess of OH^- ions over H_3O^+ ions makes the solution basic. Neutral solutions have equal concentrations of these two ions. Some substances, most notably water and also acid salts such as NaH_2PO_4 , can act as either acids or bases, depending on what other species are present. According to the Brønsted theory, an acid reacts with a base to produce a conjugate base of the original acid and a conjugate acid of the original base. The stronger the acid, the weaker is its conjugate base. Strong acids, for example, have feeble conjugate bases. Solutions of most salts in water test acidic or basic because one of their ions reacts with the water more than the other does (Section 19.1).

For reactions of weak acids or weak bases with water, the specialized equilibrium constant is denoted K_a or K_b , respectively. Neither K_a nor K_b explicitly includes the concentration of water in its equilibrium constant expression. If initial concentrations and one equilibrium concentration are given, the equilibrium constant can be calculated. If initial concentrations and the value of the equilibrium constant are given, the equilibrium concentrations can be calculated (Section 19.2).

Water can react with itself to a very limited extent, and every aqueous solution has at least *some* concentration of hydronium ion and of hydroxide ion, enough of each to satisfy the equation

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

Given a hydronium ion concentration, the hydroxide ion concentration can be calculated using this equation, and vice versa. The pH, defined as $-\log[\text{H}_3\text{O}^+]$, is a

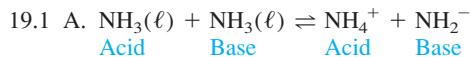
convenient way of expressing the acidity of a solution (Section 19.3).

A buffer solution resists changes in its pH due to addition of small quantities of strong acid or strong base. A buffer solution may be formed by combining a weak acid and its conjugate base or a weak base and its conjugate acid. The resistance of the buffer solution to pH changes is based on LeChâtelier's principle. For example, if a small quantity of H_3O^+ ions is added to a solution containing the conjugate base of a weak acid, the base will react with most of the added H_3O^+ ions to form more conjugate weak acid, and the pH will not change much. If a small quantity of OH^- ions is added to a solution containing an un-ionized weak acid, it will react with the acid, producing more conjugate base. The added OH^- ions are no longer present to increase the pH. Given a quantity of strong acid or base that is added to a buffer solution, first calculate how much of a reactant that is present will react completely with the added quantity, giving consideration to the limiting quantity (Chapter 10). Next deduce the new concentrations of the weak acid and its conjugate and only then proceed with the equilibrium calculation (Section 19.4).

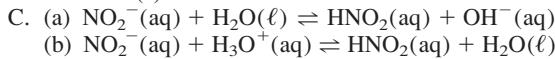
Polyprotic acids (Section 19.5) ionize stepwise, and the hydronium ion from each step represses the ionization of later steps. The second (and third) steps are essentially weaker because it is harder to remove a proton from a negatively charged species than from a neutral one. However, polyprotic acids follow the usual rules of equilibrium. For example, LeChâtelier's principle can be used to predict and explain their behavior.

Items for Special Attention

- Concentrations of strong acids or bases are usually stated without reference to their ionizations. For example, 1 M HCl contains *no* HCl molecules, but 1 M H_3O^+ and 1 M Cl^- .
 - Weak acids react extensively with Arrhenius bases. It is their incomplete reactions with *water* that differentiate them from strong acids.
 - Values of K_a and K_b given in tables are for reactions with the un-ionized molecules on the left. However, weak acids and bases can be products of the reactions of their ions. For example:
- $$\text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$$
- The pH is the negative logarithm of the *hydronium ion* concentration, not the hydroxide ion concentration, the nitrate ion concentration, or any other concentration.
 - Not every substance added to a buffer solution will react with the weak acid or base; some substances simply affect the position of the equilibrium already present. For example, sodium fluoride added to a solution containing HF and F^- reacts with neither of these but shifts the equilibrium toward the side on which HF is present because the added F^- from NaF partially reacts with some of the H_3O^+ ions present.
 - A 0.100 M solution of H_2S does not provide 0.200 M H_3O^+ because it is not a strong acid, and it does not provide twice the concentration that the first step provides because K_2 is lower than K_1 .

Answers to Snapshot Reviews

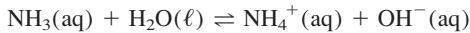
B. Reaction (a)



Reaction (b) is expected to go nearly to completion.

D. H_2PO_3^-

19.2 A.



Initial	0.0165 M	0.000 M	0.000 M
Change	-x	+x	+x
Final	0.0165 - x	x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.0165} = 1.77 \times 10^{-5}$$

$$x^2 = 2.92 \times 10^{-7}$$

$$x = 5.40 \times 10^{-4} = [\text{NH}_4^+] = [\text{OH}^-]$$

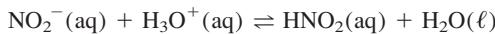
19.3 A. (a) 3.000 (b) 11.000

B.

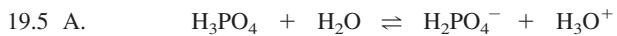
$$[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-] = (1.00 \times 10^{-14})/(5.40 \times 10^{-4}) = 1.85 \times 10^{-11}$$

$$\text{pH} = 10.732$$

19.4 A. Add hydrochloric acid to twice the number of moles of sodium nitrite.



Half of the nitrite ion will be converted to nitrous acid and half will remain. Thus there will be present nitrous acid and nitrite ion, forming a buffer solution.



Initial	1.00	0.000	0.000
Change	-x	+x	+x
Final	1.00 - x	x	x

$$K_1 = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{1.00} = 7.52 \times 10^{-3}$$

$$x = 8.67 \times 10^{-2} = [\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 1.062$$



Initial	0.100	0.100	0.000
Change	-x	+x	+x
Final	0.100 - x	0.100 + x	x

$$K_2 = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = \frac{0.100x}{0.100} = 6.23 \times 10^{-8}$$

$$x = 6.23 \times 10^{-8}$$

$$\text{pH} = 7.206$$

Self-Tutorial Problems

19.1 Write the following compounds as they would appear (in aqueous solution) in an ionic equation:

- (a) KClO_2 (b) HBrO_3 (c) CH_3OH
 (d) NH_4ClO_4 (e) $\text{Mg}(\text{HCO}_3)_2$ (f) H_3PO_3

19.2 What ions are 0.100 M after 0.100 mol of each of the following is dissolved in enough water to make 1.00 L of solution?

- (a) HNO_2 (b) NaNO_3 (c) HClO (d) NaClO

19.3 What ions or molecules are present in solution after 0.100 mol of each of the following is dissolved in enough water to make 1.00 L of solution?

- (a) $\text{Mg}(\text{ClO}_2)_2$ (b) HNO_2 (c) KClO_2
 (d) $(\text{NH}_4)_2\text{SO}_4$ (e) H_2O_2 (f) NH_3

19.4 Which of the following are weak acids, and which are strong acids?

- (a) HNO_3 (b) H_2S (c) H_2SO_3
 (d) H_2SO_4 (e) H_3PO_4 (f) HBr
 (g) HIO (h) HI

19.5 Which of the following are weak acids, and which are strong acids?

- (a) HClO_4 (b) HClO_3 (c) HClO_2
 (d) HClO (e) HCl

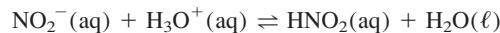
19.6 A salt in Arrhenius terminology is composed of two types of ions. Describe them in terms of the Brønsted theory.

19.7 List six singly charged cations that are feeble acids.

19.8 A solution is described as a 0.433 M solution of $\text{Al}(\text{NO}_3)_3$. What are the actual solutes? What is the meaning of 0.433 M? What are the actual concentrations?

19.9 A solution is described as a 0.900 M solution of $\text{Ca}(\text{NO}_3)_2$. What are the actual solutes? What is the meaning of 0.900 M? What are the actual concentrations?

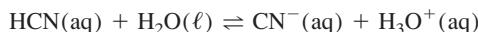
19.10 Give three examples of compounds that could provide the ions to make the following reaction proceed to the right (reverse of the ionization of nitrous acid):



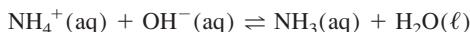
■ Problems

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- 19.11** Label each of the species in the following equilibrium system as either an acid or base in the Brønsted sense:



- 19.12** Label each of the species in the following equilibrium system as either an acid or base in the Brønsted sense:



- 19.13** Calculate the pH of each of the following solutions:

(a) 0.400 M H_3O^+ (b) 0.400 M HCl

- 19.14** Calculate the pH of each of the following:

(a) 0.100 M OH^- (b) 0.100 M NaOH

- 19.15** Calculate the pH of a solution having each of the following hydronium ion concentrations:

(a) 4.56×10^{-4} M (b) 1.77×10^{-7} M
 (c) 6.05×10^{-4} M (d) 3.33×10^{-9} M
 (e) 1.00 M (f) 2.00 M

- 19.16** Classify the following solutions as acidic, basic, or neutral:

(a) pH = 13.00
 (b) $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4}$ M
 (c) pH = 8.00
 (d) $[\text{OH}^-] = 1.0 \times 10^{-7}$ M
 (e) pH = 7.00
 (f) $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-12}$

- 19.17** What is the pH of a 8.14×10^{-4} M KCl solution?

- 19.18** Calculate the pH of a solution having each of the following hydronium ion concentrations:

(a) 1.29×10^{-6} M (b) 4.68×10^{-11} M
 (c) 3.15×10^{-3} M (d) 6.94×10^{-3} M
 (e) 1.214×10^{-12} M

- 19.19** Calculate the hydronium ion concentration of a solution having each of the following pH values:

(a) 7.331 (b) 6.44 (c) 13.333
 (d) 4.22 (e) 0.997 (f) 6.06

- 19.20** Explain why 0.100 M H_2S is not 0.200 M in H_3O^+ .

- 19.21** Since the first ionization of H_2S in 0.100 M solution produces 9.5×10^{-5} M H_3O^+ , why don't both steps together produce twice that concentration?

- 19.22** A 0.100 M solution of which acid in Table 19.4 has the highest pH?

- 19.23** Which one(s) of the following is (are) diprotic acids?



- 19.24** (a) What percentage of the total hydronium ion concentration in 0.100 M H_2S solution is contributed by the second ionization step? (See Example 19.21.) (b) What percentage of the total sulfide ion concentration?

- 19.25** What is the principal product of adding 0.100 mol of sodium oxalate to 1.00 L of 0.100 M oxalic acid solution?

Problems

19.1 The Brønsted Theory

- 19.26** What is the conjugate of each of the following?

(a) HNO_2 (b) H_2SO_3 (c) H_2SO_4

- 19.27** Write the formula for the conjugate of each of the following:

(a) CO_3^{2-} (b) ClO_2^- (c) NO_3^- (d) Br^-

- 19.28** Write the formula for a molecule that is the conjugate of each of the following:

(a) OH^- (b) H_3O^+ (c) NO_2^- (d) NH_4^+

- 19.29** What is the conjugate of each of the following?

(a) HClO_2 (b) CH_3NH_2 (a weak base like NH_3)
 (c) PO_4^{3-} (d) CN^-

- 19.30** Which of the following 0.100 M solutions are acidic, which are basic, and which are neutral?

(a) $\text{NaC}_2\text{H}_3\text{O}_2$ (b) K_2S (c) NaNO_2
 (d) LiClO_3 (e) NH_4ClO_3

- 19.31** Which of the following 0.100 M solutions are acidic, which are basic, and which are neutral?

(a) MgCl_2 (b) NH_4HSO_4 (c) K_2CO_3
 (d) NH_4NO_3 (e) CaSO_3 (f) LiNO_3

- 19.32** (a) Draw an electron dot diagram for each of the following molecules: NH_3 and CH_3NH_2 .

(b) Explain how each can act as a Brønsted base.

(c) Write the electron dot diagram for the conjugate acid of each.

- 19.33** Write formulas for the conjugate acid and the conjugate base of each of the following:

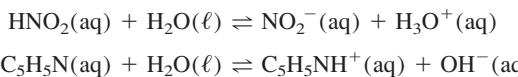
(a) H_2O (b) HSO_4^-

- 19.34** Write formulas for the conjugate acid and the conjugate base of each of the following:

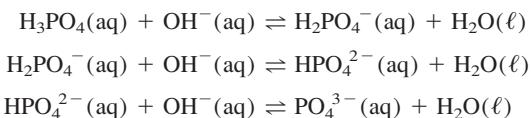
(a) HPO_4^{2-} (b) H_2PO_4^-

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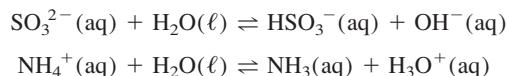
- 19.35** Label each of the species in the following equations as an acid or a base, and connect the conjugate pairs:



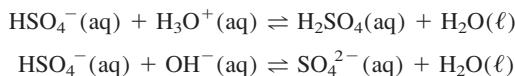
- 19.36** Label each of the species in the following equations as an acid or a base, and connect the conjugate pairs:



- 19.37** Label each of the species in the following equations as an acid or a base, and connect the conjugate pairs:



- 19.38** Label each of the species in the following equations as an acid or a base, and connect the conjugate pairs:

**19.2 Dissociation Constants**

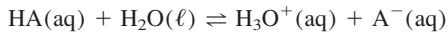
- 19.39** Calculate the ammonia concentration and the ammonium ion concentration in each of the following solutions:

- (a) 0.180 mol of NH₃ and 0.060 mol of NH₄Cl in 1.00 L of solution
- (b) 0.240 mol of NH₃ and 0.060 mol of HCl in 1.00 L of solution
- (c) Do you need to use K_b for these calculations?

- 19.40** A 0.200 M solution of a weak base, represented as B, has a hydroxide ion concentration of 6.74×10^{-5} M. Calculate the value of K_b for B. The equation for the ionization of this base is

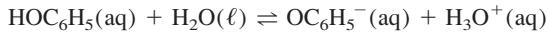


- 19.41** A 0.100 M solution of a weak acid, represented as HA, has a hydronium ion concentration of 2.50×10^{-5} M. Calculate the value of K_a for HA. The equation for the ionization of this acid is



- 19.42** Calculate the hydronium ion concentration of 0.350 M formic acid, HCHO₂. $K_a = 1.7 \times 10^{-4}$

- 19.43** Calculate the hydronium ion concentration of 0.100 M phenol, HOCH₃. $K_a = 1.3 \times 10^{-10}$



- 19.44** Calculate the percent ionization of pyridine, C₅H₅N, in (a) a 1.00 M solution, (b) a 0.100 M solution, and (c) a 0.0500 M solution. Tabulate the initial concentration of pyridine, the hydroxide ion concentration, and the percent ionization for these cases. Explain the state-

ment: Dilution of a weak base causes an increase in percentage of ionization.

- 19.45** Which base in Table 19.2 has the highest hydroxide ion concentration in 0.180 M solution?

19.3 Autoionization of Water

- 19.46** Calculate the pH of a solution having each of the following hydroxide ion concentrations:

- (a) 1.17×10^{-6} M
- (b) 5.00×10^{-13} M
- (c) 4.14×10^{-7} M

- 19.47** Calculate the hydronium ion concentration of a solution having each of the following pH values:

- (a) 2.000
- (b) 12.000
- (c) 0.000
- (d) 14.000
- (e) 7.000

- 19.48** Calculate the hydroxide ion concentration of a solution having each of the following pH values:

- (a) 4.419
- (b) 12.509
- (c) 6.39

- 19.49** What is the hydroxide ion concentration of a solution having each of the following pH values?

- (a) 3.414
- (b) 8.010
- (c) 13.595

- 19.50** Calculate the pH of a solution having each of the following hydroxide ion concentrations:

- (a) 6.2×10^{-4} M
- (b) 9.93×10^{-8} M
- (c) 4.55×10^{-12} M

- 19.51** Calculate the hydronium ion concentration of a solution having each of the following pH values:

- (a) 5.113
- (b) 13.017
- (c) 4.640

- 19.52** Calculate the pH of each of the following solutions:

- (a) 6.16×10^{-3} M KOH
- (b) 1.73×10^{-4} M HClO₃
- (c) 5.00×10^{-3} M Ba(OH)₂

- 19.53** Calculate the pH of each of the following solutions:

- (a) 0.00100 M H₂SO₄
- (b) 0.0250 M NaOH
- (c) 0.330 M NaCl

- 19.54** What is the hydroxide ion concentration of a solution having each of the following pH values?

- (a) 0.500
- (b) 9.73
- (c) 13.73

- 19.55** Calculate the pH of each of the following solutions:

- (a) 7.15×10^{-3} M HNO₃
- (b) 2.42×10^{-3} M Ba(OH)₂

- 19.56** Calculate the pH of each of the following solutions:

- (a) 0.0100 M HBr
- (b) 0.0100 M KOH
- (c) 0.0100 M NaBr

- 19.57** A 0.199 M solution of a weak base, represented as B, has a pH of 11.57. Calculate the value of K_b for B.

■ General Problems

- 19.58 A 0.110 M solution of a weak acid, represented as HA, has a pH of 4.35. Calculate the value of K_a for HA.
- 19.59 A 0.344 M solution of a weak acid, represented as HA, has a pH of 5.13. Calculate the value of K_a for HA.
- 19.60 Calculate $[H_3O^+]$ and pH for a 0.117 M solution of HF.
- 19.61 A 0.100 M solution of a weak acid, represented as HA, has a pH of 3.88. Calculate the value of K_a for HA.
- 19.62 Calculate $[H_3O^+]$ and pH for a 0.228 M solution of NH_3 .
- 19.63 Calculate the pH of a solution prepared by mixing equal volumes of 0.500 M HNO_3 and 0.150 M $Ba(OH)_2$.
- 19.64 Calculate the pH of 0.0100 M HNO_2 .

19.4 Buffer Solutions

- 19.65 Explain why each of the following solutions is a buffer solution. Write a balanced chemical equation where appropriate.
- 0.150 mol $HC_2H_3O_2$ and 0.150 mol $NaC_2H_3O_2$
 - 0.300 mol $HC_2H_3O_2$ and 0.150 mol NaOH
 - 0.300 mol $NaC_2H_3O_2$ and 0.150 mol HCl
 - 0.150 mol NH_3 and 0.150 mol NH_4Cl
 - 0.300 mol NH_3 and 0.150 mol HCl
 - 0.300 mol NH_4Cl and 0.150 mol NaOH
 - 0.150 mol H_3PO_4 and 0.150 mol NaH_2PO_4
 - 0.300 mol H_3PO_4 and 0.150 mol NaOH
- 19.66 Calculate the pH of each solution in Problem 19.39.
- 19.67 Calculate the pH of each solution in Problem 19.65.
- 19.68 A 0.115 M solution of a weak base, represented as B, is also 0.135 M in BH^+ and has a pH of 10.456. Calculate the value of K_b for B.
- 19.69 A 0.175 M solution of a weak base, represented as B, is also 0.250 M in BH^+ and has a pH of 12.22. Calculate the value of K_b for B.
- 19.70 A 0.311 M solution of a weak acid, represented as HA, is also 0.417 M in NaA and has a pH of 4.94. Calculate the value of K_a for HA.
- 19.71 A 0.139 M solution of a weak acid, represented as HA, is also 0.237 M in NaA and has a pH of 3.171. Calculate the value of K_a for HA.

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- 19.72 Calculate the acetic acid concentration, the acetate ion concentration, and the hydronium ion concentration
- After 0.105 mol of acetic acid and 0.125 mol of sodium acetate are dissolved in enough water to make 1.00 L of solution
 - After 0.230 mol of acetic acid and 0.125 mol of sodium hydroxide are dissolved in enough water to make 1.00 L of solution
 - Explain why your answer to Problem 11.77 was correct even though the equilibrium was not considered there.
- 19.73 Calculate the concentration of ammonium ion, ammonia, and hydroxide ion in solution after 0.322 mol of NH_3 and 0.202 mol of HCl are dissolved in enough water to make 1.00 L of solution.
- 19.74 Calculate the hydronium ion concentration of 1.00 L of a solution made from each of the following combinations:
- 0.190 mol of hydrofluoric acid, HF, and 0.140 mol of sodium fluoride, NaF
 - 0.330 mol of hydrofluoric acid and 0.140 mol of NaOH
- 19.75 Calculate the hydronium ion concentration of 1.00 L of a solution prepared with each of the following combinations:
- 0.215 mol of NH_3 and 0.285 mol of NH_4NO_3
 - 0.500 mol of NH_3 and 0.285 mol of HNO_3

19.5 Polyprotic Acids

- 19.76 Calculate the pH of a solution of 0.100 M sodium hydrogen oxalate and 0.100 M sodium oxalate.
- 19.77 Calculate the pH of 1.00 L of solution of 0.100 M H_2S to which 0.0500 mol NaOH has been added. Assume no change in volume.
- 19.78 Calculate the sulfide ion concentration of a solution buffered at pH 7.00 to which H_2S is bubbled into until it is saturated (0.100 M).
- 19.79 Calculate the phosphate ion concentration in 2.00 M H_3PO_4 .
- 19.80 Calculate the ascorbate ion concentration in 0.200 M ascorbic acid (vitamin C) solution.

General Problems

- 19.81 Calculate the pH of 0.100 M citric acid, $H_3C_6H_5O_7$.
- 19.82 Calculate the pH of a 0.100 M solution of Na_2HPO_4 also containing 0.100 M Na_3PO_4 .
- 19.83 Other than adding a weak molecular base to its conjugate acid, what are two ways in which a buffer solution involving the same equilibrium system can be made?

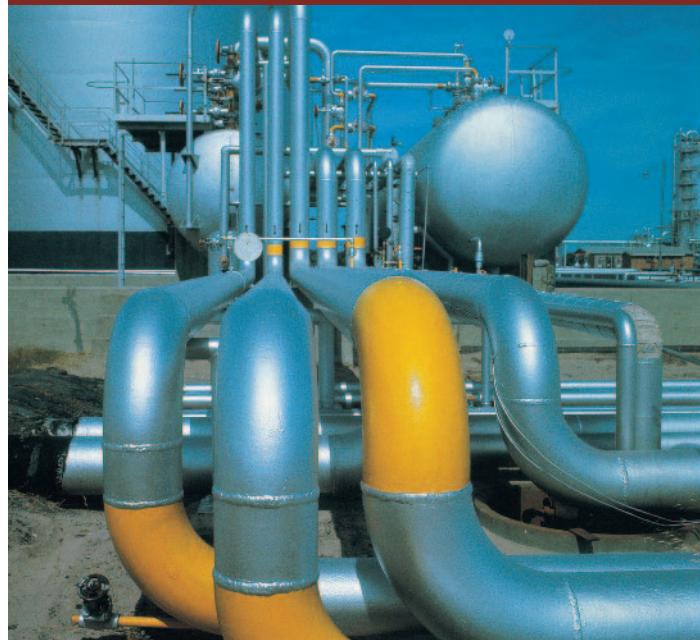
- 19.84 Which of the following will form a buffer solution when added to water?
- 0.100 mol $HC_2H_3O_2$ plus 0.100 mol $C_2H_3O_2^-$
 - 0.200 mol $NaC_2H_3O_2$ plus 0.100 mol HCl
 - 0.200 mol $NaC_2H_3O_2$ plus 0.200 mol HCl

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- (d) 0.200 mol $\text{HC}_2\text{H}_3\text{O}_2$ plus 0.100 mol NaOH
(e) 0.200 mol $\text{HC}_2\text{H}_3\text{O}_2$ plus 0.200 mol NaOH
(f) 0.200 mol NH_3 plus 0.300 mol NH_4Cl
- 19.85** Calculate the concentration of acetic acid produced and the concentration of any excess reactant by reaction in 1.000 L of solution of each of the following pairs. Also calculate the concentration of hydronium ion produced.
- (a) 1.00 mol $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq})$ + 0.500 mol $\text{HCl}(\text{aq})$
(b) 1.00 mol $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq})$ + 1.00 mol $\text{HCl}(\text{aq})$
- 19.86** Calculate the concentration of acetate ion, acetic acid, and hydronium ion in solution after 0.250 mol of $\text{HC}_2\text{H}_3\text{O}_2$ and 0.150 mol of NaOH are dissolved in enough water to make 1.00 L of solution.
- 19.87** Calculate the pH of 1.00 L of solution prepared with 0.1000 mol of oxalic acid to which has been added (a) 0.0500 mol of NaOH. (b) 0.1500 mol of NaOH. Assume no change in volume.
- 19.88** Which of the following will form a buffer solution when added to water?
- (a) 0.200 mol NaCl plus 0.100 mol HCl
(b) 0.200 mol NaOH plus 0.100 mol HCl
(c) 0.200 mol NH_3 plus 0.200 mol NH_4NO_3
(d) 0.100 mol HCl plus 0.200 mol NaOH
(e) 0.100 mol $\text{HC}_2\text{H}_3\text{O}_2$ plus 0.100 mol HCl
(f) 0.200 mol NH_3 plus 0.100 mol NaOH
(g) 0.200 mol NaCl plus 0.200 mol NaOH
- 19.89** What is the pH of a solution in which 0.200 M formic acid, HCHO_2 , is exactly half-neutralized with 0.100 M NaOH during a titration? Assume a doubling of the initial volume.
- 19.90** Calculate the acetate ion concentration in 1.00 L of a solution prepared with 0.300 mol of acetic acid and 0.100 mol of HCl. Explain the statement, “a weaker acid ionizes less in solution with a stronger acid.”

CHAPTER 19 ■ Acid-Base Theory

- 19.91** Calculate the ammonium ion concentration in 1.00 L of a solution prepared with 0.100 mol of NH_3 and 0.200 mol of NaOH.
- 19.92** A solution containing 0.100 mol of phenol, $\text{HO}\text{C}_6\text{H}_5$, and 0.100 mol of its conjugate base, OC_6H_5^- (phenolate ion), has a hydronium concentration $1.3 \times 10^{-10} \text{ M}$. The solution is basic. Explain how a solution with *any* acid in it can be basic.
- 19.93** Explain why each of the following solutions is *not* a buffer solution.
- (a) 0.100 mol NaCl and 0.100 mol HCl
(b) 0.200 mol HCl and 0.100 mol NaOH
(c) 0.200 mol $\text{HC}_2\text{H}_3\text{O}_2$ and 0.200 mol NaOH
(d) 0.200 mol $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.200 mol HCl
(e) 0.200 mol NH_3 and 0.200 mol HCl
(f) 0.200 mol NH_4Cl and 0.200 mol NaOH
(g) 0.200 mol H_3PO_4 and 0.600 mol NaOH
- 19.94** (a) A 1.00-L solution contains 0.120 mol of $\text{HC}_2\text{H}_3\text{O}_2$ and 0.120 mol of $\text{NaC}_2\text{H}_3\text{O}_2$. Calculate the hydronium ion concentration of the solution.
(b) The solution is diluted to 2.00 L. Calculate the new hydronium ion concentration.
- 19.95** What is the approximate pH of a solution of ammonium acetate?
- 19.96** Calculate the hydronium ion concentration in 0.0100 M H_3PO_4 .
- 19.97** So far throughout this book, H_2SO_4 has been treated as if *both* hydrogen atoms of each molecule ionize completely in water. Actually, only the first hydrogen atom ionizes completely, and the second ionizes fairly well. $K_a = 1.20 \times 10^{-2}$ (a) Calculate the pH of 0.100 M NaHSO_4 . (b) Calculate the sulfate ion concentration in 1.00 M H_2SO_4 .



Oil refinery

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Organic Chemistry

- 20.1 Hydrocarbons
- 20.2 Isomerism
- 20.3 Other Classes of Organic Compounds
- 20.4 Polymers
- 20.5 Foods

Review Clues

- Chapter 20 Section 5.5
Section 20.2 Section 13.4

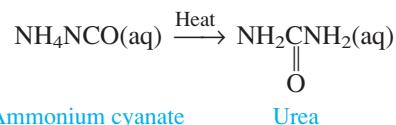
Objectives

- 20.1 To write general formulas for the different series of hydrocarbons, to write formulas for the individual members of the series, and to describe a few of their properties
- 20.2 To write formulas for isomers and to distinguish formulas for isomers from formulas that represent a single compound written in different orientations
- 20.3 To write general formulas for several classes of organic compounds, to identify their functional groups, and to write equations for a few of their reactions
- 20.4 To write equations for the formation of macromolecules called polymers and to describe some of the properties of the compounds they comprise
- 20.5 To apply the principles of organic chemistry to some of the foods we eat

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CHAPTER 20 ■ Organic Chemistry

Organic chemistry is often defined as the chemistry of carbon and its compounds. However, this definition is too broad because many compounds of carbon, such as carbon dioxide and metal carbonates, are regarded as inorganic. Until almost 200 years ago, organic chemistry was defined as the chemistry of compounds derived from living things. In 1828, Friedrich Wöhler (1800–1882) did a laboratory experiment that converted ammonium cyanate (an inorganic compound) to **urea** (an **organic compound**), which showed that the “life force” was not necessary to make organic compounds:



Structural formulas for organic compounds are often written without the Lewis dots for unshared electrons.

Note that structural formulas for organic compounds are often written without the Lewis dots representing unshared electrons. Perhaps the best definition of an organic compound is that it is a compound that contains at least one carbon-carbon or carbon-hydrogen bond. However, this definition excludes urea and thiourea, so it is not perfect.

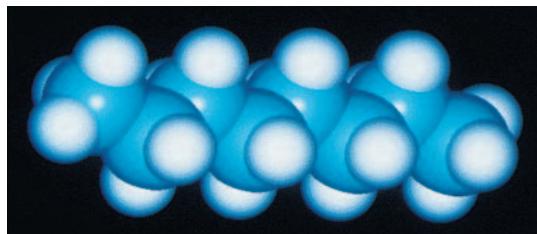
Hydrocarbons, the simplest class of organic compounds, are described in Section 20.1. The four major series of hydrocarbons and the most modern system for naming them are presented. The basic geometry of the simplest molecules is also introduced. Section 20.2 examines isomers, different compounds that have the same molecular formula. The discussion in this section is limited to isomerism of hydrocarbons, but the phenomenon exists in all classes of organic compounds. Organic compounds containing elements in addition to carbon and hydrogen are covered in Section 20.3. With the inclusion of oxygen, nitrogen, and the halogens, nine additional classes of organic compounds are formed. Section 20.4 briefly describes polymers, which have huge molecules formed from simpler molecules by ordinary types of reactions such as those described in the preceding sections. A brief look at the organic chemistry of foods is presented in Section 20.5.

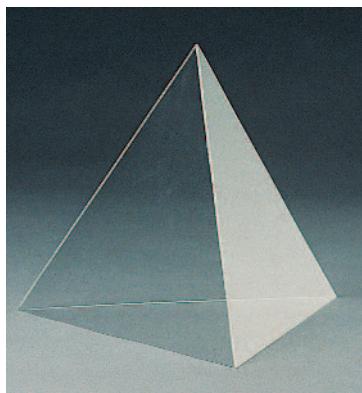
20.1 Hydrocarbons

Hydrocarbons are compounds containing only carbon and hydrogen. Not only are hydrocarbons important in themselves, but they are the foundation of all the other classes of organic compounds. We must learn how to name and write formulas for the hydrocarbons and learn a few of their simple reactions. The number of such compounds is almost uncountable because carbon atoms can bond to other carbon atoms in seemingly limitless numbers. (An eight-carbon chain is shown in Figure 20.1. Compounds with extremely long chains are discussed in

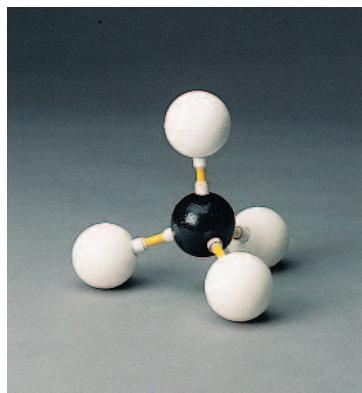
Figure 20.1 Octane, an Eight-Carbon Unbranched Hydrocarbon

This computer-generated image of an octane molecule shows that its eight carbon atoms (blue) form a continuous chain and have a total of 18 hydrogen atoms (white) attached. (Image from HyperChem software, © Autodesk, Inc.)

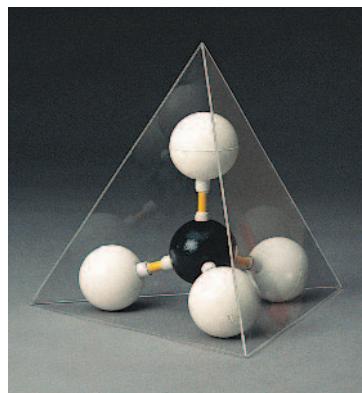


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(a)



(b)



(c)

Figure 20.2 Tetrahedral Nature of the Carbon Atom

(a) A tetrahedron has four triangular sides (including the base). (b) The carbon atom of CH_4 is typical of carbon atoms in alkanes. (c) The tetrahedral nature of the carbon atom is apparent in that its bonds with four hydrogen atoms point toward the corners of a tetrahedron. (Model courtesy of Molecular Models Co.)

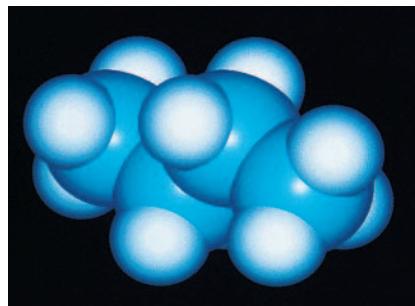
Section 20.4.) Moreover, the atoms can bond in different ways (see Section 20.2), which greatly increases the number of possible compounds.

When a carbon atom is connected to four other atoms with single bonds, those bonds are oriented toward the corners of a tetrahedron (Figure 20.2). The angle between any two of the bonds is 109.5° . A chain of such atoms in a hydrocarbon can assume a zigzag shape (see Figure 20.1). Organic molecules are usually represented in one of six different ways (Figure 20.3).

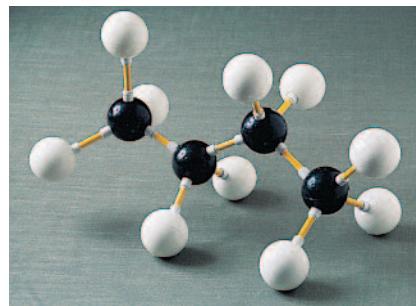
Figure 20.3 Representations of Butane

(a) Space-filling model, shown with blue carbon atoms and white hydrogen atoms. (Image from HyperChem software, © Autodesk, Inc.) (b) Ball-and-stick model, with black carbon atoms and white hydrogen atoms. (Model courtesy of Molecular Models Co.) (c) Structural formula indicating actual bond angles. (d) “Two-dimensional” structural formula. (e) Line formula. (f) Molecular formula.

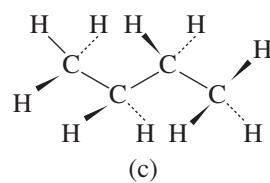
Condensed formulas are introduced on page 520.



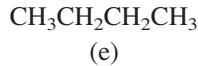
(a)



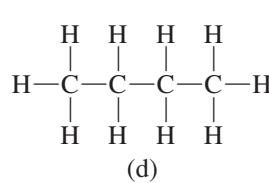
(b)



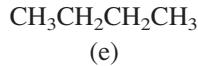
(c)



(c)



(d)



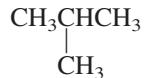
(e)



(f)

Models of the molecule are easiest to visualize but hardest to produce (see Figure 20.3a). A ball-and-stick model (Figure 20.3b) shows the bond angles best, but the space-filling model (Figure 20.3a) is more realistic and it better shows the relative sizes of the atoms and the distances between them. Chemists could draw pictures of these two types of models, of course. To save time and trouble, however, they often draw structural formulas. The actual geometry of the molecule may be indicated in a structural formula (Figure 20.3c), but usually it is not (Figure 20.3d). Figure 20.3d is similar to an electron dot diagram, with the shared pairs of electrons represented by lines, rather than pairs of dots, and the unshared pairs, if any, generally not shown. In a **line formula**, so called because it is written on a single line, groups of atoms that are connected in the molecule are written together (Figure 20.3e). This representation is easier to write than a structural formula, but it requires the chemist to remember more about the bonding of the atoms in the molecule. Finally, a molecular formula (Figure 20.3f) is the easiest to write but gives far less information. A molecular formula may even represent more than one compound.

A variation of the line formula, called a **condensed formula**, is often used for molecules with branches on a carbon chain. For example, the condensed formula for a compound with a three-carbon chain and a one-carbon branch is represented



It has a line formula $\text{CH}_3\text{CH}(\text{CH}_3)_2$ or $\text{CH}(\text{CH}_3)_3$.

Study of the chemistry of such a huge collection of compounds is kept manageable by dividing the hydrocarbons into four main series: alkanes, alkenes, alkynes, and aromatic hydrocarbons.

The Alkanes

Extra Help

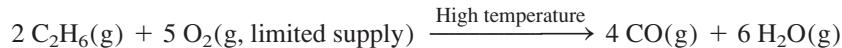
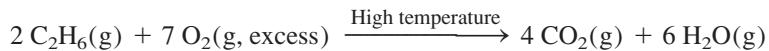
$$\begin{aligned} 2n + 2 &= 2(4) + 2 = 10 \\ 2n + 2 &= 2(6) + 2 = 14 \end{aligned}$$

The **alkanes** are the most fundamental class of hydrocarbons. Their molecular formulas may be represented as $\text{C}_n\text{H}_{2n+2}$, where n represents some integer. For example, if $n = 4$, the formula is C_4H_{10} , and if $n = 6$, the formula is C_6H_{14} . Characterized by having only *single* covalent bonds within their molecules, these compounds are said to be **saturated hydrocarbons**, because their carbon backbones cannot hold any more hydrogen atoms. Because they are relatively inert, alkanes are also known as *paraffins* (from the Latin, meaning “against reaction”). The names and formulas of the first 10 unbranched alkanes are given in Table 20.1. [The unbranched hydrocarbons are sometimes called “straight-chain” hydrocarbons, despite their actual geometries, as typified by octane (see Figure 20.1).] Each of the alkanes has a name that ends in *-ane*. The beginnings of the names of the fifth through tenth alkanes are Greek or Latin prefixes for the numbers that correspond to the numbers of carbon atoms in these molecules. For example, *octane* has *eight* carbon atoms in each of its molecules. We must learn the names of the first 10 unbranched alkanes and the associated numbers of carbon atoms in their molecules, especially because the names of the other classes of hydrocarbons and other types of organic compounds are based on these names.

Table 20.1 The First 10 Unbranched Alkanes

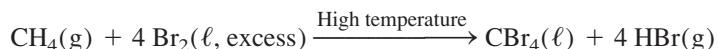
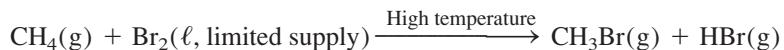
Name	Molecular Formula	Line Formula
Methane	CH ₄	CH ₄
Ethane	C ₂ H ₆	CH ₃ CH ₃
Propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃
Butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃
Pentane	C ₅ H ₁₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃
Hexane	C ₆ H ₁₄	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Heptane	C ₇ H ₁₆	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Octane	C ₈ H ₁₈	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Nonane	C ₉ H ₂₀	CH ₃ CH ₂ CH ₃
Decane	C ₁₀ H ₂₂	CH ₃ CH ₂ CH ₃

At high temperatures, the alkanes react with excess oxygen to yield water and carbon dioxide or with limited oxygen to yield water and carbon monoxide:



Alkanes are widely used as fuels: Methane is familiar as natural gas, propane is used as bottled gas and as a fuel for welding torches, butane is used as cigarette lighter fluid, and octane is a major component in gasoline.

The alkanes also react with elemental halogens at high temperatures to produce halogenated hydrocarbons. For example:



The reactions of all the alkanes are similar; they differ in degree, rather than kind. That fact makes the study of the alkanes the study of a single class of compounds, rather than of the millions of individual compounds that make up the class.



ITEM OF INTEREST

Ignorance is not bliss! Burning charcoal or hydrocarbons in a limited supply of oxygen produces carbon monoxide, a deadly poisonous gas. Internal combustion engines also produce carbon monoxide. *Don't* run automobiles in closed spaces such as garages. *Don't* heat an RV or station wagon with a charcoal or propane heater with all the windows closed or nearly closed. *Don't* weather-strip the doors and windows of a home too well, especially if gas is used for cooking or heating. *Do* check the furnace for proper functioning periodically and keep the chimney in good repair and unblocked. Failure to follow these rules has already cost too many human lives.

EXAMPLE 20.1

Write equations for the reaction of (a) propane with oxygen in limited supply and (b) ethane with bromine in limited supply.

Solution

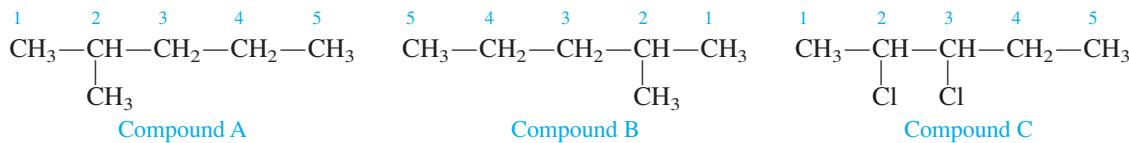
- (a) $2 \text{C}_3\text{H}_8(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}(\text{g}) + 8 \text{H}_2\text{O}(\text{g})$
(b) $\text{C}_2\text{H}_6(\text{g}) + \text{Br}_2(\ell) \rightarrow \text{C}_2\text{H}_5\text{Br}(\ell) + \text{HBr}(\text{g})$

Practice Problem 20.1 Write equations for the reaction of methane with (a) excess bromine and (b) excess oxygen.

The most modern rules for the systematic naming of alkanes follow:

1. The name is based on the longest continuous chain of carbon atoms in the molecule.
2. Branches consisting of a hydrocarbon molecule with one hydrogen atom removed are named with the *-ane* ending replaced by *-yl*. Thus a one-carbon branch, CH_3- , is called methyl.
3. A branch, functional group (Section 20.3), or multiple bond involving a carbon atom in such a chain (see next subsection) is given an “address,” or position on the carbon chain, which is the number of that carbon atom counting from the *nearer end* of the chain.

For example, consider the following condensed formulas:

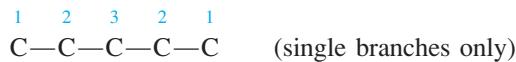


In compound A, the longest continuous chain is five carbon atoms long, and there are no multiple bonds, so this compound is named as a *pentane* (see Table 20.1). The carbon atom to which the methyl group (CH_3-) is attached is identified with the number 2 because that carbon is the second from the nearer end of the chain. The name is 2-methylpentane. Note that the number 2 is an *address* and does *not* mean two methyl groups.

The formula for compound B represents the same compound as compound A but written in the reverse direction. We start numbering the carbon chain from the end nearer the methyl group, and we get the same name, 2-methylpentane.

We name organic compounds containing chlorine in an analogous manner; compound C is 2,3-dichloropentane.

For a compound with only one branch, the carbon chain might be numbered as follows:



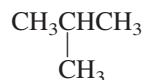
20.1 ■ Hydrocarbons**523**

Then, no matter which end the branch is nearer to, the position number is correct. The previous example showing compounds A and B may easily be seen to both be 2-methylpentane using this numbering scheme.



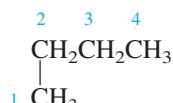
Caution: Numbering from both ends is used for single branches only.

- When no ambiguity would result from the lack of an address, none is given. For example, the following compound is called simply methylpropane:



No address is needed for the methyl group because there is only one carbon atom where a branch may occur.

- If the methyl group is attached to either carbon atom at the end of the chain, a longer continuous chain is formed:



This compound is butane. Note that since we saved work by writing formulas on a line, we have to remember that they are not really linear—the bonds are tetrahedrally oriented around each carbon atom.

The Alkenes

An **alkene** is a hydrocarbon that has one carbon-to-carbon double bond in each molecule. The general molecular formula for this class of hydrocarbons is C_nH_{2n} . The two electrons involved as the second pair of the double bond are not shared with hydrogen atoms, so each molecule of an alkene has two fewer hydrogen atoms than that of the corresponding alkane. Alkenes are therefore said to be **unsaturated hydrocarbons**. The alkenes are also named systematically:

- We use the name of the alkane having the same number of carbon atoms but change the ending to *-ene*.
- The location of the double bond is indicated when necessary. Of the two carbon atoms involved in the double bond, we use the address of the carbon closer to the nearer end of the longest chain in the name. For example,



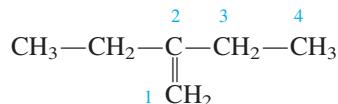
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CHAPTER 20 ■ Organic Chemistry

Table 20.2 The First Four Unbranched Alkenes

Systematic Name	Common Name	Molecular Formula	Structural Formula	Line Formula
Ethene	Ethylene	C ₂ H ₄	$\begin{array}{c} \text{H}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	CH ₂ =CH ₂
Propene	Propylene	C ₃ H ₆	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C}=\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH ₃ CH=CH ₂
1-Butene		C ₄ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH ₂ =CHCH ₂ CH ₃
2-Butene		C ₄ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}=\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH ₃ CH=CHCH ₃

3. If the double bond is not in the longest continuous chain, we name the compound with a shorter chain including the double bond. For example,



is called 2-ethyl-1-butene. This and other more complicated naming rules will be left for more advanced courses.

The names and formulas of the first four unbranched alkenes are presented in Table 20.2. (Common names are often used for the smallest members of each class.) **Ethylene** (ethene) and propylene (propene) are the raw materials used in the manufacture of the common plastics polyethylene and polypropylene.

EXAMPLE 20.2

Name each of the following alkenes:

- (a) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
 (c) $\text{CH}_2=\text{CH}_2$

Solution

- (a) 2-Pentene (b) 1-Hexene (c) Ethene

Practice Problem 20.2 Write line formulas for (a) 2-heptene and (b) 4-nonene.

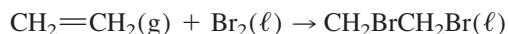
EXAMPLE 20.3

Explain why no alkene has only one carbon atom.

Solution

By definition, an alkene is a hydrocarbon with a carbon-to-carbon double bond. Therefore, it must have at least two carbon atoms.

The alkenes are more reactive than the alkanes. For example, alkene molecules undergo addition reactions in which the atoms from halogen molecules or from hydrogen halides bond to the carbon atoms involved in the double bond:

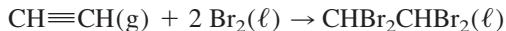


These reactions can take place at room temperature, in contrast to the high temperatures needed for an alkane to react with a halogen molecule.

The Alkynes

An **alkyne** is a hydrocarbon with one carbon-to-carbon triple bond per molecule. The series has molecules with the general molecular formula $\text{C}_n\text{H}_{2n-2}$. The first alkyne, called ethyne and commonly known as acetylene, has the formula C_2H_2 or $\text{HC}\equiv\text{CH}$, also written $\text{CH}\equiv\text{CH}$. Acetylene is used as a fuel in high-temperature welding torches. The alkynes are named similarly to the alkanes and alkenes, but with the ending *-yne*.

Like the alkenes, the alkynes are unsaturated and more reactive than the alkanes. Alkynes can add two molecules of halogen across the triple bond:

**EXAMPLE 20.4**

Name $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$.

Solution

The name is 3-octyne. (The carbon atom involved in the triple bond that is nearer the end of the chain is the *third* from the *right*.)

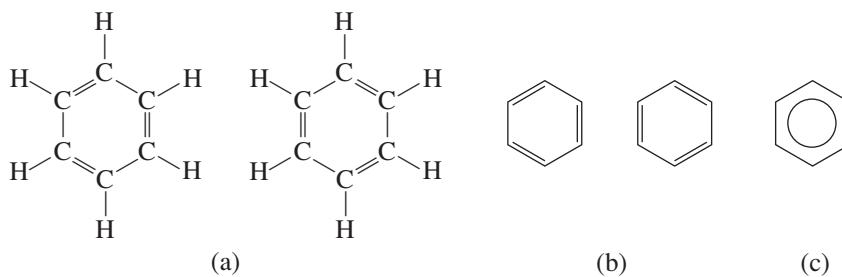
Practice Problem 20.4 Write two line formulas each for (a) 3-heptyne and (b) 2-pentyne.

The Aromatic Hydrocarbons

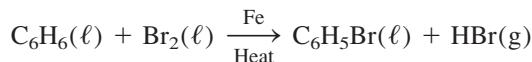
A class of hydrocarbons whose molecules contain a ring of six carbon atoms, each with only one hydrogen atom (or other group) attached, has special properties. The class is known as the **aromatic hydrocarbons**. The simplest member is **benzene**, and all other members have at least one benzene ring included

Figure 20.4 Several Representations of Benzene

- (a) Note that the alternating double bonds can be in different locations.
 (b) The letters representing the carbon and hydrogen atoms are often omitted.
 (c) The circle represents the possible locations of the double bonds averaged over time—delocalized double bonds.

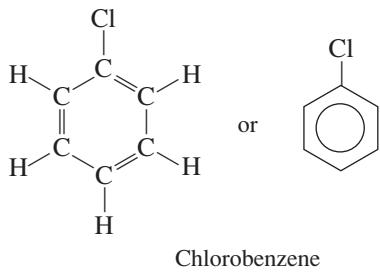


in their structures (Figure 20.4). Alternating double and single bonds yield two possible structures that obey the octet rule, but the aromatic hydrocarbons have more stability than is expected for similar compounds with ordinary double bonds. For example, benzene reacts with a halogen molecule by substitution, in a manner that is more like the reaction of an alkane than of an alkene. Iron is used as a catalyst in this substitution reaction:



Delocalized double bonding, represented by the circle within the hexagon, is responsible for the special stability of benzene and its derivatives.

EXAMPLE 20.5

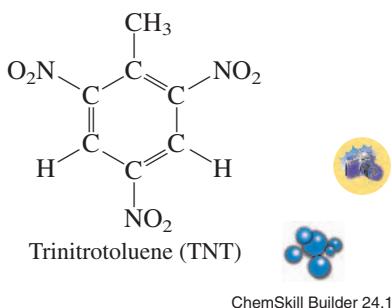


Draw the structure of chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, an aromatic organic halide. (Organic halides are defined in Section 20.3.)

Solution

The chlorine atom might have replaced any of the other hydrogen atoms as well.

Practice Problem 20.5 How many hydrogen atoms remain in dichlorobenzene?



Compounds such as trinitrotoluene, known familiarly as TNT, are derived from simple aromatic hydrocarbons.

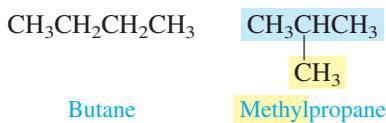
Snapshot Review

- Carbon is unique in its ability to form long chains of like atoms. Its compounds within each series react similarly, but not identically.
- Aromatic hydrocarbons do not react very similarly to alkenes or alkynes.

- A. Give the molecular formula for the member of each series with six carbon atoms.
- B. Which series of hydrocarbons is most inert?
- C. What makes the aromatic series different from the others?
- D. Name (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$
 (b) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$

20.2 Isomerism

In hydrocarbons with more than three carbon atoms per molecule, more than one compound may exist with a given formula. The compounds have the same number of carbon atoms and the same number of hydrogen atoms. Such compounds are **isomers** of each other. Each isomer is a separate compound; isomers are related only by having the same molecular formula. (Of course, their properties are similar because they are in the same class of hydrocarbons.) For example, the molecular formula C_4H_{10} corresponds to the following two compounds, which are isomers of each other:



Isomers with at least some atoms connected to different other atoms in the two (or more) compounds, such as butane and methylpropane, are said to be **structural isomers** of each other. (The fourth carbon atom is added to the end of a three-carbon chain to get butane, but in the middle of a three-carbon chain to get methylpropane.) *Only structural isomers will be considered in this text.* (Other types of isomers, in which all the atoms are bonded to the same other atoms in each of the isomers but in different spatial arrangements, will be taken up in more advanced texts.)

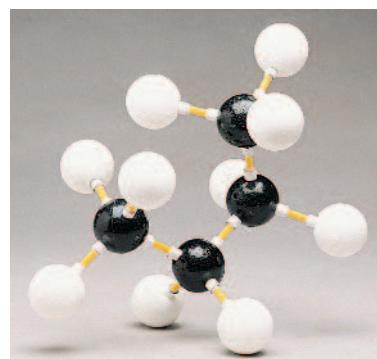
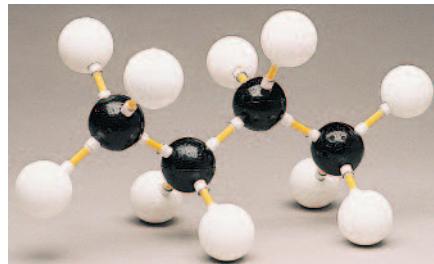
In an alkane molecule, one part of the molecule can rotate about one (or more) of the single bonds to assume different shapes (Figure 20.5). Such different orientations are different forms of the same molecule, not isomers. We must be careful not to identify two different orientations of one molecule as isomers when they really are representations of the same molecule.

EXAMPLE 20.6

Write condensed formulas that show the two different orientations for butane illustrated in Figure 20.5.

Figure 20.5 Two Different Orientations of Butane

(Model courtesy of Molecular Models Co.)



Solution

These formulas look less like the same molecule than do the models in Figure 20.5. Be aware, however, that they are representations of the same molecule.

Practice Problem 20.6 Write another condensed formula for butane that shows both ends of the molecule rotated from the zigzag shape in Figure 20.3c.

As stated previously, compounds with branches on the longest continuous chain of carbon atoms are named as derivatives of that chain. Each branch is named using the stem of the alkane having the same number of carbon atoms with the ending changed to *-yl*. Thus, for the branched chain compound whose structural formula was illustrated at the beginning of this section, the side chain CH_3- is called methyl, and the three-carbon continuous chain is called propane. Two, three, or four identical side chains are named using the prefix *di*-, *tri*-, or *tetra*-, respectively.

EXAMPLE 20.7

Does the formula of methylpropane shown previously represent another orientation of the molecule in Example 20.6, or is it another molecule?

Solution

It is another molecule. No amount of rotation about bonds can move the last carbon atom of the four-carbon chain of butane from the third to the second carbon atom in the molecule.

Practice Problem 20.7 A student incorrectly named two compounds (a) 3-methylbutane and (b) 1-methylhexane. Write formulas corresponding to these names, and give the correct names for the compounds.

EXAMPLE 20.8

Write line formulas for (a) heptane and (b) dimethylbenzene.

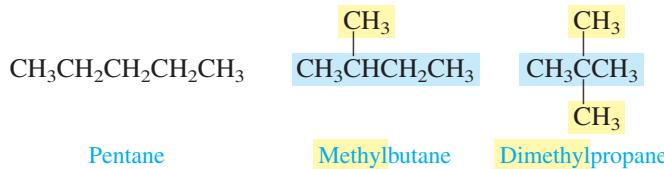
Solution

(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $\text{C}_6\text{H}_4(\text{CH}_3)_2$

Practice Problem 20.8 Write a line formula for 2,3,3-trimethylheptane.

EXAMPLE 20.9

Write condensed formulas for three compounds with the molecular formula C_5H_{12} . Name these compounds.

Solution

Practice Problem 20.9 Write formulas for the two compounds with the molecular formula C_3H_7Br . Name these compounds.

In unsaturated hydrocarbons, isomerism can occur because of the position of the double or triple bond.

EXAMPLE 20.10

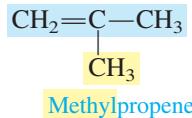
Draw line formulas for two compounds with the molecular formula C_5H_{10} having the five carbon atoms in a continuous chain. Name them.

Solution

These two compounds are called 1-pentene and 2-pentene, respectively.

EXAMPLE 20.11

Draw a condensed formula for an unsaturated isomer with the molecular formula C_4H_8 , and with a branch. Name the compound.

Solution

Practice Problem 20.11 Write line formulas representing all alkynes with the molecular formula C_4H_6 .



ENRICHMENT

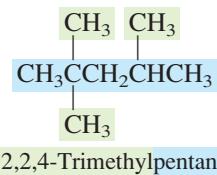
Petroleum is a mixture of many compounds, mainly hydrocarbons containing varying numbers of carbon atoms per molecule. Hydrocarbons with more than 12 carbon atoms per molecule are oily, greasy, or waxy substances. To produce smaller molecules, which are characteristic of hydrocarbons used as fuels, oil companies *crack* the petroleum by heating it in the absence of air. The heating causes some of the carbon–carbon bonds to break and results in the production of

a range of smaller molecules. Cracking in the presence of certain catalysts optimizes the yield of those isomers that are useful as fuels. The cracking process is followed by distillation, in which various types of petroleum products are separated from one another by means of their different boiling points. Two isomers of octane, C_8H_{18} , are shown in Figure 20.6. The fuel known as “100 octane” is 2,2,4-trimethylpentane.

Figure 20.6 Two Isomers of Octane



Octane



Isomers exist in all classes of organic compounds, some of which are described in the next section.



Snapshot Review



ChemSkill Builder 24.1

- Isomers of hydrocarbons are produced by differences in the position of carbon atoms or of multiple bonds or both.
- Numbering of carbon chains starting at both ends is done for single branches only.

- A. What is the molecular formula of the smallest member of each nonaromatic series that exists in isomeric forms?
- B. Write the line formula of each of the three unbranched heptynes, and tell how their names distinguish them.

20.3 Other Classes of Organic Compounds

A wide variety of organic compounds contain at least one other element in addition to carbon and hydrogen. The other elements most commonly found in organic compounds are all nonmetals—oxygen, nitrogen, fluorine, chlorine, bromine, iodine, sulfur, and phosphorus. The **total bond order** of an atom is its number of bonding electron pairs. Just as a hydrogen atom always shares one electron pair to form one covalent bond and a carbon atom shares four electron pairs in organic compounds (in four single bonds, two double bonds, two single bonds and one double bond, or one single bond and one triple bond), these other elements also have characteristic total bond orders in neutral molecules (Table 20.3). Knowing these total bond orders is essential to interpreting line formulas correctly.

20.3 ■ Other Classes of Organic Compounds**531****Table 20.3** Total Bond Orders of Atoms in Uncharged Organic Molecules

Atom	Total Bond Order
C	4
H	1
O	2
S	2
N	3
P	3
X*	1

*X refers to any halogen atom: F, Cl, Br, or I. Except for hydrogen, the total bond order of each element in the table is 8 minus its group number.

Because the hydrocarbon portion of an alkane or aromatic hydrocarbon is relatively inert, the atoms of the other elements form the centers of reaction. The hydrocarbon portion is termed a **radical** and is often represented by the symbol R. The radical is essentially the parent hydrocarbon with a hydrogen atom removed. The reactive portion of the molecule, containing the other element(s), is called the **functional group**. Radicals are named just like side chains (see Section 20.2): The name of the parent hydrocarbon has its ending changed to -yl. However, C₆H₅—, the radical derived from benzene, C₆H₆, is called the *phenyl radical*. Radicals derived from alkanes are called **alkyl radicals**. (A radical may be a hydrogen atom in some classes containing carbon atoms in the functional group.)

EXAMPLE 20.12

What are the names of the radicals formed when a hydrogen atom is removed from one end of each of the first four unbranched alkanes? (See Table 20.1 if necessary.)

Solution

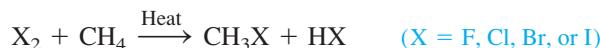
The names are methyl, ethyl, propyl, and butyl, respectively.

Practice Problem 20.12 What are the names of the radicals formed from the unbranched alkanes with nine and ten carbon atoms?

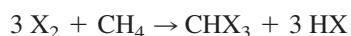
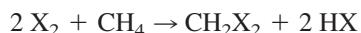
The subsections that follow briefly describe nine different classes of organic compounds: organic halides, alcohols, ethers, aldehydes, ketones, acids, esters, amines, and amides.

Organic Halides

Organic halide is a general term that refers to any fluoride, chloride, bromide, or iodide of a hydrocarbon. The halogen atom is bonded with a single covalent bond to one carbon atom. The symbol X is often used to represent any one of the halogen atoms: F, Cl, Br, or I. Organic halides may be produced by the reaction of the elemental halogen and a hydrocarbon or by the reaction of a hydrogen halide and an unsaturated hydrocarbon, among other methods:



Reaction of excess halogen with an alkane can result in replacement of more than one hydrogen atom:



Chloroform, CHCl₃, and carbon tetrachloride, CCl₄, are familiar products of the chlorination of methane. Halogenated hydrocarbons are intermediates in the production of many other types of organic compounds.

ITEM OF INTEREST

Freons are organic halides in which fluorine and chlorine atoms are substituted for all the hydrogen atoms of methane or ethane. An example is Freon 12, CCl_2F_2 . Such compounds had been used as refrigerants. They are relatively inert, boil in a suitable temperature range, and have a relatively high heat of vaporization. The Freon is allowed to evaporate in the coils in the inner part of the refrigerator; the evaporation process cools. (Chapter 14) The Freon is then pumped as a gas to coils outside the food compartment, where it is compressed back to the liquid state. The liquefaction gives off heat, which is discharged into the room. The whole process is repeated over and over. (The refrigeration process is an example of heat being moved from a cold place to a warmer place, but the process is not spontaneous. Energy is required to accomplish this change.)

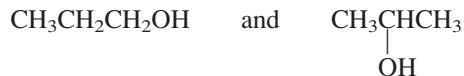
The escape of Freons into the atmosphere is thought to contribute to the destruction of the ozone layer of the Earth's atmosphere. For this reason, Freons are no longer used in aerosol cans for shaving cream, hair spray, and other products, and they have been phased out of refrigeration systems.

DDT (Figure 20.7) is short for dichlorodiphenyltrichloroethane, an old name for 1,1-di(4-chlorophenyl)-2,2,2-trichloroethane. It is a chlorinated hydrocarbon that has had widespread success in controlling mosquitoes and preventing thousands of deaths from malaria. The insecticide is not easily decomposed in the environment, however, and finds its way into the food chain of higher animals, with harmful results. For this reason, its use has been banned in the United States, and substitute insecticides are being used.

Alcohols and Ethers

If a hydrogen atom on a hydrocarbon is replaced by a functional group consisting of covalently bonded oxygen and hydrogen ($-\text{OH}$), an **alcohol** is formed. Because the $-\text{OH}$ group is covalently bonded, the alcohols do not act as bases.

The systematic name of each alcohol is formed from the name of the parent hydrocarbon by changing the ending to *-ol*. For example, the compound $\text{CH}_3\text{CH}_2\text{OH}$ is *ethanol*. If necessary, the “address” of the functional group is indicated. Thus



are 1-propanol and 2-propanol, respectively.

An older nomenclature system used the name of the radical (the name of the parent hydrocarbon with the *-yl* ending) plus the word *alcohol*. Thus, ethanol is also known as ethyl alcohol and, because it is the most familiar alcohol, even simply as alcohol. The formulas of organic compounds can be written in the reverse direction, so ethanol can be represented by HOCH_2CH_3 , as well as by $\text{CH}_3\text{CH}_2\text{OH}$.

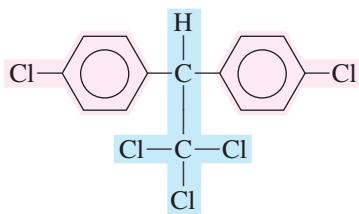
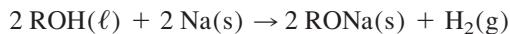


Figure 20.7 Structural Formula of DDT

20.3 ■ Other Classes of Organic Compounds**533**

The reaction of ethane, CH_3CH_3 , to produce ethanol is not easy to accomplish directly; the previously mentioned “replacement” of a hydrogen is a mental replacement. The CH_3CH_2- part of the molecule is the radical, and the $-\text{OH}$ part is the functional group. Because the radical is not very reactive and because radicals of similar hydrocarbons have very similar properties, the characteristic properties of an alcohol come from its functional group. For example, methanol, CH_3OH , and 1-propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, have chemical properties very similar to those of ethanol. Moreover, most alcohols behave rather similarly. Thus, we can write general reactions of all alcohols:

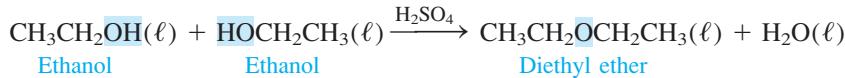
1. They react with very active metals, such as sodium, to produce hydrogen and the corresponding organic salt.



2. They react when heated in the presence of a dehydrating agent, like concentrated H_2SO_4 , to produce ethers:



For example:

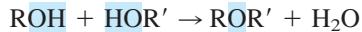


3. They react with organic acids, as described later in this section.

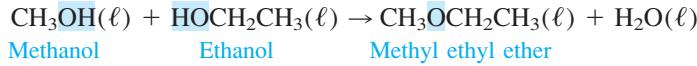
Caution: The physiological effects of ethanol ingestion are different from those of other alcohols. Even ethanol must be used with extreme caution, but the other alcohols are deadly poisonous if ingested.

Several alcohols have commercial importance. Ethanol is used in intoxicating beverages. (Other alcohols are poisonous.) A dialcohol, ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is the major ingredient in permanent antifreeze for cars. 2-Propanol, $\text{CH}_3\text{CHOHCH}_3$, is used as rubbing alcohol. Methanol, CH_3OH , is used as a portable source of heat (Sterno), among many other uses.

Ethers are formed by the reaction of alcohols, as just shown in item 2 of the previous list. If two different alcohol molecules combine, a mixed ether is formed:



For example:



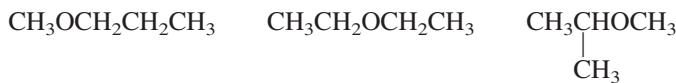
Ethers are named using the radical names derived from their parent hydrocarbons. Their names end with the word *ether*. Diethyl ether was used as an anesthetic until compounds with fewer undesirable side effects were found. It is still widely known as ether, just as ethanol is known as alcohol. Ethers and alcohols can be isomers of each other because both classes have the general molecular formula $\text{C}_n\text{H}_{2n+2}\text{O}$.

EXAMPLE 20.13

Write condensed formulas for the three ethers that are isomers of 1-butanol.

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CHAPTER 20 ■ Organic Chemistry

Solution

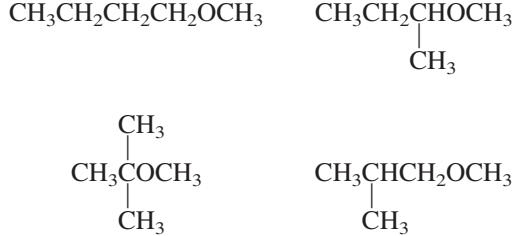
Practice Problem 20.13 Write line formulas for all alcohols that are isomers of methyl ethyl ether.

EXAMPLE 20.14

Write condensed formulas for all ethers that have the molecular formula $\text{C}_5\text{H}_{12}\text{O}$.

Solution

It is best to answer questions like this systematically. Every ether has an —O— functional group with at least one carbon atom on each side of the oxygen atom. Therefore, in the present problem, the most carbon atoms on one side will be four, corresponding to the formula $\text{CH}_3\text{OC}_4\text{H}_9$. There are four ethers corresponding to this formula:



Next we consider the ethers with three carbon atoms on one side of the oxygen atom, leaving two on the other. There are two such formulas:



There are no other combinations.

Practice Problem 20.14 What classes of compounds must be included in the answers to the following problems?

- Write structural formulas for all ethers having molecular formula $\text{C}_5\text{H}_{12}\text{O}$.
- Write structural formulas for all isomers having molecular formula $\text{C}_5\text{H}_{12}\text{O}$.

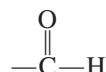
Aldehydes and Ketones

Both aldehydes and ketones have the carbonyl group as the functional group:

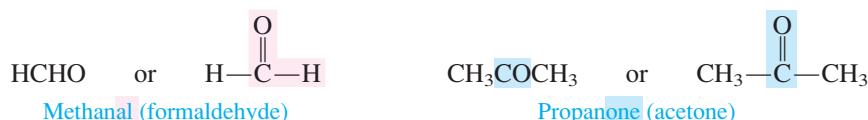


20.3 ■ Other Classes of Organic Compounds**535**

Aldehydes have the carbonyl group on the end of a carbon chain, and **ketones** have it somewhere other than the end. Because the end carbon atom also has a hydrogen atom attached, the formal functional group for aldehydes is written:



The systematic names of *aldehydes* end in *-al*; the systematic names of *ketones* end in *-one*. The simplest ketone, propanone, known familiarly as acetone, has three carbon atoms. Because of its solvent properties, acetone is used in nail polish remover. The simplest aldehyde, methanal, also known as formaldehyde, is perhaps most familiar because it was formerly routinely used as a preservative for biological specimens.



The CO in the line formula for propanone must be



because the total bond order of carbon is four.

Aldehydes and ketones are produced by the mild oxidation of alcohols. If the —OH group of the alcohol is on the end carbon atom, an aldehyde is produced; if that functional group is on a carbon atom that is connected to two other carbon atoms, a ketone is produced. Aldehydes and ketones can be isomers of each other because both have the general molecular formula $\text{C}_n\text{H}_{2n}\text{O}$.

EXAMPLE 20.15

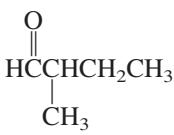
Draw condensed formulas for four aldehydes that are isomers of 2-pentanone. Name these compounds.

Solution

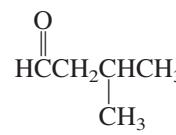
The carbonyl group must be at the end of the carbon chain.



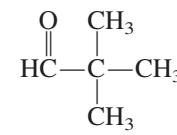
Pentanal



2-Methylbutanal



3-Methylbutanal

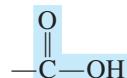


2,2-Dimethylpropanal

Practice Problem 20.15 Name and draw condensed formulas for the three ketones that are isomers of pentanal.

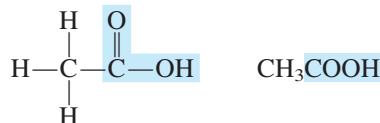
Organic Acids and Esters

An **organic acid** has the functional group —COOH:

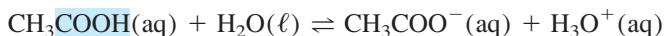


Molecules with covalently bonded —OH groups are not bases.

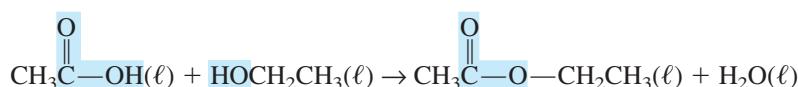
The systematic name of an organic acid ends in *-oic acid*. The hydrogen is not necessarily written first in formulas for organic acids, and hydrogen written first in organic compounds does not necessarily indicate that the compound is an acid. Although the ionizable hydrogen atom of such an acid looks as if it is part of an —OH group, the —OH group is not a hydroxide ion, and the compound is not a base. The —OH group is covalently bonded to a carbon atom that is also doubly bonded to an oxygen atom. As a rule, organic acids are weak; the hydrogen atom ionizes to a slight extent in water. Perhaps the most familiar organic acid is ethanoic acid, also called acetic acid, denoted $\text{HC}_2\text{H}_3\text{O}_2$ earlier in this book. Ethanoic acid has the following structural and line formulas:



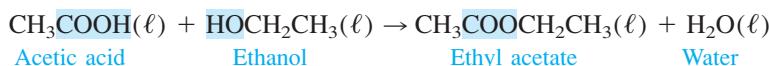
Acetic acid is the most abundant acid in vinegar. Its equilibrium reaction with water may be written as follows (compare Chapter 19):



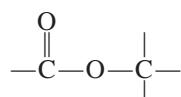
Acetic acid reacts with NaOH to produce sodium acetate, a salt, CH_3COONa . Organic acids also react with alcohols to produce **esters** plus water:



or



The functional group of the ester is related to that of the acid group, with the hydrogen atom replaced by a carbon atom:



The name of an ester is a combination of the name of the hydrocarbon radical of the alcohol plus the name of the parent acid with its ending changed to *-ate*. The ester of *ethyl* alcohol plus *acetic* acid is thus *ethyl acetate*. Many simple esters have pleasant odors. Ethyl acetate is used to provide an odor to artificial fruits, as a solvent for lacquers and varnishes, in the manufacture of photo-

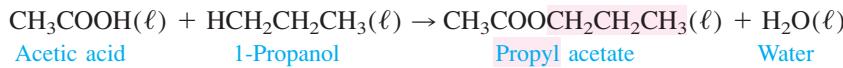
20.3 ■ Other Classes of Organic Compounds**537**

graphic films, and for many other purposes. Many esters occur naturally; their sweet odors are responsible for the fragrances of flowers and fruits. Esters, especially those containing more than one ester linkage in a molecule, are components of fats (Section 20.5) and many polymers (Section 20.4).

EXAMPLE 20.16

Write an equation for the reaction of 1-propanol with acetic acid, and name the products.

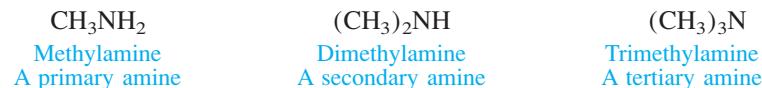
Solution



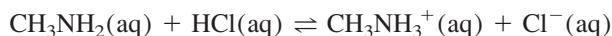
Practice Problem 20.16 Write an equation for the reaction of ethanol with butanoic acid, and name the products.

Amines and Amides

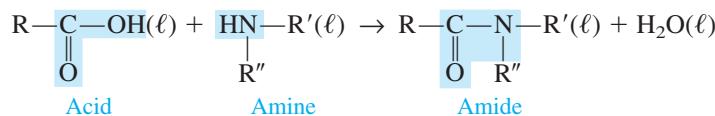
Amines may be regarded as organic derivatives of ammonia. One or more of the hydrogen atoms of ammonia may be replaced with a radical to produce an **amine**. If one H atom is replaced, a *primary* amine is produced; if two are replaced, a *secondary* amine is produced; if three are replaced, a *tertiary* amine is produced:



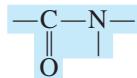
Like ammonia, the amines as a class act as weak bases in water solution (see Table 19.2):



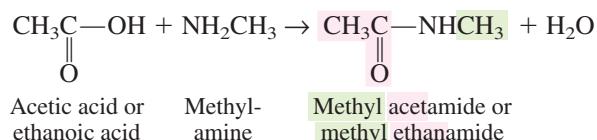
When amines are not in water solution, they can react with organic acids to produce another class of organic compounds. **Amides** are formed by the reaction of organic acids with ammonia or primary or secondary amines:



(Here R, R', and R" on the amide represent radicals that may be the same or different from one another; any or all of them may be hydrogen atoms instead.) Note that in contrast to the product of reaction of an acid and a base, this product is covalently bonded. The reaction is reversible if the reaction conditions are changed. The functional group that characterizes an amide is



Amides are named from the acid and amine from which they are prepared. The characteristic name ending is *amide*, replacing the *-oic acid* of the parent acid. For example:



The classes of organic compounds introduced in this section are summarized in Table 20.4.

In addition to the most modern systematic nomenclature system, several older nomenclature systems are still in use in organic chemistry. The simplest compounds are more often known by their older names than their most modern names, especially in commerce. For example, ethanol is often called ethyl alcohol or just alcohol, and methanol is called methyl alcohol. Even older names, grain alcohol and wood alcohol, respectively, are still used for these two compounds. Similarly, methanal is more generally called formaldehyde, methanoic acid is frequently referred to as formic acid, and methylpropane is often called isobutane.



Snapshot Review



ChemSkill Builder 24.2

- Isomerism can exist between classes as well as within each class.
- The radicals of organic compounds with functional groups are relatively inert; therefore the compounds in each class have similar chemical properties, characteristic of the functional group.

Table 20.4 Classes of Organic Compounds

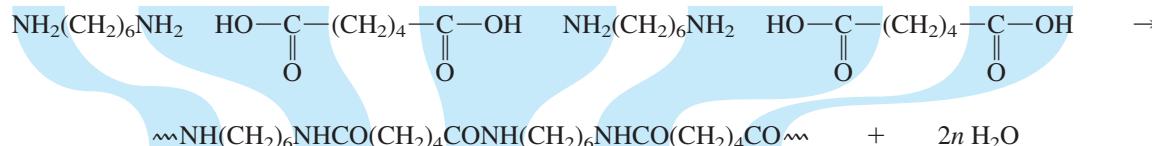
Class	Functional Group	General Formula*	Ending for Name	Example
Organic halides	$—X$	RX		CH_3Cl , chloromethane (methyl chloride)
Alcohols	$—\text{OH}$	ROH	-ol	$\text{CH}_3\text{CH}_2\text{OH}$, ethanol (ethyl alcohol)
Ethers	$—\text{O}—$	ROR'	ether	CH_3OCH_3 dimethyl ether (methyl ether)
Aldehydes	$\begin{array}{c} \text{—C=O} \\ \\ \text{H} \end{array}$	RCHO	-al	CH_3CHO , ethanal (acetaldehyde)
Ketones	$\begin{array}{c} \text{—C=O} \\ \\ \text{R}' \end{array}$	RC=O R'	-one	CH_3COCH_3 , propanone (acetone)
Organic acids	$\begin{array}{c} \text{—C—OH} \\ \\ \text{O} \end{array}$	RCOOH O	-oic acid	$\text{CH}_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—OH}$, ethanoic acid (acetic acid)
Esters	$\begin{array}{c} \text{—C—O—} \\ \\ \text{O} \end{array}$	RCOR' O	-ate	$\text{CH}_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—OCH}_3$, methyl ethanoate (methyl acetate)
Amines	$—\text{NH}_2$	RNH ₂	amine	CH_3NH_2 , aminomethane (methylamine)
Amides	$\begin{array}{c} \text{—C—N—} \\ \\ \text{O} \end{array}$	RC—NR' O R''	amide	$\text{CH}_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—NHCH}_3$, methyl ethanamide (methyl acetamide)

*The radicals designated R, R', and R'' can be the same as or different from each other.

- Give the functional group and name ending for each of the following:
(a) alcohol, (b) aldehyde, and (c) amine.
- Write condensed formulas for all alcohols that are isomeric with diethyl ether.
- Which two classes of compounds in a given subsection of this section *cannot* be isomers of each other?

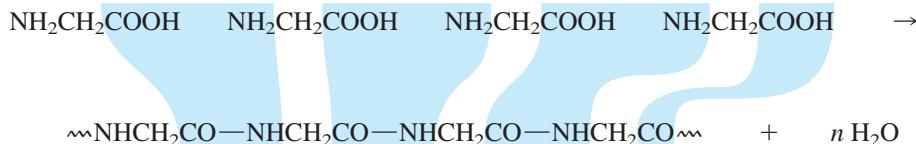
20.4 Polymers

Polymers are familiar to the general public in the form of plastics and **synthetic fibers**, such as nylon, Teflon, polyethylene, and polyester. When two organic molecules that each contain one functional group react with each other, they usually form a new molecule whose size is about that of the two reacting molecules combined. However, an organic molecule can have more than one functional group. In such a molecule, each functional group acts more or less independently of the other(s). When such molecules react, a huge molecule can result. For example, consider the reaction of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ with $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, each of which has two functional groups. Note that only two molecules of each reactant are pictured in the following equation, representing a large number (n) of each:

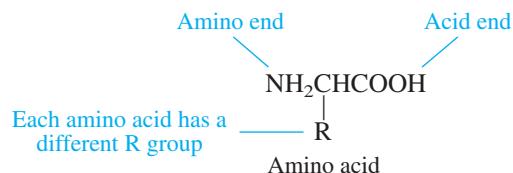


When the $-\text{NH}_2$ group of the first molecule reacts with the $-\text{COOH}$ group of the second molecule, an amide linkage (see Section 20.3) is formed, and the resulting molecule is about twice the size of each of the reacting molecules. That molecule still has functional groups on its two ends and is capable of further reaction. When the $-\text{COOH}$ group at the right reacts with the adjacent $-\text{NH}_2$ group, a still larger molecule is formed. This sort of reaction can continue until the supply of reactant molecules, called **monomers**, is exhausted (or until a ring is formed). The large molecule that is the product of such a reaction is called a **polymer** (from the Greek *poly*, meaning “many,” and *mer*, meaning “parts”). A polymer can have a molecular mass of hundreds of thousands of atomic mass units (amu) or even more. The polymer formed in the preceding reaction is called **nylon**.

A similar reaction takes place when molecules of amino acid (each with both an amine and an acid group) react with others:

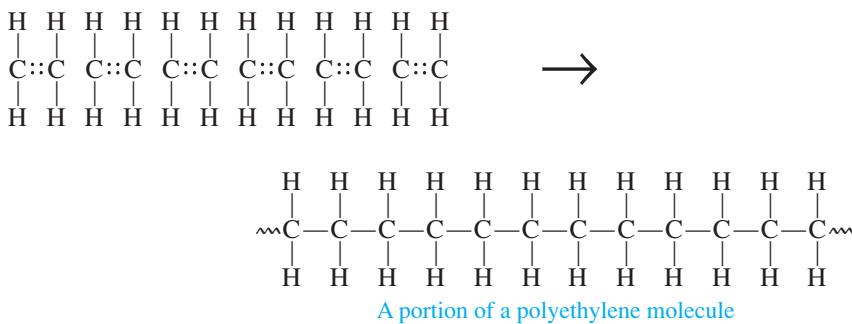


Protein is a product of the polymerization of amino acids. Twenty different natural amino acids, each with a different R group in the formula, are components of human proteins.



A polymerization reaction can also take place between molecules containing two organic acid groups and molecules containing two alcohol groups; a **polyester**, widely used in clothing manufacture, is formed.

The reactions described so far are examples of condensation polymerization. In such reactions, small molecules (in these cases, water molecules) are eliminated from the reacting functional groups. Another type of polymerization is addition polymerization, illustrated by the polymerization of ethylene:

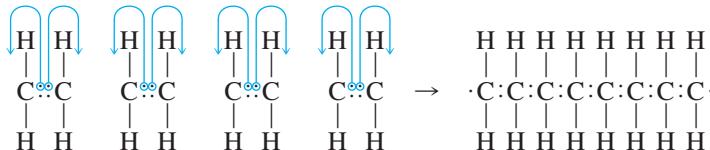


In this polymerization process, no small molecules are produced. The monomer molecules add together by shifting electrons from their double bonds to form new carbon-carbon single bonds.

EXAMPLE 20.17

Show how shifting the electrons of four C_2H_4 molecules causes reaction leading to polymerization.

Solution



This process continues until a polymer is formed.

Practice Problem 20.17 If one hydrogen on each monomer is replaced with a CH_3- group, (a) what difference does this change make to the electron shifting process? (b) what polymer results?

Table 20.5 Commercial Polymers Related to Polyethylene

Name and Formula of Monomer	Polymer	Use
Ethylene, $\text{CH}_2=\text{CH}_2$	Polyethylene	Wrapping film
Propylene, $\text{CH}_3\text{CH}=\text{CH}_2$	Polypropylene	Wrapping film
Vinyl chloride, $\text{CH}_2=\text{CHCl}$	Polyvinylchloride (PVC)	Raincoats, bottles
Styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Polystyrene	Molded plastic insulation
Tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$	Teflon	Chemical- and heat- resistant plastics

Several commercial polymers are related to polyethylene (Table 20.5). For example, fluorinated polymers, such as Teflon, are familiar commercial products. Having fluorine atoms in place of all the hydrogen atoms makes the polymer nonflammable and much more resistant to oxidation and thermal decomposition.



Snapshot Review

ChemSkill Builder
25.1, 25.2, 25.3

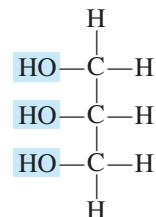
- The functional groups of compounds with more than one functional group behave rather independently of one another. Reactions of two or more functional groups on each molecule can yield very long chain products, upward of 100,000 or more.

- A. What other type of compound is required to react with a dialcohol to yield a polyester?
- B. If we wanted to experiment to make a polyamide, what type of monomer or monomers should we use?

20.5 Foods

Fats

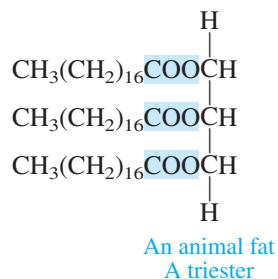
Fats are triesters of the **trialcohol** glycerine:



Glycerine, or glycerol
A trialcohol

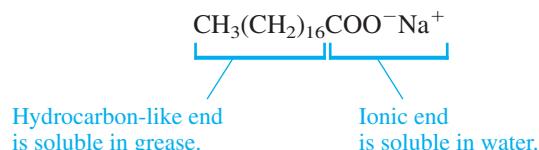
The radicals of acid molecules that react with glycerine to make animal fats have long chains of carbon atoms. Perhaps most typical of these so-called fatty

acids is stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$. The reaction of three stearic acid molecules with a molecule of glycerine produces a triester (see Section 20.3) that is a fat:



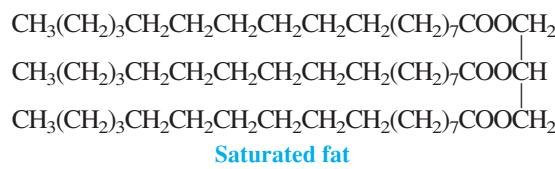
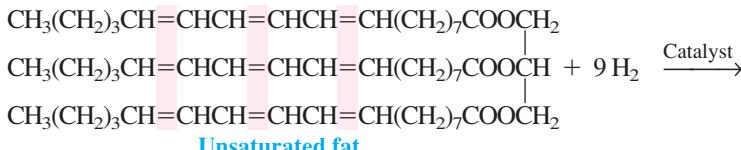
This fat can be broken down into glycerine and the sodium salt of the acid (sodium stearate) by treating it with NaOH.

Sodium stearate is a **soap**. It has a long-chain hydrocarbon-like end, which dissolves well in greases and oils, and it has an ionic end, which dissolves well in water:



Such a molecule can cause particles of grease or oil to mix somewhat with water and to be washed from a dirty article. Calcium and magnesium ions in hard water react with stearate ions to form a solid, yielding soap scum. To avoid this problem, chemists developed synthetic detergents that do not form insoluble salts with calcium and magnesium ions. Synthetic detergents are similar to soaps in that they have an ionic end and a large hydrocarbon-like end.

If triesters are made with unsaturated fatty acids—ones with double bonds in their hydrocarbon-like parts—oils are produced. If only single bonds are in the fatty acids, fats are produced. Because consumers seem to prefer solid fats (such as butter) to liquid oils, some food manufacturers hydrogenate the unsaturated oils to reduce the number of double bonds in the molecules and produce a more solid product:

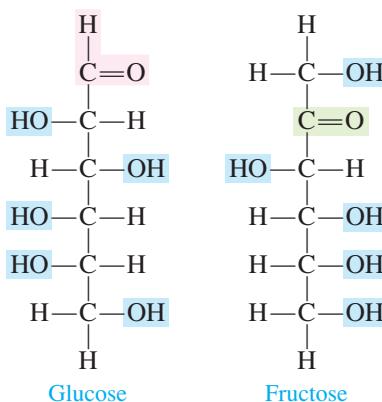


Unsaturated fats seem to be more healthful than saturated ones, especially in reducing the buildup of deposits in the arteries. Do not expect to reap the benefits of unsaturated fats, however, by eating fully hydrogenated triesters.

Carbohydrates

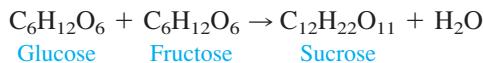
Sugars and starches are two classes of **carbohydrates**, compounds containing carbon, hydrogen, and oxygen in which the hydrogen-to-oxygen ratio is 2:1. Despite the word *hydrate* in the name, a carbohydrate molecule contains no water. **Sugars** are compounds whose molecules have many **alcohol groups**, plus an **aldehyde** or **ketone** group.

Glucose and fructose, two isomeric simple sugars, have the following (simplified) structures:



These sugars are highly water-soluble because of the hydrogen bonding between their —OH groups and water molecules.

Molecules of two of these simple sugars, examples of **monosaccharides**, can react by eliminating one water molecule to produce a double molecule. Sucrose, ordinary table sugar, is an example of such a double molecule, formed from a glucose molecule and a fructose molecule; it is a **disaccharide**. Its molecular formula is $C_{12}H_{22}O_{11}$. The two simple sugars that make it up both have the formula $C_6H_{12}O_6$, and twice that formula yields $C_{12}H_{24}O_{12}$. Elimination of one water molecule, H_2O , yields the correct molecular formula for sucrose:



Starches and cellulose are polymers of monosaccharides linked together. They are **polysaccharides**.



Snapshot Review

- Foods are somewhat more complex organic compounds, but chemically they still follow the general behavior of their class(es) of compounds.

- A. Classify the following foods as a class of organic compound from Section 20.3:
(a) fat and (b) protein.

Key Terms

Key terms are defined in the Glossary.

alcohol (20.3)	ethylene (20.1)	polysaccharide (20.5)
aldehyde (20.3)	fat (20.5)	protein (20.4)
alkane (20.1)	functional group (20.3)	radical (20.3)
alkene (20.1)	hydrocarbon (20.1)	saturated fat (20.5)
alkyl radical (20.3)	isomers (20.2)	saturated hydrocarbon (20.1)
alkyne (20.1)	ketone (20.3)	soap (20.5)
amide (20.3)	line formula (20.1)	structural isomers (20.2)
amine (20.3)	monomer (20.4)	sugar (20.5)
aromatic hydrocarbon (20.1)	monosaccharide (20.5)	synthetic fiber (20.4)
benzene (20.1)	nylon (20.4)	total bond order (20.3)
carbohydrate (20.5)	organic acid (20.3)	unsaturated fat (20.5)
condensed formula (20.1)	organic compound (intro)	unsaturated hydrocarbon (20.1)
disaccharide (20.5)	organic halide (20.3)	urea (intro)
ester (20.3)	polyester (20.4)	
ether (20.3)	polymer (20.4)	

ethene (20.1)
fat (20.5)
functional group (20.3)
hydrocarbon (20.1)
isomers (20.2)
ketone (20.3)
line formula (20.1)
monomer (20.4)
monosaccharide (20.5)
nylon (20.4)
organic acid (20.3)
organic compound (intro)
organic halide (20.3)
polyester (20.4)
polymer (20.4)

Symbols/Suffixes

 (benzene) (20.1)	-ane (20.1)	-ol (20.3)
R (radical) (20.3)	-ate (20.3)	-one (20.3)
X (halogen) (20.3)	-ene (20.1)	-yl (20.2)
-al (20.3)	-oic acid (20.3)	-yne (20.1)

Summary

Organic compounds (with very few exceptions) are compounds containing at least one carbon-carbon or carbon-hydrogen bond. Hydrocarbons are compounds containing only carbon and hydrogen. The hydrocarbons to learn first are the alkanes, which have single bonds only. Their systematic names end in *-ane*, and their general molecular formula is C_nH_{2n+2} . The systematic names of other organic compounds are based on the names of the alkanes. The alkanes are relatively inert, but they do react with oxygen to form water and carbon monoxide or carbon dioxide, or with a halogen to form a hydrogen halide and the halogenated alkane.

The unsaturated hydrocarbons include the alkenes, which contain one double bond per molecule, and the alkynes, which contain one triple bond per molecule. Their systematic names begin as the names of the corresponding alkanes do, but they end with *-ene* or *-yne*, respectively. The location of the multiple bond may have to be specified in the name by including the address of the multiple-bonded carbon atom that is closer to the end of the chain. The alkenes and alkynes are more active than the alkanes; for example, they react with halogens to form halogenated hydrocarbons under much less severe

conditions than are required for the reactions of alkanes with halogens.

Aromatic hydrocarbons are compounds containing a benzene ring. The ring structure and special bonding in benzene give the aromatic hydrocarbons added stability (Section 20.1).

Molecules with the same molecular formula but different structures are isomers of one another. They are different compounds, with different properties. Structural isomers exist because of different points of attachment of groups on a chain of carbon atoms or because of different locations of multiple bonds in the chain. Determining whether two structures represent the same molecule or are isomers of each other may seem difficult at first, because two-dimensional representations do not accurately portray the three-dimensional molecules (Section 20.2).

In addition to the hydrocarbons are nine other important classes of organic compounds to learn: organic halides, alcohols, ethers, aldehydes, ketones, organic acids, esters, amines, and amides. The hydrocarbon-like part of such molecules is called the radical; the other part is called the functional group. The names of radicals

■ Self-Tutorial Problems**545**

are derived from the names of the corresponding alkanes, with the ending changed to *-yl*. The functional groups are named as shown in Table 20.4; all of those characteristic functional groups and their names must be learned. Isomerism exists within all classes of organic compounds and between certain classes as well. For example, most aldehydes have isomers among the ketones (Section 20.3).

Each functional group in any organic molecule can react more or less independently of any others in the molecule. Therefore, many molecules with two or more functional groups can react in sequences to form very large molecules, called polymers. Nylon, polyethylene, and protein are familiar examples of polymers (Section 20.4).

The foods we consume are mainly organic compounds. Proteins are polymers of amino acids. Fats are triesters of glycerine, a trialcohol. When fats are treated with a strong base, soaps and glycerine result. Unsaturated fats contain double bonds in the hydrocarbon-like part of the ester; saturated fats have only single bonds there. Carbohydrates are compounds of carbon, hydrogen, and oxygen, in which hydrogen and oxygen occur in a 2 : 1 mole ratio of atoms. Despite the name, water molecules are not present in carbohydrates. Molecules of the simplest carbohydrates contain alcohol and either aldehyde or ketone functional groups. Carbohydrates include sugars, starches, and cellulose; the last two are polymers of simpler carbohydrates (Section 20.5).

Items for Special Attention

- Hydrocarbons are compounds containing only carbon and hydrogen. Carbohydrates are compounds of carbon, hydrogen, and oxygen.
- The formulas $\text{CH}_3\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{CHCH}_3$ both represent the same compound, propene. They are simply written in the opposite order.
- Hydrogen is not necessarily written first in the formula for an organic acid, nor is an organic compound whose formula has hydrogen written first necessarily an acid.
- In a line formula, an oxygen atom doubly bonded to a carbon atom is usually written to the right of the carbon atom.

Answers to Snapshot Reviews

20.1 A. Alkane, C_6H_{14} ; alkene, C_6H_{12} ; alkyne, C_6H_{10} ; aromatic, C_6H_6
B. Alkanes

C. The alternating single and double bonds in the ring give benzene a special stability.
D. (a) 3-Methylhexane (b) 2,5-dimethylhexane

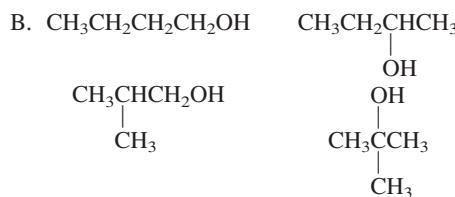
20.2 A. Alkane, C_4H_{10} ; alkene, C_4H_8 ; alkyne, C_4H_6
B. $\text{CH}=\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 1-Heptyne
 $\text{CH}_3\text{C}=\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 2- Heptyne
 $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ 3- Heptyne

The number denoting the location of the triple bond distinguishes them.

20.3 A. (a) $-\text{OH}$, -ol (b)

$$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H}, \text{-al} \end{array}$$

(c) $-\text{NH}_2$, amine



C. Amines and amides (Amides contain oxygen.)
20.4 A. A diacid
B. An amino acid or a diamine plus a diacid

20.5 A. (a) Triester
B. Polyamide

Self-Tutorial Problems

- 20.1 How many carbon atoms are in (a) hexane, (b) 1-hexene, (c) 2-hexyne, and (d) a hexyl radical?
- 20.2 How many hydrogen atoms are present in an alkane with 14 carbon atoms?
- 20.3 In which classes of Table 20.4 must the radical R be different from a hydrogen atom?

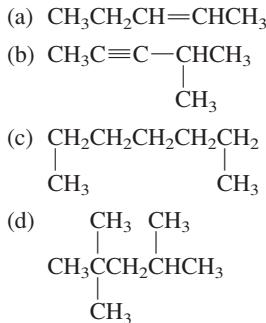
- 20.4 Name each of the following:
 (a) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ (b) $\text{CH}\equiv\text{CCH}_2\text{CH}_3$
 (c) $(\text{CH}_3\text{CH}_2)_3\text{CH}$ (d) 
- 20.5 Write condensed formulas for (a) 2-methylhexane, (b) 3-chloropentane, and (c) ethylbenzene.

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- 20.6** We can picture methanol, CH_3OH , as a water molecule with one hydrogen atom replaced by a radical (CH_3-). How can each of the following be similarly described?
- $\text{CH}_3\text{CH}_2\text{NH}_2$
 - $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$
 - $\text{ClCH}_2\text{CH}_2\text{CH}_3$
- 20.7** Name each of the following two ways:
- CH_3COCH_3
 - CH_3NH_2
 - CH_3CHO
 - CH_3COOH
 - $\text{CH}_2=\text{CH}_2$
 - CH_3OH
- 20.8** What is the *inorganic* product of the reaction of (a) an organic acid with an amine, (b) an alcohol with an organic acid, and (c) an alcohol with another alcohol?
- 20.9** Write condensed formulas for (a) propanone, (b) ethanoic acid, (c) methyl ethanoate, (d) ethanol, (e) aminomethane, and (f) methanal.
- 20.10** Write a condensed formula for (a) butane, (b) 2-butene, (c) 1-butyne, (d) 1-butanol, (e) butanal, (f) butanone, (g) butanoic acid, (h) butanamide.

Problems**20.1 Hydrocarbons**

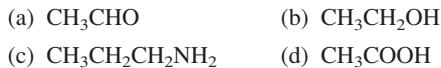
- 20.16** Identify each of the following as an alkane, alkene, or alkyne:
- $\text{C}_{10}\text{H}_{18}$
 - C_9H_{20}
 - C_8H_{16}
- 20.17** Identify each of the following as an alkane, alkene, or alkyne:
- $\text{C}_{35}\text{H}_{72}$
 - $\text{C}_{30}\text{H}_{60}$
 - $\text{C}_{40}\text{H}_{78}$
- 20.18** Draw a condensed formula for (a) $\text{C}(\text{CH}_3)_4$ and (b) $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$.
- 20.19** Draw a condensed formula for (a) $\text{CH}_2(\text{C}_6\text{H}_5)_2$, (b) C_3H_6 , and (c) $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$.
- 20.20** Name each of the following compounds:



- 20.21** Write a line formula for each of the following compounds:
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CHCH}_2\text{CH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \\ || \\ \text{CH}_3\text{CCH}_3 \\ || \\ \text{CHCH}_3 \end{array}$

- 20.11** Explain why no location numbers are needed in the names (a) propanone and (b) propanal.

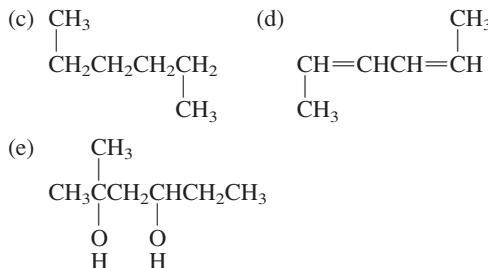
- 20.12** Write the line formula for each of the following compounds in the reverse order.



- 20.13** Write condensed formulas for (a) acetone, (b) acetic acid, (c) methyl acetate, (d) ethyl alcohol, (e) methyl amine, and (f) formaldehyde.

- 20.14** What functional group is common to both nylon and proteins?

- 20.15** Using molecular formulas, write an equation for the combination of fructose and glucose (each $\text{C}_6\text{H}_{12}\text{O}_6$) into sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$).



- 20.22** Complete the following table by writing the molecular formula for each compound or the formula for radical. If none exists for a particular place in the table, write "None."

Number of Carbon Atoms	Alkane	Alkene	Alkyne	Alkyl Radical
1	—	—	—	—
2	—	—	—	—
3	—	—	—	—
4	—	—	—	—
5	—	—	—	—

- 20.23** How many carbon atoms are in (a) 3-ethylhexane, (b) 3,3-diethylheptane, and (c) 2,4,6-trimethylheptane?

- 20.24** How many hydrogen atoms are in each of the compounds in the prior problem?

- 20.25** How many carbon atoms are in (a) 3,4-diethyl-2-heptene, (b) 3-methyl-4-propyl-1-nonyne, and (c) 2,2,3,4-tetramethyl-3-ethylheptane?

■ Problems

- 20.26 How many hydrogen atoms are in each of the compounds in the prior problem?

20.2 Isomerism

- 20.27 Write a condensed formula for (a) 2,3-dimethylbutane and (b) 3,3-dimethylhexane. (c) Explain why 3,4-dimethylpentane does not exist.
- 20.28 Write a line formula for (a) 2-methyl-2-pentene, (b) 3-methyl-1-pentene, and (c) 4-methyl-2-pentene. (d) Explain why 4-ethyl-2-pentene does not exist.
- 20.29 Write condensed formulas for the isomers of C_7H_{16} that have two methyl branches only.
- 20.30 Draw condensed formulas for all unbranched isomers of C_5H_8 . (*Hint:* Consider more than one multiple bond.)
- 20.31 Draw condensed formulas for all structural isomers of C_6H_{14} . Name each one.
- 20.32 Draw condensed formulas for five noncyclic structural isomers of C_5H_{10} . Name each one.
- 20.33 Draw line formulas for all unbranched isomers of C_6H_{12} .
- 20.34 Draw all isomers named methylnaphthalene (with a position number). Naphthalene, a planar aromatic hydrocarbon, has the structure,



where each corner of a hexagon represents a carbon atom, and eight hydrogen atoms are connected to the carbon atoms not in both hexagons.

- 20.35 Draw condensed formulas for (a) all four noncyclic isomers of C_4H_6 and (b) all aromatic isomers of $C_6H_4(CH_3)_2$.

20.3 Other Classes of Organic Compounds

- 20.36 Write the line formula of the simplest member of each of the following classes:
- | | |
|------------------|------------------|
| (a) Ether | (b) Aldehyde |
| (c) Amine | (d) Amide |
| (e) Ketone | (f) Organic acid |
| (g) Alkyl iodide | (h) Alcohol |
- 20.37 Name the compounds that were the answers in the prior problem.
- 20.38 Give the systematic name for (a) ethyl alcohol, (b) acetone, (c) acetaldehyde, and (d) formic acid.
- 20.39 Identify the class of each of the following compounds:
- | | | |
|----------------|-----------------|------------------|
| (a) $HCOOH$ | (b) CH_3OCH_3 | (c) CH_3COCH_3 |
| (d) CH_3NH_2 | (e) CH_3OH | (f) $HCHO$ |
- 20.40 Which aldehyde(s) do(es) not have (an) isomer(s) that is a (are) ketone(s)?

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- 20.41 Write the condensed formula for an isomer of each of the following:
- | | |
|---------------------|--------------------|
| (a) $CH_3OCH_2CH_3$ | (b) $NH_2CH_2CH_3$ |
| (c) $HCONHCH_3$ | (d) CH_3CH_2OH |
- 20.42 Identify the class of compound of both isomers (in the problem and the answer) for each part of the prior problem.
- 20.43 Name both compounds in each part of Problem 20.41.
- 20.44 Draw condensed formulas for all alcohols with the formula $C_4H_{10}O$.
- 20.45 Draw condensed formulas for all ethers with the formula $C_4H_{10}O$.
- 20.46 Write the line formula for one unbranched isomer of each of the following in a different class of organic compound.
- | | |
|------------------------|-------------------------|
| (a) $CH_3CH_2CHOHCH_3$ | (b) $CH_3CH_2CH_2OCH_3$ |
| (c) $CH_3CH_2COCH_3$ | (d) $CH_3CH_2COOCH_3$ |
- 20.47 Identify the class of compound of each isomer (in the problem and the answer) in each part of the prior problem.
- 20.48 Name both compounds in each part of Problem 20.46.
- 20.49 Write a condensed formula for (a) 3-chlorohexane and (b) 2-chlorohexane. (c) Explain why there is no compound named 4-chlorohexane.
- 20.50 Give the common name for each of the following:
- | | | |
|-------------|-------------|-------------------|
| (a) Ethanol | (b) Ethanal | (c) Ethanoic acid |
|-------------|-------------|-------------------|
- 20.51 Draw condensed formulas for all unbranched isomers of $C_6H_{13}Cl$.
- 20.52 Write condensed formulas for all alcohols with molecular formulas
- | | |
|---------------|------------------|
| (a) CH_4O | (b) C_2H_6O |
| (c) C_3H_8O | (d) $C_4H_{10}O$ |
- 20.53 Write the structural formula for the simplest amide, a compound prepared from ammonia and an organic acid.
- 20.54 Write condensed formulas for all compounds with the formula
- | | | |
|----------------|----------------|----------------|
| (a) C_2H_5Cl | (b) C_3H_7Cl | (c) C_4H_9Cl |
|----------------|----------------|----------------|
- 20.55 For which pair of groups discussed in the subsections of Section 20.3 is isomerism between a member of one class and a member of the other impossible?
- 20.56 Write the line formulas of two isomers of each of the following:
- | | |
|-------------------------|----------------------|
| (a) $CH_3CH_2OCH_2CH_3$ | (b) $CH_3N(CH_3)_2$ |
| (c) $CH_3CONHCH_3$ | (d) $(CH_3)_2CHCOOH$ |
- 20.57 What is the class of the compound whose line formula is given in each part of the prior problem?
- 20.58 Name the compounds whose line formulas are given in Problem 20.56.
- 20.59 Name the compounds that were answers in Problem 20.56.

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- 20.60 A styrene molecule can be considered to be an ethylene molecule with one hydrogen replaced by a phenyl radical (C_6H_5-). Using R for C_6H_5 , draw a representation of polystyrene like that of polyethylene shown in Section 20.4.
- 20.61 A propylene molecule can be considered to be an ethylene molecule with one hydrogen replaced by a methyl radical. Using R for CH_3 , draw a representation of polypropylene like that of polyethylene shown in Section 20.4.
- 20.62 Are polymers expected to be gaseous at room temperature and atmospheric pressure? Explain.
- 20.63 Name all the plastic materials that existed in 1900.
- 20.64 Draw a section of polymer formed from a diamine and a diacid. Have at least two molecules of each in your section.

CHAPTER 20 ■ Organic Chemistry**20.5 Foods**

- 20.65 Explain the difference between an amino acid and an amide.
- 20.66 What elements are contained in each of the following?
(a) Fats (b) Sugars (c) Proteins
- 20.67 Draw a line formula for each of the following:
(a) Glycerine (glycerol) (b) A soap
(c) The simplest amino acid (d) A fatty acid
- 20.68 Draw a section of polymer formed from an amino acid. Have at least three molecules of monomer in your section.

General Problems

- 20.69 Draw a condensed formula for $(C_6H_5)_2CH_2$.
- 20.70 Draw condensed formulas for four primary amines with molecular formula $C_4H_{11}N$.
- 20.71 Calculate the oxidation number of the carbon atom in each of the following:
(a) $HCONH_2$ (b) $HCOOH$
(c) $HCHO$ (d) CH_3OH
(e) CH_2Br_2 (f) CH_3Br
- 20.72 Write the line formula for the largest (a) alcohol that cannot have an ether isomer, (b) aldehyde that cannot have a ketone isomer, and (c) acid that cannot have an ester isomer.
- 20.73 (a) Calculate the oxidation number of the carbon atoms in each of the following molecules:
 CH_3OCH_3 CH_3COOH
 CH_3CH_2OH $HCOOCH_3$
(b) Deduce a generalization about oxidation numbers and isomerism.
- 20.74 (a) Deduce the numbering system for the benzene rings in DDT (see Figure 20.7) from the systematic name given.
(b) Draw a structural formula for di(2-chlorophenyl)-methane.
- 20.75 Explain how the following compound can act as a detergent, making grease and water mix:
- $$CH_3(CH_2)_nCH_2SO_3^-K^+$$
- 20.76 TNT (end of Section 20.1) is more precisely known as 2,4,6-trinitrotoluene. Define the numbering system for the benzene ring of toluene.

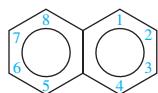
- 20.77 Which structural isomer of dichloroethene has a dipole?
(Hint: consider Section 13.4.)
- 20.78 Which isomers of difluorobenzene have dipoles?
- 20.79 Which classes of organic compounds do *not* need positional numbers for the functional groups in any of their names?
- 20.80 Does difluoroethyne, a linear molecule, have a dipole?
- 20.81 Write a formula for a portion of a protein formed solely from glycine monomers. Glycine is NH_2CH_2COOH .
- 20.82 Draw a condensed formula for (a) 1-chlorobutane and (b) 2-chlorobutane. (c) Explain why there is no 3-chlorobutane.
- 20.83 Draw formulas for all structural isomers of the monochloro compound produced by treating a limited quantity of Cl_2 with (a) 2-methylhexane and (b) 3-methylhexane. (c) Why are fewer isomers produced for one of these than for the other?
- 20.84 Would it be worth paying extra to get the “health benefits” of a fully hydrogenated unsaturated fat compared with a saturated fat? Explain.
- 20.85 Write condensed formulas for all esters with molecular formulas
(a) $C_2H_4O_2$ (b) $C_3H_6O_2$ (c) $C_4H_8O_2$
- 20.86 Which food groups can be considered polymers?
- 20.87 Write a formula for a portion of a protein formed from monomers represented by $NH_2CHRCOOH$.
- 20.88 Draw a representation of a protein molecule consisting of four amino acid residues and containing two different amino acids, differentiated by R and R' radicals. How many different four-residue structures can be drawn?

■ General Problems

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Comment on the number of possible proteins with 20 different amino acids in a molecule containing 100 or more residues. (*Hint:* The amino acids are different on each end of each molecule.)

- 20.89** Give the position numbers of the methyl groups in each isomer of dimethylnaphthalene, a planar molecule. The positions on naphthalene are



20.90 In dilute aqueous solution, the amino end of an amino acid molecule acts as a base, and the acid end acts as an acid. Write a line formula for an amino acid in neutral solution after the two ends of the same molecule have reacted with each other.

20.91 Explain why no addresses (positional numbers) need to be used in the names (a) butanal and (b) butanone.

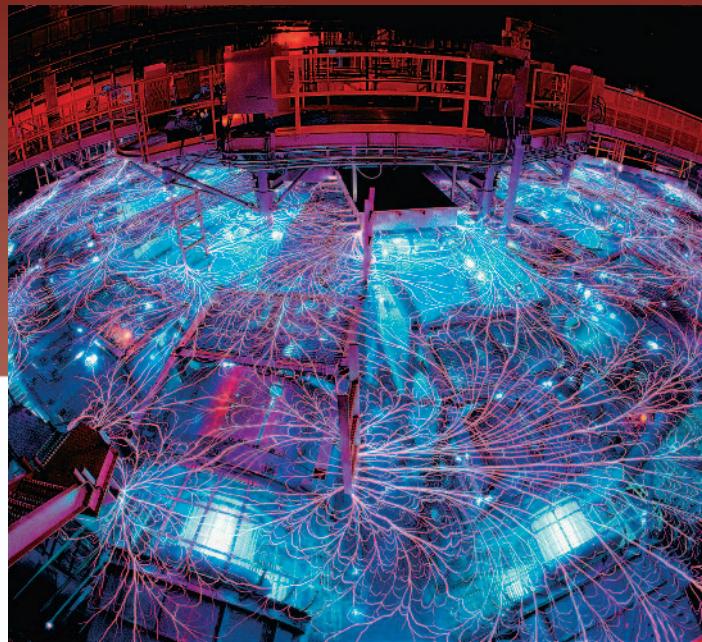
20.92 Write a condensed formula for methyl 2-propyl ether.

20.93 Write the line formula for 1,3-butadiene.

21

Nuclear Reactions

- 21.1 Natural Radioactivity
- 21.2 Half-Life
- 21.3 Nuclear Fission
- 21.4 Nuclear Fusion



X-ray generator at Sandia National Lab

Review Clues

- Section 21.1** Sections 3.3, 4.1
Section 21.2 Section 19.3, Appendix A.2
(logarithms)
Section 21.4 Section 1.3

Objectives

- 21.1** To write equations describing how certain isotopes disintegrate naturally and spontaneously and to describe how these processes occur
21.2 To predict the time in which a given fraction of a naturally radioactive sample will disintegrate
21.3 To predict the products of artificially induced reactions in which nuclei break down into smaller nuclei and subatomic particles
21.4 To describe the principles of reactions in which nuclei are combined into larger nuclei

21.1 ■ Natural Radioactivity**551**

None of the reactions or processes studied in previous chapters affected the nucleus of an atom. No atom changed from one element to another. This chapter considers the effects of nuclear change. In most cases, such changes cause a transformation from one element to another. They include the natural radioactivity of certain isotopes (Section 3.3), as well as the artificial nuclear reactions discovered during the twentieth century. Nuclear reactions differ from ordinary chemical reactions in the following ways:

Chemical Reactions

1. Atomic numbers do not change.
2. Isotopes of a given element behave almost identically.
3. The total quantity of matter does not change measurably.
4. Mole quantities are usually used in calculations.

Nuclear Reactions

1. Atomic numbers almost always change.
2. Isotopes of an element have different properties.
3. The total quantity of matter in the reaction changes in a very small but significant way; some matter is converted to energy.
4. Individual atoms are usually used in calculations.

We live amid constant and natural radiation due to natural radioactive processes, which is normal and not harmful. (For example, the carbon which makes up so much of our bodies contains a tiny fraction of radioactive carbon-14.) Natural radioactivity, the spontaneous disintegration of unstable nuclei, is described in Section 21.1. The subatomic particles involved, the balancing of nuclear equations, and a practical use of such reactions are also discussed. Section 21.2 examines half-life, the time it takes for half of any particular sample of a given radioactive isotope to disintegrate spontaneously. Artificially induced nuclear reactions are introduced in Section 21.3. Many such reactions produce two large product nuclei from each target nucleus, a process called nuclear fission. The subatomic products of some of these reactions cause further reactions, producing a chain reaction. Nuclear fusion, the formation of larger nuclei from smaller ones, is discussed in Section 21.4.

This chapter deals with *reactions* of nuclei; it has nothing to do with magnetic resonance imaging (MRI) or nuclear magnetic resonance, which are the effects of the magnetic properties of some nuclei.

21.1 Natural Radioactivity

The subatomic particles that are the major components of the atom were introduced in Section 3.3. Protons, neutrons, and electrons have the properties presented in Table 21.1. The atomic number of an atom is the number of protons in its nucleus, and the mass number of an atom is the number of protons plus neutrons in the atom's nucleus. **Isotopes** are atoms having the same number of protons (the same atomic number) and different numbers of neutrons (and therefore different mass numbers).

The symbol for an isotope stands for the *nucleus* of that isotope. Recall that the mass number of an isotope is written as a left superscript on the symbol of the element and that the atomic number may appear as a left subscript. For example, cobalt-60 may be represented as either ^{60}Co or $_{27}^{60}\text{Co}$. The symbol of

Table 21.1 Properties of Subatomic Particles

	Charge (e)*	Mass (amu) [†]	Location in the Atom
Proton	1 +	1.0073	In the nucleus
Neutron	0	1.0087	In the nucleus
Electron	1 -	0.000549	Outside the nucleus

*The charges given are the relative charges, based on the charge of the electron, e , as the fundamental unit of charge ($1 e = 1.60 \times 10^{-19}$ coulomb).

[†]The masses are given in atomic mass units (amu), described in Section 3.4.

the element tells the atomic number, but for balancing nuclear equations, writing the subscripts explicitly is very convenient.

Some naturally occurring isotopes of certain elements have nuclei that disintegrate (break down) spontaneously, and we have no control over these processes. These include most isotopes with atomic numbers greater than 83. Each of these disintegrations occurs with the emission of one of three types of **nuclear radiation**—alpha particles, beta particles, and gamma particles—as well as a considerable quantity of energy. The properties of these particles are presented in Table 21.2. **Alpha particles** are identical to helium-4 nuclei. **Beta particles** are electrons with extremely high energies. **Gamma particles** are identical to very high-energy electromagnetic radiation (a form of light, but with much higher energy than visible light). Gamma radiation was originally referred to as a ray, but because electromagnetic radiation is now known to have the characteristics of particles as well as of waves, a gamma ray can also be thought of as a stream of gamma particles, called photons (Section 4.1). Similarly, a stream of alpha or beta particles is often called an alpha ray or a beta ray, respectively. When alpha and beta particles slow down enough after being emitted from the nucleus, they become ordinary ${}^4\text{He}$ nuclei and ordinary electrons, respectively.

The process involving spontaneous emission of particles from nuclei is called **radioactivity**, or **radioactive decay**. The isotopes that undergo such **disintegration** are said to be radioactive. Each disintegration is called an **event**. Because the nucleus of the atom is undergoing the change, the chemical environment of the atom makes little difference to the process of radioactive decay. For example, uranium-238 metal or uranium-238 in any one of its compounds undergoes nuclear disintegration in the same manner and at the same rate.

Superscripts and subscripts may be used with the Greek letters that represent alpha, beta, and gamma particles. For example, an alpha particle can be represented by the Greek letter alpha (α) or the symbol ${}^4\text{He}$. In either case, the subscript can be used or omitted. With the Greek letter, the superscript is also

Table 21.2 Products of Natural Radioactivity

Particle*	Symbol	Charge	Mass Number	Identity
Alpha	α	2 +	4	Helium nucleus
Beta	β	1 -	0	Electron
Gamma	γ	0	0	Photon of light

*Sometimes, a stream of any of these types of particles is called a ray, as in gamma ray.

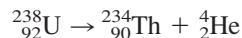
21.1 ■ Natural Radioactivity**553**

optional. In short, the alpha particle can be represented as α , ${}^4\alpha$, ${}^4_2\alpha$, ${}^4\text{He}$, or ${}^4_2\text{He}$. In this book, we will usually use ${}^4_2\text{He}$. Similarly, the beta particle can be represented β , -1β , ${}^0\beta$, ${}^0_1\beta$, e , $-e$, ${}^0-e$, or ${}^0_{-1}e$. The gamma particle is usually represented γ or ${}^0\gamma$.

Nuclear radiation must be distinguished from electromagnetic radiation. **Electromagnetic radiation** is light in its various forms, including visible light, ultraviolet light, infrared light, microwaves, X-rays, and gamma rays. Radiation emitted from the nuclei of atoms can be dangerous, as can electromagnetic radiation. Except for gamma rays, however, the two forms of radiation are not the same. Gamma rays consist of a stream of high-energy light particles (Section 4.1).

During a nuclear disintegration, the total of the charges and the total of the mass numbers of the particles involved do not change, but the quantity of matter does change as a tiny portion of the matter is transformed into energy. The isotope undergoing decay is called the **parent isotope**, and the isotope produced (along with a small particle from Table 21.2) is called the **daughter isotope**. For example, the natural decay of ${}^{238}_{92}\text{U}$ produces ${}^{234}_{90}\text{Th}$ and an alpha particle. The ${}^{238}_{92}\text{U}$ is the parent isotope, and the ${}^{234}_{90}\text{Th}$ is the daughter isotope. In an equation written to represent this process, the subscripts on the left and right sides of the arrow total to the same number, and the superscripts also have the same totals:

Superscripts: $238 = 234 + 4$



Subscripts: $92 = 90 + 2$

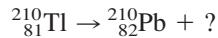
The superscripts represent the mass numbers, and the (optional) subscripts represent the atomic numbers or charges. Knowing that the superscripts and subscripts must balance allows us to deduce one species involved in a reaction if all the others are given. The process is often called “balancing a nuclear equation.”

EXAMPLE 21.1

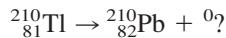
In addition to ${}^{210}\text{Pb}$, what is the other product of disintegration of ${}^{210}\text{Tl}$?

Solution

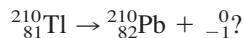
Because the charges must balance, we should write the subscripts for each isotope. We determine the atomic numbers from the periodic table and start to write an equation:



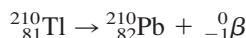
We see that the superscript of the unknown product must be 0 for the superscripts to balance:



The subscript of the unknown product must be -1 for the charges to balance:

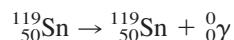


The particle in Table 21.2 that has a single negative charge and a zero mass number is a beta particle (electron), so we can complete the equation:



Practice Problem 21.1 Determine what isotope is produced along with a beta particle by the decomposition of ^{234}Th .

The emission of a gamma particle does not change the atomic number or the mass number of the parent isotope because the gamma particle has zero charge and zero mass number. For example, the emission of a gamma particle from $^{119}_{50}\text{Sn}$ yields a lower-energy form of the *same isotope*:



Thus, in gamma particle emission, the identity of the element does not change.

EXAMPLE 21.2

Show that the emission of a gamma particle does not change the atomic number or the mass number of the parent isotope.

Solution

Because the superscript and the subscript on the symbol for the gamma particle are both zero, the superscript and the subscript of the daughter isotope must be the same as those of the parent isotope for the mass numbers and charges to balance.

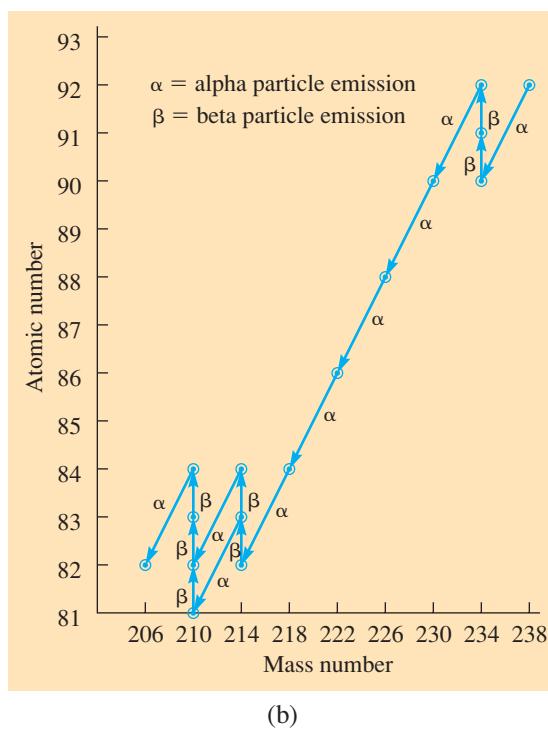
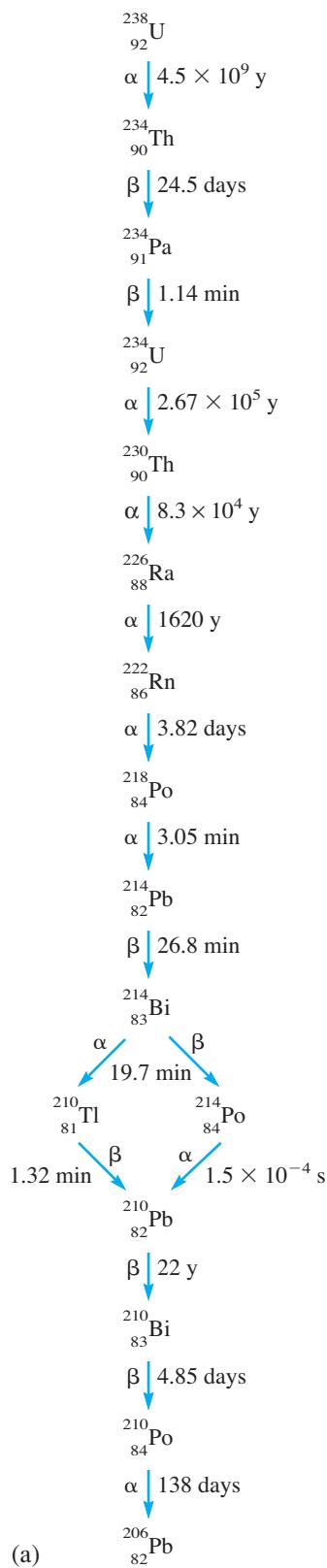
Radioactive Series

The daughters of most radioactive isotopes with very high atomic numbers will themselves disintegrate, and a whole series of disintegrations takes place. All the isotopes involved form a **radioactive series**. For example, ^{235}U loses seven alpha particles and four beta particles (as well as some gamma particles) as it successively disintegrates into stable ^{207}Pb . The disintegration series of ^{238}U , including reactions involving only the alpha and beta particles, is shown in Figure 21.1a. Gamma particle emissions are not shown in the figure because the emission of a gamma particle does not change the atomic number or the mass number of the isotope (only its energy). A graph of the mass number versus the atomic number for these isotopes is presented in Figure 21.1b. ^{214}Bi one of the isotopes in this series, can disintegrate in either of two ways.

The mass number changes by 4 when an alpha particle is emitted but does not change at all when a beta or a gamma particle is emitted. Therefore, the mass numbers of all the isotopes in a given series differ from one another by some integral multiple (0, 1, 2, ...) of 4. Because of this fact, there are four different series. One of them has mass numbers evenly divisible by 4; it is called the $4n$ series. In another series, all of the mass numbers exceed a multiple of 4 by 1; it is called the $4n + 1$ series. Similarly, the other two series are the $4n + 2$ and the $4n + 3$ series. The disintegrations in the $4n$, $4n + 1$, and $4n + 3$ series are shown in Figure 21.2.

EXAMPLE 21.3

Without looking at any of the figures, determine the designation of the series that starts with ^{237}Np .

21.1 ■ Natural Radioactivity**555****Figure 21.1** Disintegration Series for Uranium-238

(a) The diagram shows the particle emitted and the half-life (Section 21.2) for each event. (b) Atomic number is plotted versus mass number for each isotope in the series diagrammed in part (a).

Solution

Because ^{237}Np has a mass number that is 1 greater than an even multiple of 4, the series is the $4n + 1$ series:

$$237 = 4(59) + 1$$

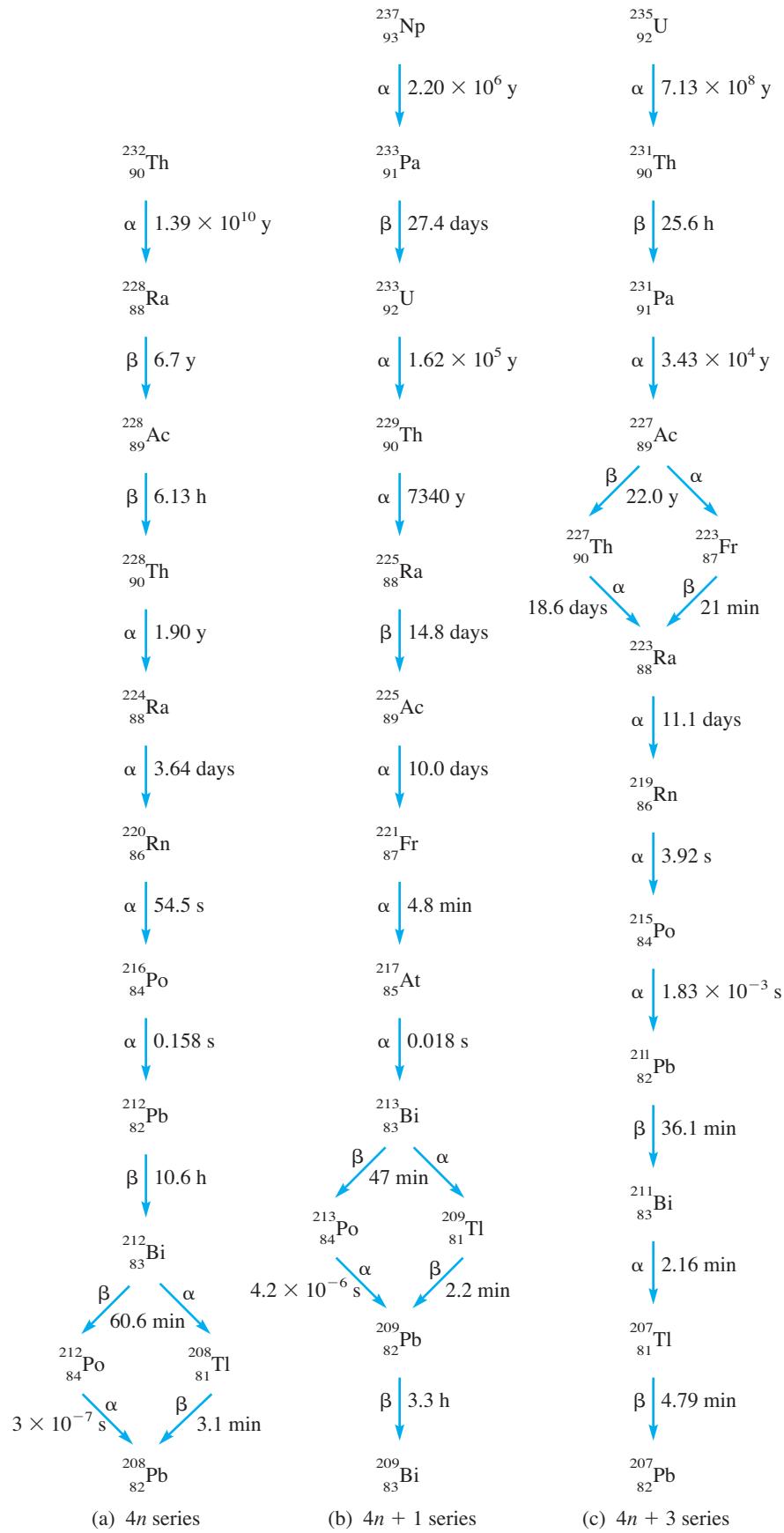
Practice Problem 21.3 What series involves ^{231}Th ?

EXAMPLE 21.4

Radium was discovered by Marie Curie (1867–1934) in pitchblende, a uranium ore. Radium is produced from a series of disintegrations, starting with ^{238}U and each producing an alpha particle or a beta particle (and possibly a gamma particle). Without looking at any figure or table, but using the mass number of ^{226}Ra , deduce how many alpha particles have been emitted from ^{238}U to produce this isotope of radium.

Solution

The emission of an alpha particle lowers the mass number of the daughter isotope by 4; the emission of a beta particle or a gamma particle produces no loss

Figure 21.2 Other Disintegration Series

ITEM OF INTEREST

The general public has a great deal of fear of nuclear energy and nuclear reactions of any type. The concept of radioactivity is unfamiliar to many people and therefore frightens them. For example, a suburban New York legislator introduced a bill in the county legislature that would have banned transportation of *any amount* of *any radioactive material* through the county. The legislator withdrew the bill when he was informed that a tiny percentage of the carbon in *every human being* is radioactive ^{14}C . If his bill had passed, no one would have been allowed to use the county highways.

in mass number. Because the mass number of $^{226}_{88}\text{Ra}$ is 12 less than that of $^{238}_{92}\text{U}$, three alpha particles must have been lost.

Practice Problem 21.4 How many alpha particles are emitted from $^{237}_{93}\text{Np}$ in its disintegration to $^{209}_{83}\text{Bi}$?

EXAMPLE 21.5

How many beta particles are emitted in the disintegration of $^{238}_{92}\text{U}$ to $^{226}_{88}\text{Ra}$?

Solution

The emission of the three alpha particles (see Example 21.4) lowers the atomic number by 6; however, radium's atomic number is only 4 units lower than uranium's. Therefore, two beta particles must also have been emitted, each event raising the atomic number by 1.

Practice Problem 21.5 How many beta particles are emitted from $^{237}_{93}\text{Np}$ in its disintegration to $^{209}_{83}\text{Bi}$?

Tracers

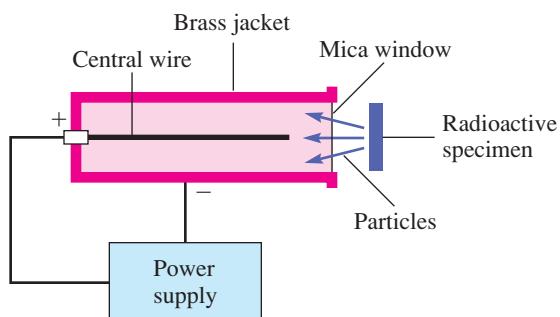
A **Geiger counter** is a device that can detect radioactive disintegrations (Figure 21.3). The high-energy particles emitted from a radioactive sample cause the gas in a Geiger counter's tube to be ionized and to carry an electric current for a short period of time. The "blip" of the Geiger counter signals a radioactive event. Other more modern devices, such as scintillation counters and film badges, are now used to detect and measure disintegrations.

Radioactive isotopes have the same chemical properties as the nonradioactive isotopes of the same element. Because they undergo the same chemical reactions, radioactive atoms are often used as **tracers** to determine what ordinary atoms are doing. For example, to detect problems in the human thyroid gland, physicians often prescribe iodine that includes a tiny fraction of $^{131}_{53}\text{I}$, a radioactive isotope of iodine. The body should utilize all the iodine in the thyroid gland. With a Geiger counter, the physician can follow the path of the radioactive isotope. If the radioactive iodine is not absorbed by the thyroid, then the regular iodine has not been absorbed either, and the physician has confirmed that a certain problem exists.

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CHAPTER 21 ■ Nuclear Reactions

Figure 21.3 Simplified Diagram of a Geiger Counter



ChemSkill Builder 23.2

Snapshot Review

- Most naturally occurring nuclei of atomic number greater than 83 disintegrate spontaneously, and we have no control over these reactions.
- Nuclear equations are balanced by balancing the superscripts and balancing the subscripts. We must know the charge and mass characteristics of the small particles for this purpose; charges (but not masses) of the atoms can be obtained from the periodic table.

- A. Give the charge and mass characteristics of (a) the alpha particle, (b) the beta particle, and (c) the gamma particle.
- B. Complete the following equations:
(a) $^{231}_{91}\text{Pa} \rightarrow ^{227}_{89}\text{Ac} +$
(b) $^{228}_{88}\text{Ra} \rightarrow {}_{-1}\beta +$

21.2 Half-Life

Radioactive isotopes have widely different stabilities. They disintegrate in times ranging from tiny fractions of a second to hours to months to years to billions of years. The atoms of a given isotope do not disintegrate all at once; they undergo their particle emissions in a pattern that is statistically predictable. Although scientists cannot tell when any particular atom of an isotope will disintegrate, they can predict what fraction of the atoms in any given sample of the isotope will disintegrate during a given period of time. Life insurance companies work on the same principle; they cannot predict accurately whether any particular individual will die in a given year, but they can tell what fraction of a particular age group (in a given state of health, etc.) will die within the year. Their statistics are quite accurate (and have to be if the companies are to survive), even though they are based on only a few million people. The statistics for radioactive decay are based on billions of billions of atoms and thus are very precise indeed.

The number of radioactive disintegrations that will occur in a given unit of time in a given sample depends not only on the relative instability of the isotope but also on the number of atoms in the sample. The number of disintegrations per unit time is called the activity, A , and is directly proportional to the number of atoms of the radioactive isotope present: $A = kN$. As a sample of an isotope disintegrates, the number of atoms of the isotope gets smaller. As the number of atoms gets smaller, the number of disintegrations per second gets smaller. The time it takes for a sample of an isotope to get to half of its original

21.2 ■ Half-Life**559**

number of atoms is called the **half-life** of the isotope. The size of the original sample does not affect the length of the half-life. Bigger samples will disintegrate faster, and half of a larger sample will disintegrate in the same time as half of a smaller sample. For example, a 1.0-kg sample of an isotope, which we can designate X, will have twice as many disintegrations per second as a 0.50-kg sample of the same isotope, which we can designate Z. In the time it takes 0.50 kg of sample X to disintegrate, only 0.25 kg of sample Z disintegrates because it is disintegrating only half as fast:

<i>Sample X</i>	1.0 kg	0.50 kg	<i>Sample Z</i>
↓	}	1 half-life	↓
	0.50 kg		0.25 kg

After that first half-life, sample X will contain 0.50 kg of the original isotope (plus other products) and that 0.50 kg will disintegrate only as fast as sample Z did *originally*.

EXAMPLE 21.6

A quiz show gives away 50% of its current jackpot to each contestant who answers a question correctly. Show how much is left in the jackpot after four contestants answer correctly if the jackpot starts at (a) \$1,000,000 and (b) \$500,000.

Solution

(a) \$1,000,000 → \$500,000 Give away \$500,000 to first contestant	→ \$250,000 Give away \$250,000 to second contestant	→ \$125,000 Give away \$125,000 to third contestant	→ \$62,500 Give away \$62,500 to fourth contestant
(b) \$500,000 → \$250,000 Give away \$250,000 to first contestant	→ \$125,000 Give away \$125,000 to second contestant	→ \$62,500 Give away \$62,500 to third contestant	→ \$31,250 Give away \$31,250 to fourth contestant

We see that the value after the first contestant in part (a) is the same as the value at the beginning of part (b). At each stage, the jackpot for part (a) and the amount given away are twice as great as those for part (b). The same principle works in the case of natural radioactivity.

Half-lives of some typical isotopes are listed in Table 21.3.

EXAMPLE 21.7

From the data in Table 21.3, calculate the time required for a 60.0-g sample of $^{14}_6\text{C}$ to be reduced to 7.50 g of $^{14}_6\text{C}$.

Solution

The half-life of $^{14}_6\text{C}$ is 5730 years. That means that in 5730 years, half of the 60.0-g sample will have disintegrated; 30.0 g of $^{14}_6\text{C}$ will remain. After another

Table 21.3 Half-Lives of Some Radioactive Isotopes

Isotope	Half-life	Particle Emitted
¹⁸⁷ Re	7×10^{10} years = 70 billion years	
²³² Th	1.41×10^{10} years = 14.1 billion years	Alpha
²³⁸ U	4.51×10^9 years = 4.51 billion years	Alpha
²³⁵ U	7.13×10^8 years = 713 million years	Alpha
¹⁴ C	5.73×10^3 years = 5730 years	Beta
⁹⁰ Sr	28.1 years	Beta
³ H	12.3 years	Beta
²²⁸ Th	1.90 years	Alpha
¹³¹ I	8.0 days	Beta
¹⁴⁰ La	40 h	Beta
⁹⁴ Kr	1.4 s	Beta
²¹⁶ Po	0.158 s	Alpha

Extra Help

60.0 g

↓1

30.0 g

↓2

15.0 g

↓3

7.50 g

5730 years, half of *that sample* of ¹⁴C—that is, 15.0 g of ¹⁴C—will remain. In a third half-life, 7.50 g will decompose and an equal mass will remain. It takes three half-lives to get to one-eighth of the original sample size, so the time required is 17,190 years.

Practice Problem 21.7 From the data in Table 21.3, calculate the time required for seven-eighths of a 60.0-g sample of ¹⁴C to disintegrate. What is the difference between this problem and the one in Example 21.7?

EXAMPLE 21.8

- (a) If 43.2 mg of a certain radioactive isotope disintegrates to 10.8 mg in 59.6 seconds, what is the half-life of the isotope?
 (b) How long would it take for 64.8 g of the isotope to disintegrate to 8.10 g?

Solution

- (a) The fraction of the original sample remaining is

$$\frac{10.8 \text{ mg}}{43.2 \text{ mg}} = 0.250 = \frac{1}{4}$$

The isotope in the sample has disintegrated to one-fourth of its original mass, so one-fourth of its original number of atoms must remain. Two half-lives must have elapsed:

$$1 \rightarrow \frac{1}{2} \rightarrow \frac{1}{4}$$

The 59.6 seconds represents two half-lives; therefore, one half-life is 29.8 seconds.

Be sure to count the arrows.

21.2 ■ Half-Life**561**

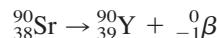
(b)

$$\frac{8.10 \text{ g}}{64.8 \text{ g}} = 0.125 = \frac{1}{8}$$

The isotope in the sample has disintegrated to one-eighth of its original size, which takes three half-lives. The time necessary is thus

$$3(29.8 \text{ s}) = 89.4 \text{ s}$$

Note that although the mass of the parent isotope drops to one-half of its original value in one half-life, the total mass of the sample is reduced only slightly. In addition to the mass of the parent isotope that remains, the masses of the daughter isotope and the alpha or beta particles must be included in the total mass. For example, if 2.00 mol of ^{90}Sr is allowed to disintegrate for 28.1 years (one half-life), 1.00 mol of ^{90}Sr remains:



However, 1.00 mol of ^{90}Y and 1.00 mol of electrons are formed in the process, and the total mass of the remaining ^{90}Sr , the ^{90}Y , and the electrons is only slightly less than the original mass of the ^{90}Sr .

For times that are not an integral multiple of the half-life, the following equation can be used to calculate disintegration times (t), half-lives ($t_{1/2}$), the original number of atoms (N_o), or the number of atoms at time t (N):

$$\ln\left(\frac{N_o}{N}\right) = \left(\frac{0.693}{t_{1/2}}\right)t$$

Using the natural logarithm key (LN) on a scientific calculator, it is relatively easy to solve for an unknown given values for the other three variables. For example, to get the time required for 6.22×10^{15} atoms of a certain isotope with half-life 55.4 min to disintegrate to 8.88×10^{14} atoms, follow the steps in the left column to get the answers in the right column:

Note that
 $\ln 2 = 0.693$

Steps

Step 1: Substitute the values given into the equation.

Step 2: Solve the left side of the equation, with both values known, by dividing the numerator of the ln term by the denominator and then taking the natural logarithm.

Step 3: Solve the resulting equation the usual way.

Step 4: Check the reasonableness of the result.

Example

$$\ln\left(\frac{6.22 \times 10^{15}}{8.88 \times 10^{14}}\right) = \left(\frac{0.693}{55.4 \text{ min}}\right)t$$

$$1.9466 = \left(\frac{0.693}{55.4 \text{ min}}\right)t$$

$$t = \left(\frac{1.9466}{0.693}\right)(55.4 \text{ min})$$

$$= 156 \text{ min}$$

It takes a little less than three half-lives to reduce the number of atoms to a little more than one-eighth of the original number.

EXAMPLE 21.9

Calculate the time it will take for 6.75×10^{18} atoms of an isotope to disintegrate to a point at which 8.90×10^{17} atoms of the isotope remain. The half-life of the isotope is 73.5 h.

Solution

$$\ln\left(\frac{N_o}{N}\right) = \left(\frac{0.693}{t_{1/2}}\right)t$$

$$\text{Step 1: } \ln\left(\frac{6.75 \times 10^{18}}{8.90 \times 10^{17}}\right) = \left(\frac{0.693}{73.5 \text{ h}}\right)t$$

$$\text{Step 2: } 2.026I = \left(\frac{0.693}{73.5 \text{ h}}\right)t$$

$$\text{Step 3: } t = 215 \text{ h}$$

Step 4: This is a reasonable time—almost three half-lives—because the number of atoms of the isotope has been reduced to a little more than one-eighth of the original number.

Practice Problem 21.9 Calculate the time it takes for a sample of an isotope to be reduced to exactly one-fifth of its original number of atoms if the half-life is 6.79 y.

First simplify the side without the unknown. Then take ln or anti ln.

EXAMPLE 21.10

Calculate the number of atoms remaining after a sample containing 4.00×10^{19} atoms with half-life 17.9 min is left for 21.2 min.

Solution

$$\ln\frac{N_o}{N} = \left(\frac{0.693}{t_{1/2}}\right)t$$

$$\ln\left(\frac{4.00 \times 10^{19}}{N}\right) = \left(\frac{0.693}{17.9 \text{ min}}\right)21.2 \text{ min}$$

$$\ln\left(\frac{4.00 \times 10^{19}}{N}\right) = 0.8208$$

$$\frac{4.00 \times 10^{19}}{N} = 2.272$$

$$N = 1.76 \times 10^{19} \text{ atoms}$$

In a little more than one half-life, a little more than half of the atoms have disintegrated and fewer than half remain.

Practice Problem 21.10

- (a) Calculate the time it takes an isotope with a half-life 47.2 years to disintegrate from 1.77×10^{15} atoms to 5.59×10^{14} atoms.
- (b) Calculate the original number of atoms of this isotope if 1.77×10^{15} atoms remain after 112 years.

Extra Help

Activity ratio:

$$\frac{A_o}{A} = \frac{kN_o}{kN} = \frac{N_o}{N}$$

Mole ratio:

$$\frac{n_o}{n} = \frac{N_o/\text{Avogadro's number}}{N/\text{Avogadro's number}} = \frac{N_o}{N}$$

Mass ratio:

$$\frac{m_o}{m} = \frac{n_o(\text{MM})}{n(\text{MM})} = \frac{n_o}{n} = \frac{N_o}{N}$$

The ratio N_o/N , the original number of atoms of the isotope (N_o) divided by the number of atoms (N) at time t , is equal to the activity ratio, to the mole ratio, and also to the mass ratio of the same isotope, and so those quantities may be used instead if they are given in a problem. Thus we can calculate a disintegration time, given a half-life and the numbers of atoms or activities or masses of an isotope at the start and at the end of the period of time.

EXAMPLE 21.11

Calculate the half-life of an isotope if the activity of a sample was reduced to 45.0% of its original activity in 1.08 years.

Solution

Here, the ratio of activities, A_o/A , is equal to 100/45.0:

$$\ln\left(\frac{100}{45.0}\right) = \left(\frac{0.693}{t_{1/2}}\right)(1.08 \text{ years})$$

The left side of this equation is evaluated first:

$$0.7985 = \left(\frac{0.693}{t_{1/2}}\right)(1.08 \text{ years})$$

Rearranging gives

$$t_{1/2} = \frac{(0.693)(1.08 \text{ years})}{0.7985} = 0.937 \text{ year}$$

This answer is reasonable, because more than one but less than two half-lives are required.

Practice Problem 21.11 Calculate the half-life of an isotope if a sample was reduced to 45.0% its original mass of the isotope in 1.08 years.

EXAMPLE 21.12

- (a) Krypton-94 has a half-life of 1.4 s. Starting with 1.00 mol of $^{94}_{36}\text{Kr}$ atoms, calculate the number of atoms of $^{94}_{36}\text{Kr}$ that will remain after 0.500 min.
- (b) Discuss how many atoms would remain after 2.00 min.

Solution

$$(a) \ln\left(\frac{N_o}{N}\right) = \left(\frac{0.693}{t_{1/2}}\right)t = \left(\frac{0.693}{1.4 \text{ s}}\right)(0.500 \text{ min})(60 \text{ s/min}) = 14.9$$



ChemSkill Builder 23.4

Taking the natural antilogarithm gives

$$\left(\frac{N_o}{N}\right) = \frac{6.02 \times 10^{23} \text{ atoms}}{N} = 3 \times 10^6$$

Solving for N yields

$$N = 2 \times 10^{17} \text{ atoms}$$

Of every mole of atoms (6.02 thousand billion billion atoms), 2×10^{17} will remain after 0.500 min.

- (b) A similar calculation with a time of 120 s shows that 1×10^{-2} atom would remain after 2.00 min, but a fraction of an atom cannot exist. During the last half-minute, the number of atoms of the isotope becomes so small that the statistics involved break down. The isotope virtually disappears.

• • • • •

ITEM OF INTEREST

Exposure to isotopes with a half-life of intermediate length is the most dangerous to human beings. Isotopes of long half-life, such as uranium-238 (4.5 billion years), do not undergo many nuclear reactions in a short period of time. Isotopes of short half-life are not around long enough to do major damage. (See Example 21.12.) Although the isotopes of intermediate half-life are dangerous if not handled with great care, even they can be beneficial. For example, ^{60}Co , with a half-life of 5.26 years, has been used in nuclear medicine in a treatment called *radiation therapy* because its radiation kills a greater percentage of cancer cells than of ordinary cells.

The slowest step in any of the disintegration series generally determines the time in which half of the original parent is converted to the final, stable product. For example, if we add up the half-lives of all the isotopes in Figure 21.1a, we get a sum equal to the half-life of ^{238}U , within the rules of significant digits.

Archaeologists and geologists apply the principles of half-life measurement to determine the age of samples of interest to them. The method they use is called **radioactive dating**. For example, a geologist might be interested in the age of a certain rock formation. If the rock contained uranium-238 but no lead when it solidified from a molten state, the geologist can tell how long ago the rock solidified assuming no daughter atoms escaped from the rock. Uranium-238 disintegrates in a series of events to lead-206, which is stable. Eight alpha particles and six beta particles are emitted in the process. The atoms of lead-206 currently in the rock were formed by the disintegration of the uranium-238 that was originally present. Thus, we can assume that N_o is equal to the number of atoms of lead plus the number of atoms of uranium present now, and N is the number of atoms of uranium present now. These values can be used to calculate the age of the rock. A representative sample of the rock is analyzed to discover the numbers of atoms.

EXAMPLE 21.13

A geologist analyzes a sample of rock and finds that it contains 1.25×10^{16} atoms of ^{207}Pb for every 4.16×10^{15} atoms of ^{235}U . Calculate the age of the rock, assuming that no lead was present when the rock solidified and no uranium or its daughter elements escaped from the rock.

Solution

The number of atoms of ^{235}U originally present was

$$\begin{aligned} 1.25 \times 10^{16} + 4.16 \times 10^{15} &= 1.666 \times 10^{16} \\ 1.666 \times 10^{16} &\xrightarrow[1]{\quad} 8.33 \times 10^{15} \xrightarrow[2]{\quad} 4.17 \times 10^{15} \end{aligned}$$

It took two half-lives, or $2(7.13 \times 10^8 \text{ years}) = 1.43 \times 10^9 \text{ years}$. The rock is 1.43 billion years old.

Practice Problem 21.13 Calculate the age of a sample of rock containing 2.57×10^{17} atoms of ^{40}K for every 7.71×10^{17} atoms of ^{40}Ar , its stable daughter isotope. Assume that no argon was in the rock when it solidified and that no argon escaped from the rock since its solidification. The half-life of ^{40}K is $1.3 \times 10^9 \text{ years}$.

EXAMPLE 21.14

Calculate the age of a sample of rock containing 25.5 g of ^{206}Pb for every 29.5 g of ^{238}U .

Solution

Although the ratio of masses of *a given isotope* is equal to the ratio of numbers of atoms (because each atom of a given isotope has the same mass at time zero as at time t), the ratio of the masses of different isotopes (^{206}Pb and ^{238}U , for example) is *not* equal to the ratio of atoms. We must change each mass to moles of atoms. To three significant digits, the mass of a mole of each of the isotopes involved in this problem is equal to its mass number (in grams):

$$25.5 \text{ g } ^{206}\text{Pb} \left(\frac{1 \text{ mol } ^{206}\text{Pb}}{206 \text{ g } ^{206}\text{Pb}} \right) = 0.1238 \text{ mol } ^{206}\text{Pb}$$

$$29.5 \text{ g } ^{238}\text{U} \left(\frac{1 \text{ mol } ^{238}\text{U}}{238 \text{ g } ^{238}\text{U}} \right) = 0.1239 \text{ mol } ^{238}\text{U}$$

Half of the ^{238}U has disintegrated, so one half-life has passed, and the rock is $4.51 \times 10^9 \text{ years old}$.

Practice Problem 21.14 Calculate the age of a sample of rock containing 9.11 g of ^{40}K and 9.11 g of ^{40}Ar , its daughter isotope. Assume that no argon was in the rock when it solidified and that no potassium or argon escaped from the rock since its solidification. The half-life of ^{40}K is $1.3 \times 10^9 \text{ years}$.

Carbon-14 is created continuously in the upper atmosphere by bombardment of $^{14}_7\text{N}$ atoms by cosmic rays:



The carbon finds its way into carbon dioxide and eventually into living things through the process of photosynthesis. An archaeologist can date a sample of wood by analyzing the amount of ${}_{6}^{14}\text{C}$ in it because after a tree has died, it no longer takes in ${}_{6}^{14}\text{C}$ in carbon dioxide.

EXAMPLE 21.15

Calculate the age of a piece of wood that is disintegrating at a rate of 1.91 counts per minute per gram of carbon. A modern sample of carbon disintegrates at a rate of 15.3 dis/min·g. Assume that the ratio of ${}_{6}^{14}\text{C}$ to ${}_{6}^{12}\text{C}$ in the atmosphere was the same when the tree was alive as it is today.

Solution

$$\frac{15.3 \text{ dis}}{\text{min}\cdot\text{g}} \xrightarrow{1} \frac{7.65 \text{ dis}}{\text{min}\cdot\text{g}} \xrightarrow{2} \frac{3.825 \text{ dis}}{\text{min}\cdot\text{g}} \xrightarrow{3} \frac{1.91 \text{ dis}}{\text{min}\cdot\text{g}}$$

The ${}_{6}^{14}\text{C}$ in the wood disintegrated in three half-lives, or 17,190 years.

Practice Problem 21.15 At what rate would the ${}_{6}^{14}\text{C}$ in a 22,920-year-old piece of wood disintegrate?

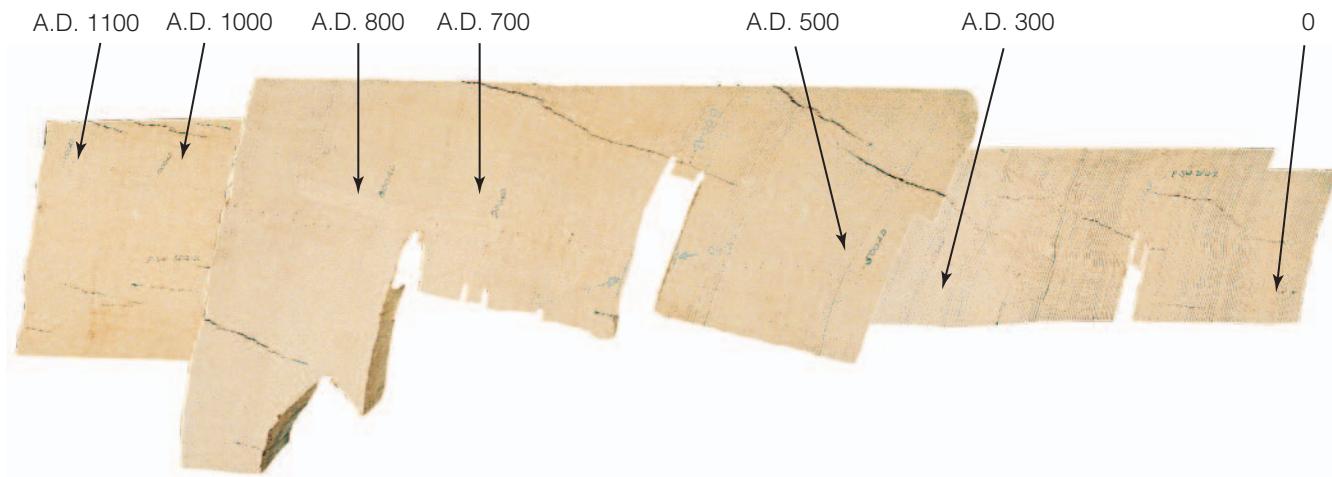
Archaeologists can test the assumption that the ratio of ${}_{6}^{14}\text{C}$ to ${}_{6}^{12}\text{C}$ was the same in ancient times as it is now by dating a sample of wood of known age. The age of a particular sample of wood from the cross section of a tree (Figure 21.4) can be determined by counting the annual rings, and then testing a portion of the wood from an inner ring.



Snapshot Review

- The rate of spontaneous radioactive decay is directly proportional to the number of atoms of the isotope present (and thus to the number of moles of the isotope or the mass of the isotope). Half of any given sample will disintegrate in one half-life period.

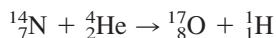
- A. Calculate the number of ${}^{232}\text{Th}$ atoms that will remain in a rock 4.23×10^{10} years after it formed if initially there were 6.78×10^{19} atoms present.
- B. Calculate the number of ${}^{232}\text{Th}$ atoms that will remain in a rock 1.00×10^{10} years after it formed if initially there were 6.78×10^{19} atoms present.
- C. Show that $\ln 2 = 0.693$, using $t = t_{\frac{1}{2}} = 4.00 \text{ y}$, and $N_o = 2.0 \times 10^{20}$, and $N = 1.0 \times 10^{20}$.

21.3 ■ Nuclear Fission**567****Figure 21.4** Cross Section of a Tree

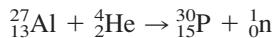
The age of a tree can be determined by counting the rings, each of which is formed in a year's growth.

21.3 Nuclear Fission

Scientists have learned how to make some isotopes undergo nuclear reactions. Artificial radioactivity is induced by bombardment of certain nuclei with subatomic particles (or atoms), which are produced either by other nuclear reactions or in machines called **particle accelerators**. For example, the first artificially induced nuclear reaction was produced by Ernest Rutherford (1871–1937) in 1919:



Nitrogen-14 was bombarded by alpha particles (helium nuclei), producing oxygen-17 and protons (hydrogen nuclei). In 1934, Irène Joliot-Curie (1897–1956), the daughter of Marie Curie, produced an isotope of phosphorus by bombarding aluminum-27 with alpha particles from polonium:



These reactions are examples of artificial **transmutation**—the change of one element into another. Several small particles, in addition to those involved in natural radioactivity, are involved in artificial nuclear reactions. Some of these additional particles are listed in Table 21.4. They are used as projectiles to bombard nuclei or are produced along with other products of such reactions, or both.

When an isotope of large mass number undergoes a nuclear reaction to produce two isotopes of much lower mass numbers plus some subatomic particles, the isotope is said to have undergone **nuclear fission**.

After such transmutations, the product nucleus often disintegrates spontaneously in further nuclear reactions. For example, the ${}_{15}^{30}\text{P}$ produced in the reaction described previously disintegrates with a half-life of 2.50 min, producing ${}_{14}^{30}\text{Si}$:



Table 21.4 Small Particles Involved in Artificial Radioactivity

Particle	Symbol	Charge	Mass Number	Identity
Neutron	n	0	1	Uncharged nuclear particle
Proton	p	1+	1	Hydrogen nucleus
Deuteron	d	1+	2	Nucleus of ${}^2\text{H}$
Positron	${}^0_+ \beta$ or ${}^0_+ \beta$	1+	0	Positively charged electron

The positive particle produced along with the silicon isotope is a **positron**, a particle identical to an electron except that it has a positive charge. When a positron collides with an electron, both are annihilated and a relatively large amount of energy is produced.

Just as we did for natural radioactive reactions we can balance nuclear equations for artificial reactions by making the superscripts on the left and right sides add up to the same quantity, and also the subscripts.

Chain Reactions

One of the projectiles most often used in modern times to initiate nuclear reactions is the neutron. To be effective, a neutron does not need as high an energy as an alpha particle or a proton because it is uncharged and can penetrate a nucleus more easily than a positively charged particle can. Some nuclear reactions initiated with neutrons produce more neutrons. For example, the bombardment of ${}^{235}\text{U}$ with a neutron produces two large nuclei plus two or three new neutrons. The following are examples of the many possible reactions:



When a neutron enters a sample of ${}^{235}\text{U}$, it may collide with the nucleus of one of the atoms, producing a reaction in which two or three new neutrons are produced. Each of these may react with another nucleus, producing more reactions and an increased number of neutrons (Figure 21.5). Such reactions, all started by a single neutron, can continue until the entire sample of ${}^{235}\text{U}$ has reacted. The sequence of reactions is called a **chain reaction** and is the source of energy by which nuclear power plants operate. The **atomic bomb**, which should more accurately be called the nuclear bomb, also uses a chain reaction.

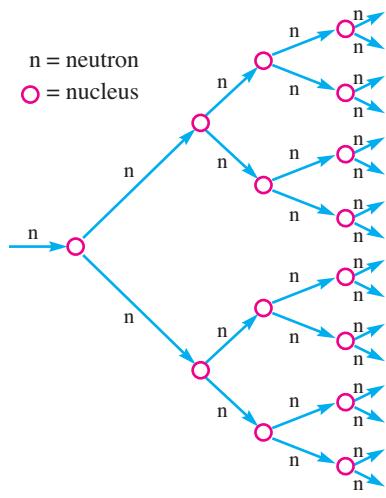


Figure 21.5 Schematic Representation of a Chain Reaction

In this representation, each collision of a neutron with a nucleus causes a reaction that produces two new neutrons (plus other products and energy). The new neutrons can cause further reactions.

EXAMPLE 21.16

How many neutrons are produced at the end if the following reaction is run through five cycles and every neutron produced in the first four cycles causes another such reaction? How many neutrons would the tenth cycle produce?



ITEM OF INTEREST

Nuclear energy supplies a significant percentage of the commercial electricity in the United States and an even greater percentage in Europe and Japan, where the cost of conventional fuels is greater. As conventional fuels are used up, nuclear energy may become even more important. Nuclear energy can be very dangerous if used incorrectly but also very beneficial if handled correctly. (The same statement can be made about electricity and automobiles, of course.) Nuclear power plants can cause problems, but conventional plants utilizing fossil fuels can also be troublesome. Conventional plants produce air pollution. Production of fossil fuels causes pollution of a different type; strip mining of coal and oil well fires are only two problems associated with the production of fuels for conventional power plants. Moreover, the world's supply of fossil fuels is rapidly being depleted. Solar energy and wind energy are two sources of energy that produce little pollution and pose little danger, but they also have their limitations. The problem of how to dispose of nuclear wastes—the products of nuclear reactions, which take thousands of years to disintegrate—is one that today's scientists and future scientists must solve.

Solution

The first reaction produces $3^1 = 3$ neutrons; those three, in the second cycle, produce $3^2 = 9$ neutrons; in the third cycle, $3^3 = 27$; in the fourth cycle, $3^4 = 81$; and in the fifth cycle, $3^5 = 243$. In the tenth cycle, $3^{10} = 59,049$ neutrons would be produced.

Practice Problem 21.16 How many neutrons are produced at the end if the following reaction is run through 20 cycles and every neutron produced in the first 19 cycles causes another such reaction?

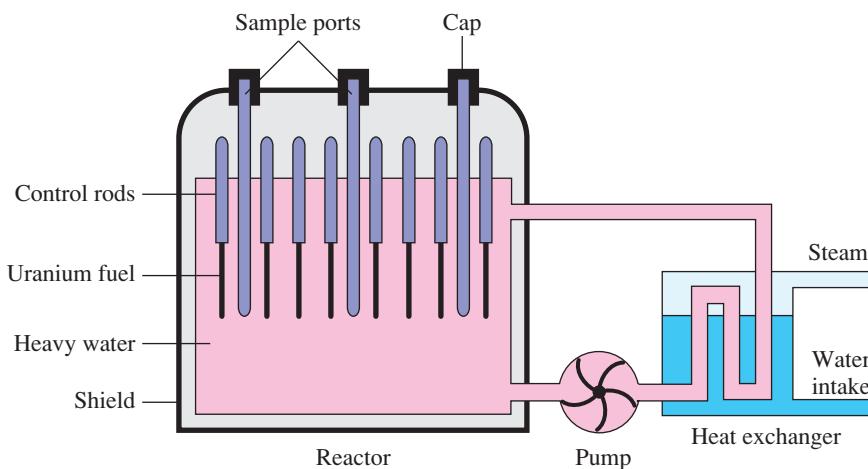


To control such a reaction, the mass of uranium may be kept small so that many of the neutrons that are produced escape from the sample without causing other nuclear reactions. The smallest mass in which a chain reaction can continue is called the **critical mass**. Another way to control such a reaction is to use rods of some material that absorbs neutrons without causing a reaction (Figure 21.6). Such **control rods** are part of nuclear reactors in which uranium is used as “fuel” to produce electricity commercially. When the reaction is to be slowed down, the control rods are inserted farther into the sample of fuel. When more energy from the reaction is desired, the rods are withdrawn somewhat. The control rods are operated automatically.

Energetics of Nuclear Reactions

In the process of changing a heavy nucleus into two lighter nuclei plus some small particles, a great deal of energy is emitted. Some matter is converted to

Figure 21.6 Simplified Diagram of a Nuclear Reactor



energy. The mass of this portion of matter is related to the energy by the famous **Einstein equation**

$$E = mc^2$$

where m is the decrease in mass of the matter, E is the energy produced, and c is the velocity of light in a vacuum, a constant equal to 3.00×10^8 m/s. The c^2 in the equation is such a large number that conversion of a small quantity of matter produces a large quantity of energy. This is the source of the energy of nuclear bombs and nuclear power plants.

EXAMPLE 21.17

How many joules of energy ($1\text{ J} = 1\text{ kg}\cdot\text{m}^2/\text{s}^2$) is produced by conversion of 1.00 kg of matter to energy?

Solution

Note that Einstein's equation is most easily used with mass in kilograms.

$$\begin{aligned} E &= mc^2 = 1.00\text{ kg} \left(\frac{3.00 \times 10^8\text{ m}}{\text{s}} \right)^2 \\ &= 9.00 \times 10^{16}\text{ kg}\cdot\text{m}^2/\text{s}^2 = 9.00 \times 10^{16}\text{ J} \\ &= 9.00 \times 10^{13}\text{ kJ} = 90.0 \text{ trillion kJ} \end{aligned}$$

Contrast that quantity of energy with the amount that can be produced by burning 1.00 kg of carbon, which is 32,800 kJ.



Snapshot Review



ChemSkill Builder 23.6

- Bombarding certain isotopes with small particles, especially neutrons, causes them to split into two isotopes of more or less equal size (plus other products), a process called nuclear fission.
- Memorize the charge and mass characteristics of the other small particles.

- A. Give the charge and mass characteristics of the (a) neutron, and
 (b) positron.
 B. Complete the following equation:



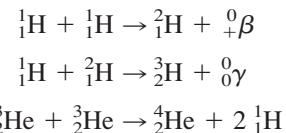
21.4 Nuclear Fusion

In contrast to nuclear fission reactions, in which large nuclei are broken into smaller nuclei, **nuclear fusion** involves the combination of small nuclei into larger ones. In nuclear fusion reactions, tremendous quantities of energy are released. The atomic bomb uses a fission reaction as its source of energy; the so-called **hydrogen bomb** uses a fusion reaction as its source of energy. In this fusion reaction, **deuterium** (${}_2^1\text{H}$) nuclei, also called **deuterons**, with symbol d, are combined into nuclei of **tritium** (${}_3^1\text{H}$) and then into nuclei of an isotope of helium. This reaction is less “dirty” than a fission reaction in that the products of fusion are not radioactive. However, fusion reactions require an extremely high temperature to get them started, so a small atomic bomb is used as the energy source to trigger a hydrogen bomb, and that bomb is a source of radioactivity.

ITEM OF INTEREST

In 1989, the scientific community was startled by the announcement of two chemists that they had succeeded in causing a fusion reaction to occur near room temperature. This *cold fusion* would have enabled the population of the Earth to be supplied with almost limitless energy without the radioactivity associated with the operation of ordinary nuclear power plants. The effect on the scientific and economic communities was profound. Unfortunately, so far, the results reported by the scientists have not been repeated or confirmed, and cold fusion is still a dream.

The energy of the Sun and stars comes from nuclear fusion reactions, which have the overall effect of transforming hydrogen nuclei to alpha particles (helium nuclei). The temperature of the particular star determines the mechanism by which this transformation takes place. The Sun, a moderately small star, is thought to be powered by the following sequence of reactions:



Each of these reactions emits energy, as well as the products listed. The positron released in the first reaction can react with an electron to yield even more energy. The net reaction is the conversion of four protons into an alpha particle plus a great deal of energy. Hotter stars convert protons to alpha particles via another series of reactions (see Problems 21.41 and 21.42 at the end of the chapter).

EXAMPLE 21.18

When a positron and an electron meet, the matter in both is totally converted to energy. (They annihilate each other.) The mass of each of these particles is 9.10×10^{-31} kg. Calculate the number of joules of energy released in each annihilation reaction ($1\text{ J} = 1\text{ kg}\cdot\text{m}^2/\text{s}^2$).

Solution

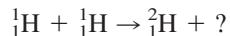
The total mass of a positron and an electron involved in the annihilation reaction is $(9.10 \times 10^{-31}\text{ kg}) + (9.10 \times 10^{-31}\text{ kg}) = 1.820 \times 10^{-30}\text{ kg}$. The energy is given by Einstein's equation:

$$\begin{aligned}E &= mc^2 = (1.820 \times 10^{-30}\text{ kg})(3.00 \times 10^8\text{ m/s})^2 \\&= 1.64 \times 10^{-13}\text{ J}\end{aligned}$$

**Snapshot Review**

- Combination of smaller nuclei into larger ones is called nuclear fusion. The reactions of the Sun and stars are fusion reactions.

A. Complete the following equation:

**Key Terms**

Key terms are defined in the Glossary.

alpha particle (21.1)
atomic bomb (21.3)
beta particle (21.1)
chain reaction (21.3)
control rod (21.3)
critical mass (21.3)
daughter isotope (21.1)
deuterium (21.4)
deuteron (21.4)
disintegration (21.1)
Einstein's equation (21.3)

electromagnetic radiation (21.1)
event (21.1)
gamma particle (21.1)
Geiger counter (21.1)
half-life (21.2)
hydrogen bomb (21.4)
isotopes (21.1)
nuclear fission (21.3)
nuclear fusion (21.4)
nuclear radiation (21.1)

parent isotope (21.1)
particle accelerator (21.3)
positron (21.3)
radioactive dating (21.2)
radioactive decay (21.1)
radioactive series (21.1)
radioactivity (21.1)
tracer (21.1)
transmutation (21.3)
tritium (21.4)

Symbols

α (alpha particle) (21.1)
 β (beta particle) (21.1)
 ${}^0_+ \beta$ or ${}^0_+ \beta$ (positron) (21.3)
 d (deuteron) (21.4)

γ (gamma particle) (21.1)
 n (neutron) (21.3)
 N (number of nuclei) (21.2)

N_o (original number of nuclei) (21.2)
 p (proton) (21.3)
 $t_{1/2}$ (half-life) (21.2)

■ Items for Special Attention

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Summary

Nuclear reactions, unlike ordinary chemical reactions, usually change one element into one or more other elements. The energy produced in nuclear reactions is much greater than that involved in any chemical reaction.

Natural radioactivity (on Earth) occurs when radioactive nuclei disintegrate spontaneously, yielding alpha, beta, and gamma particles (rays) plus daughter isotopes almost as massive as the parent isotopes. A nuclear equation can be balanced by making both the total of the mass numbers and the total of the charges the same on the two sides of the equation. When the products of a nuclear reaction are radioactive, a series of disintegrations may occur. The isotopes involved, including the original parent isotope and all daughter isotopes, constitute a radioactive series. Each member of the series differs in mass number from the other members of the series by some integral multiple of 4 (0, 4, 8, . . .). Four such series occur naturally.

Radioactive isotopes react chemically just like the nonradioactive isotopes of the same element. Because of this, physicians can add a little radioactive isotope to a sample of an element, which is then ingested or injected into the body. They can then determine the element's location in the body by detecting the particles that the radioactive isotope emits. The radioactive isotope is called a tracer, and this technique is used extensively in medicine and other fields (Section 21.1).

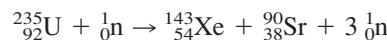
All the atoms of a radioactive isotope in a sample do not disintegrate at once but in accordance with the laws of statistics. The rate of disintegration is proportional to the number of atoms of the radioactive isotope present. The time it takes for half of a given number of atoms of the isotope to disintegrate spontaneously is called the half-life of the isotope. The half-life does *not* depend on the sample size.

The following equation, which governs radioactive disintegration, can be used to calculate the half-life from data on the numbers of atoms or to calculate the number of atoms remaining from knowledge of the half-life:

$$\ln\left(\frac{N_0}{N}\right) = \frac{(0.693)t}{t_{1/2}}$$

Here, N_0 is the original number of atoms of the isotope, N is the number at time t , and $t_{1/2}$ is the half-life. Archaeological and geological samples may be dated by half-life measurement (Section 21.2).

Bombardment of certain nuclei with small particles, such as alpha particles or neutrons, can lead to artificial nuclear reactions. The splitting of heavy atoms is one such process, called nuclear fission. Two fairly massive products plus some small particles are apt to result from splitting one large nucleus with a projectile particle. For example:



Chain reactions result when more neutrons are produced in a step of a nuclear reaction than are used up in that step. For example, for every neutron that causes a nuclear reaction of $^{235}_{92}\text{U}$, two or three new neutrons are produced. If each of these product neutrons, in turn, causes another nuclear reaction, many more neutrons will be produced, creating a chain reaction. If some of the product neutrons escape from the sample or are absorbed by other nuclei that do not split, the overall reaction can be controlled. The operation of commercial nuclear reactors is based on this principle. In nuclear reactions, a certain quantity of matter is converted to energy. The mass of the matter converted is related to the energy produced by Einstein's equation, $E = mc^2$ (Section 21.3).

In contrast to fission reactions, very small nuclei can be fused into larger ones. An example of such nuclear fusion is one of the reactions thought to power the sun:



(Section 21.4).

Items for Special Attention

- In the statement of a problem involving a half-life, be careful to distinguish between the number of atoms *remaining* and the number of atoms that *have disintegrated*.
- Remember that the mass number of an isotope is generally not given in the periodic table.
- The m in Einstein's equation $E = mc^2$ is the *change in mass* of the matter undergoing a nuclear reaction, not the total mass.
- We can use the mass number as an approximation for the mass of an isotope, but not for the mass of the naturally occurring mixture of isotopes.

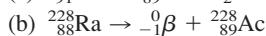
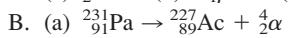
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CHAPTER 21 ■ Nuclear Reactions

Answers to Snapshot Reviews

- 21.1 A. The masses are the superscripts, charges are the subscripts:

(a) ${}^4_2\alpha$ (b) ${}^{-1}_0\beta$ (c) ${}^0_0\gamma$



21.2 A. $\frac{4.23 \times 10^{10} \text{ y}}{1.41 \times 10^{10} \text{ y}} = 3.00$ half-lives

$$6.78 \times 10^{19} \text{ atoms} \rightarrow 3.39 \times 10^{19} \text{ atoms} \rightarrow \\ 1.695 \times 10^{19} \text{ atoms} \rightarrow 8.48 \times 10^{18} \text{ atoms}$$

B. $\ln(N_o/N) = (0.693/t_{1/2})t$

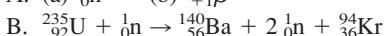
$$\ln\left(\frac{6.78 \times 10^{19}}{N}\right) = \left(\frac{0.693}{1.41 \times 10^{10} \text{ y}}\right)(1.00 \times 10^{10} \text{ y}) \\ = 0.4915$$

$$[(6.78 \times 10^{19})/N] = 1.6347$$

$$N = (6.78 \times 10^{19})/(1.6347) = 4.15 \times 10^{19} \text{ atoms}$$

$$\text{C. } \ln \frac{(2.0 \times 10^{20})}{(1.0 \times 10^{20})} = \frac{0.693(4.00 \text{ y})}{4.00 \text{ y}} \\ \ln 2.0 = 0.693$$

21.3 A. (a) ${}^1_0\text{n}$ (b) ${}^0_+1\beta$



21.4 A. ${}^1_1\text{H} + {}^1_1\text{H} \rightarrow {}^2_1\text{H} + {}^0_+\beta$

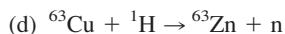
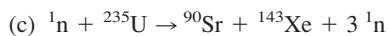
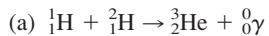
Self-Tutorial Problems

- 21.1 What is the difference, if any, in α , ${}^4_2\alpha$, and ${}^4_2\text{He}$?
- 21.2 What is the difference, if any, between the symbols U and ${}^{238}\text{U}$?
- 21.3 What is the difference between (a) β and ${}^+_-\beta$? (b) ${}^-_e$ and ${}^+_-\beta$? (c) ${}^-_e$ and ${}^-_-\beta$?
- 21.4 In a nuclear equation, the subscripts for isotopes are often omitted, but the superscripts always appear. Where can the subscripts be found? Why *can't* the superscripts be found there?
- 21.5 Substitute the correct symbol for X for each of the following particles (without looking at Tables 21.1, 21.2, and 21.4, if possible):
- | | | | |
|----------------------|----------------------|----------------------|--------------------|
| (a) ${}^1_1\text{X}$ | (b) ${}^2_1\text{X}$ | (c) ${}^3_1\text{X}$ | (d) ${}^0_+1\beta$ |
| (e) ${}^0_-\text{X}$ | (f) ${}^4_2\text{X}$ | (g) ${}^1_0\text{X}$ | (h) ${}^0_0\gamma$ |
- 21.6 Create a graph for the disintegration series that starts with ${}^{235}_{92}\text{U}$ like that for ${}^{238}_{92}\text{U}$ in Figure 21.1b.
- 21.7 Compare the *chemical* properties of radioactive cobalt-60 to those of ordinary cobalt.
- 21.8 Explain why some people buy radon detectors when radon is a noble gas and hardly undergoes any chemical reactions.
- 21.9 If half of a radioactive sample disintegrates in 2.00 y, why doesn't it all disintegrate in 4.00 y?

- 21.10 ${}^{207}_{81}\text{Tl}$ disintegrates by beta emission with a half-life of 4.79 min to give the stable isotope ${}^{207}_{82}\text{Pb}$. Calculate the approximate mass of the entire system 4.79 min after 0.100 g of ${}^{207}_{81}\text{Tl}$ starts decaying.

- 21.11 Which of the four disintegration series disintegrates to the final stable isotope with a half-life different from the half-life of its original parent isotope (with due regard to significant digits)?

- 21.12 State whether each of the following nuclear reactions is spontaneous, a fission, a fusion, or none of these:

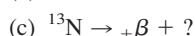
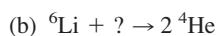


- 21.13 If the half-life of a certain isotope is 20.0 min, (a) how many atoms of 2.50×10^9 present initially will disintegrate in the first 20.0 min? (b) How many will remain? (c) How many will disintegrate in the second 20.0 min?

- 21.14 In the equation that enables us to calculate a disintegration time from a half-life, what do the symbols t and $t_{1/2}$ stand for? What do N_o and N stand for? What does \ln stand for?

Problems**21.1 Natural Radioactivity**

- 21.15 Complete each of the following nuclear equations:



■ Problems

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21.16 Complete each of the following nuclear equations:

- (a) $^{230}\text{Th} \rightarrow ? + \alpha$
- (b) $^{30}\text{P} \rightarrow ^{30}\text{S} + ?$
- (c) $^{119}_{50}\text{Sn} \rightarrow {}_0^0\gamma + ?$
- (d) $? + {}_2^4\text{He} \rightarrow {}_{13}^7\text{N} + {}_0^1\text{n}$

21.17 Complete each of the following nuclear equations:

- (a) $^{10}\text{Be} + ? \rightarrow {}^{13}\text{C} + \text{n}$
- (b) ${}^7\text{Be} \rightarrow {}^7\text{Li} + ?$
- (c) ${}^3\text{H} \rightarrow -\beta + ?$
- (d) ${}^{64}_{29}\text{Cu} \rightarrow {}_+\beta + ?$

21.18 Complete each of the following nuclear equations:

- (a) ${}^{210}_{83}\text{Bi} \rightarrow {}_0^-\beta + ?$
- (b) ${}^{106}_{47}\text{Ag} \rightarrow {}^{106}_{48}\text{Cd} + ?$
- (c) ${}^{43}_{20}\text{Ca} + {}_2^4\text{He} \rightarrow \text{p} + ?$
- (d) ${}^{23}_{11}\text{Na} + {}_2^4\text{He} \rightarrow {}^1_1\text{H} + ?$

21.19 Cobalt-60 is used for radiation treatments of certain cancers. It decays by positron emission. Write a nuclear equation for the reaction.

21.20 Iodine-131 is used for medical treatment of thyroid problems. It decays by emission of a beta particle. Write a nuclear equation for this reaction.

21.21 If one daughter isotope of uranium-238 escapes from a rock during its decay to lead-206, which isotope is it most likely to be? (*Hint:* Consider the chemical properties of the daughters.)

21.22 A certain isotope loses eight alpha particles and six beta particles to form a certain daughter isotope. As a result of the process, what is the increase or decrease in (a) mass number? (b) atomic number?

21.2 Half-Life

21.23 Explain why *month* is not used as a time unit for half-life problems.

21.24 Calculate the half-life of an isotope if 155.2 mg disintegrates to 19.40 mg in 12.9 min.

21.25 The half-life of a certain isotope is 17.5 y. Determine the time required for 74.4 g of the isotope to decay to 18.6 g.

21.26 The half-life of a certain isotope is 23.5 min. Calculate the original mass of a sample of the isotope if it takes 70.5 min to decay to 12.0 g.

21.27 A certain isotope has a half-life of 4.54 s. How much of a 29.70-mg sample of this isotope will remain after 18.2 s?

21.28 A certain isotope has a half-life of 25.5 min. How much of a 64.0-mg sample of this isotope will remain after 102 min?

21.29 Calculate the age of a sample of rock containing 1.93×10^{19} atoms of ${}^{40}\text{K}$ for every 5.79×10^{19} atoms

of ${}^{40}\text{Ar}$, its stable daughter isotope. Assume that no argon was in the rock when it solidified and that no argon escaped from the rock since its solidification. The half-life of ${}^{40}\text{K}$ is 1.3×10^9 years.

21.30 Calculate the age of a piece of wood that is disintegrating at a rate of 7.65 counts per minute per gram of carbon. A modern sample of carbon disintegrates at a rate of 15.3 dis/min·g. Assume that the ratio of ${}^{14}\text{C}$ to ${}^{12}\text{C}$ in the atmosphere when the wood formed was the same as it is today.

21.31 The half-life of a certain isotope is 20.4 y. Calculate the original mass of a sample of the isotope if it takes 102 y to decay to 27.25 mg.

21.32 The half-life of a certain isotope is 7.57×10^4 years. Calculate the time required for 7.55 mg of the isotope to decay to 0.103 mg.

21.33 The half-life of a certain isotope is 1.70 h. Calculate the time required for 6.62 mg of the isotope to decay to 4.79 mg.

21.34 Show that $A_o/A = m_o/m$, where m represents the mass of the isotope at time t , m_o represents the mass of the isotope at time zero, and A and A_o represent the corresponding activities.

21.35 Calculate the half-life of each of the following isotopes:

- (a) A 6.90-g sample of the isotope disintegrates to 1.71 g in 6.13 h.
- (b) Of a 6.90-g sample of the isotope, 1.71 g disintegrates in 6.13 h.

21.36 Calculate the half-life of each of the following isotopes:

- (a) A 17.3-mg sample of the isotope disintegrates to 12.9 mg in 214 y.
- (b) Of a 6.92-mg sample of the isotope, 0.955 mg disintegrates in 17.4 min.

21.3 Nuclear Fission

21.37 Complete each of the following nuclear equations:

- (a) ${}^{235}\text{U} + {}_0^1\text{n} \rightarrow {}^{139}_{57}\text{La} + ? + 2 {}_0^1\text{n}$
- (b) ${}^{238}\text{U} + {}_0^1\text{n} \rightarrow \gamma + ?$
- (c) $? \rightarrow \alpha + {}^{235}\text{U}$

21.38 Complete each of the following nuclear equations:

- (a) ${}^{27}_{13}\text{Al} + {}_2^4\alpha \rightarrow {}^{30}_{15}\text{P} + ?$
- (b) ${}^{239}\text{Pu} + ? \rightarrow {}^{240}\text{Pu}$
- (c) ${}^{235}_{92}\text{U} + {}_0^1\text{n} \rightarrow ? + {}^{143}_{54}\text{Xe} + 3 {}_0^1\text{n}$

21.39 Complete each of the following nuclear equations:

- (a) ${}_2^4\text{He} + ? \rightarrow {}^{17}_8\text{O} + {}_1^1\text{H}$
- (b) ${}^{235}_{92}\text{U} + {}_0^1\text{n} \rightarrow {}^{140}_{56}\text{Ba} + ? + 3 {}_0^1\text{n}$
- (c) ${}^9_4\text{Be} + {}_2^4\text{He} \rightarrow {}_0^1\text{n} + ?$
- (d) ${}^{237}_{92}\text{U} + \text{d} \rightarrow {}_0^1\text{n} + ?$

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21.40 Complete each of the following nuclear equations:

- (a) $^{235}\text{U} + \text{n} \rightarrow ^{137}\text{Te} + 2 \text{n} + ?$
 (b) $^{235}\text{U} + \text{n} \rightarrow ^{142}\text{Ba} + 2 \text{n} + ?$
 (c) $^{235}\text{U} + \text{n} \rightarrow ^{97}\text{Mo} + 2 \text{n} + ?$

21.4 Nuclear Fusion

21.41 Complete each of the following nuclear equations, the sequence of which is thought to be the source of the energy of some stars:

- (a) $^{12}\text{C} + ? \rightarrow ^{13}\text{N}$ (d) $^{14}\text{N} + ^1\text{H} \rightarrow ?$
 (b) $^{13}\text{N} \rightarrow ? + ^1\beta$ (e) $^{15}\text{O} \rightarrow ? + ^1\beta$
 (c) $^{13}\text{C} + ? \rightarrow ^{14}\text{N}$ (f) $^{15}\text{N} + ? \rightarrow ^{12}\text{C} + ^4\text{He}$

21.42 Add the equations in the answer to Problem 21.41, and cancel the species appearing on both sides. What is the net reaction?

21.43 If a neutron escapes from a sample undergoing a chain reaction, it may disintegrate into a proton plus an electron. Calculate the energy released during this process.

The masses are as follows: 1.00728 amu for a proton, 0.00054858 amu for an electron, and 1.00867 amu for a neutron.

21.44 Complete each of the following nuclear equations:

- (a) $^2\text{H} + ^2\text{H} \rightarrow ^1\text{H} + ?$
 (b) $^2\text{H} + ? \rightarrow ^3\text{He} + ^1\text{n}$
 (c) $^8\text{Be} \rightarrow ? + ^0\beta$
 (d) $^1\text{H} + ? \rightarrow ^2\text{H} + ^0\beta$
 (e) $^1\text{H} + ? \rightarrow ^3\text{He} + ^0\gamma$
 (f) $? + ^4\text{He} \rightarrow ^{13}\text{C} + ^1\text{H}$
 (g) $^2\text{H} + ? \rightarrow ^4\text{He} + ^1\text{n}$

21.45 Complete each of the following nuclear equations:

- (a) $? + ^7\text{Li} \rightarrow 2 ^4\text{He}$
 (b) $^9\text{Be} + \text{p} \rightarrow \alpha + ?$
 (c) $2 ^3\text{He} \rightarrow 2 ^1\text{H} + ?$
 (d) $^3\text{He} + ^2\text{H} \rightarrow ^4\text{He} + ?$

General Problems

21.46 Which of the following reactions represent natural radioactive decay, and which are artificially induced?

- (a) $^{218}\text{Po} \rightarrow ^{214}\text{Pb} + ^4\alpha$
 (b) $^{14}\text{N} + ^4\alpha \rightarrow ^{17}\text{O} + ^1\text{H}$
 (c) $^{238}\text{U} + ^1\text{n} \rightarrow ^{239}\text{U} + ^0\gamma$

21.47 One-fourth of the radioactive atoms of a certain sample is present 120.0 min after the original measurement. How many will be present after another 60.00 min?

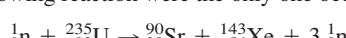
21.48 Calculate the time required for 87.5% of a sample with a 46.7 h half-life to disintegrate.

21.49 Complete each of the following nuclear equations:

- (a) $^{67}\text{Cu} + ? \rightarrow 2 ^1\text{n} + ^{66}\text{Cu}$
 (b) $^1\text{n} + ^6\text{Li} \rightarrow ^3\text{H} + ?$
 (c) $^2\text{H} + ? \rightarrow ^4\text{He} + ^{10}\text{B}$

21.50 Does boiling water in which a dangerous radioactive isotope is dissolved make the water safe to drink? Does distilling it?

- 21.51 (a) What fraction of the neutrons generated in the chain reaction illustrated in Figure 21.5 must be absorbed by control rods or must escape from the sample to keep the reaction from accelerating?
 (b) What fraction would have to be absorbed or escape if the following reaction were the only one occurring?

21.52 A certain rock contains 3.01×10^{-4} g of ^{235}U and 7.93×10^{-4} g of ^{207}Pb . Assuming that no lead was in

the rock when it solidified and that no uranium or its daughter isotopes escaped, calculate the age of the rock. (Note: To three significant digits, the masses of the atoms are equal to their mass numbers.)

21.53 A certain rock contains 1.58×10^{-3} g of ^{238}U and 2.49×10^{-4} g of ^{206}Pb . Assuming that no lead was in the rock when it solidified and that no uranium or its daughter isotopes escaped, calculate the age of the rock. (Note: To three significant digits, the masses of the atoms are equal to their mass numbers.)

21.54 It takes 7.22 min for 45.0% of a certain isotope to disintegrate. Calculate its half-life.

21.55 Calculate the number of joules emitted by the conversion of 1.00 amu of matter completely to energy.

21.56 It takes 4.94 years for 75.0% of a certain isotope to disintegrate. Calculate its half-life.

21.57 What is the mass of a gamma particle having an energy of 9.22×10^{-12} J?

21.58 What decrease in the mass of the matter accompanies the chemical combustion of 1.00 mol of carbon in oxygen to form carbon dioxide if 393 kJ of energy is produced?

21.59 From the information in Table 21.3, does the half-life seem to depend on the type of particle emitted?

21.60 Calculate the mass of a gamma particle of frequency 1.00×10^{21} /second.

21.61 $^{148}_{64}\text{Gd}$ disintegrates by alpha emission with a half-life of 130 years to give the stable isotope $^{144}_{62}\text{Sm}$. Calculate

CHAPTER 21 ■ Nuclear Reactions

■ General Problems

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the energy emitted by the system in the 130 years after 1.00 kg of ^{148}Gd starts decaying. The isotopic masses are ^{148}Gd 147.9177 amu, ^{144}Sm 143.9117 amu, ^4He 4.00260 amu.

- 21.62 Look up the number of people killed in the Chernobyl nuclear accident. Look up the number of people killed in the United States in accidents involving drunken drivers in 1999. Look up the number of people who die in one year worldwide as a result of cigarette smoking. Comment on the relative risk of mortality from nuclear

accidents as opposed to cigarette smoking and drunken driving.

- 21.63** Some texts use one of the following equations for half-life problems. Show that each one is equivalent to the equation used in this text. Choose one that is easiest to use, and explain why.

- (a) $\ln(N/N_0) = -0.693t/t_{\frac{1}{2}}$
(b) $2.303 \log(N/N_0) = -0.693t/t_{\frac{1}{2}}$
(c) $2.303 \log(N_0/N) = +0.693t/t_{\frac{1}{2}}$

Appendix 1

Scientific Calculations

- A.1 Scientific Algebra and Geometry
- A.2 The Scientific Calculator

This appendix introduces two mathematics topics important for chemistry students: (1) scientific algebra and (2) electronic calculator mathematics. The scientific algebra section (Section A.1) presents the relationships between scientific algebra and ordinary algebra. The two topics are much more similar than different; however, because everyone already knows ordinary algebra, the differences are emphasized here. The scientific calculator section (Section A.2) discusses points with which students most often have trouble. This section is not intended to replace the instruction booklet that comes with the calculator, but to emphasize the points in that booklet that are most important to science students.

For more practice with the concepts in this appendix, try recalculating the answers to some of the examples in the text.

A.1 Scientific Algebra and Geometry

Designation of Variables

We all know how to solve an algebraic equation such as

$$5x + 35 = 75$$

We first isolate the term containing the unknown ($5x$) by addition or subtraction on each side of the equation of any terms not containing the unknown. In this case, we subtract 35 from each side:

$$5x + 35 - 35 = 75 - 35$$

$$5x = 40$$

We then isolate the variable by multiplication or division. In this case, we divide by 5:

$$\frac{5x}{5} = \frac{40}{5}$$

$$x = 8$$

If values are given for some variables—for example, if $y = 121$ and $z = 11$ are given for the equation

$$x = y/z$$

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we simply substitute the given values and solve:

$$x = 121/11 = 11$$

In chemistry and other sciences, such equations are used continually. Because velocity is defined as distance divided by time, we could use the equation

$$x = y/z$$

with y representing the distance and z representing time, to solve for x , the velocity. However, we find it easier to use letters (or combinations of letters) that remind us of the quantities they represent. Thus, we write

$$v = d/t$$

with d representing the distance, t representing the time, and v representing the velocity. In this way, we do not have to keep looking at the statement of the problem to see what x represents. However, we solve this equation in exactly the same way as the equation in x , y , and z .

Chemists need to represent so many different kinds of quantities that the same letter may have to represent more than one quantity. The necessity for duplication is lessened in the following possible ways:

Method	Example
Using capital and lowercase (small) letters to mean different things	V for volume and v for velocity
Using italic letters for variables and roman (regular) letters for units	m for mass and M for meter
Using subscripts to differentiate values of the same type	V_1 for the first volume, V_2 for the second, and so on
Using Greek letters	π (pi) for osmotic pressure
Using combinations of letters	MM for molar mass

Each such symbol is handled just like an ordinary algebraic variable, such as x or y .

EXAMPLE A.1

Solve each of the following equations for the first variable, assuming that the second and third variables are equal to 30 and 5, respectively. For example, in part (a), n is the first variable, m is the second, and MM is the third. So m is set equal to 30 and MM is set equal to 5, allowing us to solve for n .

- (a) $n = m/MM$ (where MM is a single variable)
- (b) $v = \lambda\nu$ (λ and ν are the Greek letters lambda and nu.)
- (c) $M = n/V$
- (d) $P_1V_1 = P_2(12)$ (P_1 and P_2 represent different pressures.)

Solution

- (a) $n = 30/5 = 6$
- (b) $v = (30)(5) = 150$
- (c) $M = 6$
- (d) $P_1 = (5)(12)/30 = 2$

EXAMPLE A.2

Solve the following equation, in which each letter stands for a different quantity, for T :

$$PV = nRT$$

Solution

Dividing both sides of the equation by n and R yields

$$T = \frac{PV}{nR}$$

EXAMPLE A.3

Solve the following equation for t_F in terms of t :

$$\frac{t}{t_F - 32.0} = \frac{5}{9}$$

Solution

Inverting each side of the equation (dividing each side into 1) yields

$$\frac{t_F - 32.0}{t} = \frac{9}{5}$$

Simplifying gives

$$t_F = \frac{9}{5}t + 32.0$$

EXAMPLE A.4

Using the equation in Example A.3, find the value of t_F if $t = 25$.

Solution

$$t_F = \frac{9}{5}t + 32.0 = \frac{9}{5}(25) + 32.0 = 77$$

EXAMPLE A.5

Solve the following equation for t :

$$(6.00)(4.20)(t - 19.0) + (12.0)(1.0)(t - 60.0) = 0$$

Solution

$$25.2t - 479 + 12.0t - 720 = 0$$

$$37.2t - 1199 = 0$$

$$37.2t = 1199$$

$$t = 32.2$$

Extra Help:

In ordinary algebra
 $wx(y - z) = wxy - wxz$

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APPENDIX 1 ■ Scientific Calculations

Some of these steps could have been combined for a more efficient solution process.

Units

Perhaps the biggest difference between ordinary algebra and scientific algebra is that scientific measurements (and most other measurements) are always expressed *with units*. Like variables, units have standard symbols. The units are part of the measurements and can often help determine what operation to perform.

Units are often multiplied or divided but never added or subtracted. (The associated quantities may be added or subtracted, but the units are not.) For example, if we add the lengths of two ropes, each of which measures 7.5 yd (Figure A.1a), the final answer includes just the unit yards (abbreviated yd). Two units of distance are multiplied to get area, and three units of distance are multiplied to get the volume of a rectangular solid (such as a box). For example, to get the area of a carpet, we multiply its length in yards by its width in yards. The result has the unit square yards (Figure A.1b):

$$\text{yard} \times \text{yard} = \text{yard}^2$$

Be careful to distinguish between similarly worded phrases, such as “3.00 yards, squared” and “3.00 square yards” (Figure A.2).

EXAMPLE A.6

What is the unit of the volume of a cubic box whose edge measures 2.0 ft?

Solution

A cube has the same length along each of its edges, so the volume is

$$V = (2.0 \text{ ft})^3 = 8.0 \text{ ft}^3$$

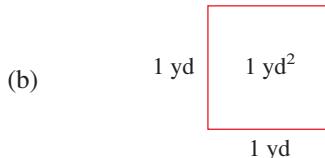
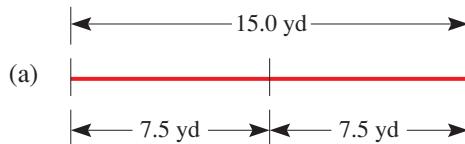
The unit is

$$\text{ft} \times \text{ft} \times \text{ft} = \text{ft}^3$$

Practice Problem A.6 What is the unit of the price of (a) eggs? (b) milk?

Figure A.1 Addition and Multiplication of Lengths

- (a) When two (or more) lengths are added, the result is a length, and the unit is a unit of length, such as yard.
(b) When two lengths are multiplied, the result is an area, and the unit is the square of the unit of length, such as square yards.
(Not drawn to scale.)

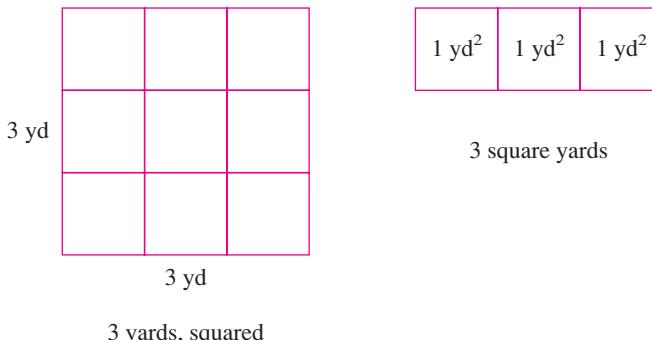


A.1 ■ Scientific Algebra and Geometry**583****Figure A.2** An Important Difference in Wording

Knowing the difference between such phrases as “3 yards, squared” and “3 square yards” is important.

Multiplying 3 yards by 3 yards gives 3 yards, squared, which is equivalent to 9 square yards, or nine blocks with sides 1 yard long, as we can see. In contrast, 3 square yards is three blocks, each having sides measuring 1 yard.

(Not drawn full size.)



The unit of a quantity may be treated like an algebraic variable. For example, how many liters of soda are purchased if someone buys three 3.00-L bottles of soda plus one 2.00-L bottle of soda?

$$3(3.00 \text{ L}) + 1(2.00 \text{ L}) = 11.00 \text{ L}$$

The same result would have been obtained if L were an algebraic variable instead of a unit. In dollars, how much will the 11.00 L of soda cost if the average price is 95 cents per liter?

$$11.00 \text{ L} \left(\frac{95 \text{ cents}}{1 \text{ L}} \right) = 1045 \text{ cents} \left(\frac{1 \text{ dollar}}{100 \text{ cents}} \right) = 10.45 \text{ dollars}$$

EXAMPLE A.7

What is the unit of the price of roast beef at the supermarket?

Solution

The price is given in dollars per pound.

If two or more quantities representing the same type of measurement—for example, a distance—are multiplied, they are usually expressed in the same unit. For example, to calculate the area of a rug that is 9.30 ft wide and 5.00 yd long, we express the length and the width in the same unit before they are multiplied. The width in yards is

$$9.30 \text{ ft} \left(\frac{1 \text{ yd}}{3 \text{ ft}} \right) = 3.10 \text{ yd}$$

The area is

$$(5.00 \text{ yd})(3.10 \text{ yd}) = 15.5 \text{ yd}^2$$

If we had multiplied the original measurements without first converting one to the unit of the other, we would have obtained an incomprehensible set of units:

$$(9.30 \text{ ft})(5.00 \text{ yd}) = 46.5 \text{ ft} \cdot \text{yd}$$

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APPENDIX 1 ■ Scientific Calculations

EXAMPLE A.8

What is the cost of 14.0 oz of hamburger if the store charges \$3.20 per pound?

Solution

Do not simply multiply:

$$14.0 \text{ oz} \left(\frac{3.25 \text{ dollars}}{1 \text{ lb}} \right) = \frac{45.5 \text{ oz} \cdot \text{dollar}}{\text{lb}}$$

Instead, first convert one of the quantities to a unit that matches that of the other quantity:

$$14.0 \text{ oz} \left(\frac{1 \text{ lb}}{16 \text{ oz}} \right) = 0.875 \text{ lb}$$

$$0.875 \text{ lb} \left(\frac{3.20 \text{ dollars}}{1 \text{ lb}} \right) = 2.80 \text{ dollars}$$

The same principles apply to the metric units used in science.

EXAMPLE A.9

A car accelerates from 0.0 mph to 45.0 mph in 5.00 s. What is the acceleration of the car? (Acceleration is the change in velocity per unit of time.)

Solution

The change in velocity is

$$45.0 \text{ miles/hour} - 0.0 \text{ miles/hour} = 45.0 \text{ miles/hour}$$

$$\frac{45.0 \text{ miles/hour}}{5.00 \text{ s}} = \frac{9.00 \text{ miles/hour}}{\text{s}}$$

The acceleration is 9.00 miles per hour per second. [This is an example of one of the few times when two different units may be used for the same quantity (time) in one value (the acceleration).]

Practice Problem A.9 A sprinter accelerates from 0.00 m/s to 13.5 m/s in 0.300 s. What is his acceleration?

Percentage

The percentage of a certain class of items within a whole group is equal to 100% times the number of items in the group divided by the number in the entire group. For example, the percentage of men within a class having 16 men and 80 students total is

$$100\% \left(\frac{16 \text{ men}}{80 \text{ students}} \right) = 20\% \text{ men}$$

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Percentage is merely a ratio, and can be used as a factor in calculations such as are done in Section 15.3. We can deduce six different factors from one percentage if there are only two types of items in the entire group. For example, if there are 55% females in a certain class, we can use any of the following ratios as a factor:

$$\begin{array}{lll} \left(\frac{55 \text{ females}}{100 \text{ students}} \right) & \left(\frac{45 \text{ males}}{100 \text{ students}} \right) & \left(\frac{55 \text{ females}}{45 \text{ males}} \right) \\ \left(\frac{100 \text{ students}}{55 \text{ females}} \right) & \left(\frac{100 \text{ students}}{45 \text{ males}} \right) & \left(\frac{45 \text{ males}}{55 \text{ females}} \right) \end{array}$$

For example, to determine the number of students in a class with 120 women, equal to 75% women, use the percentage as a factor:

$$120 \text{ women} \left(\frac{100 \text{ students}}{75 \text{ women}} \right) = 160 \text{ students}$$

Similarly, to calculate the number of women in a class of 250 with 48% women,

$$250 \text{ students} \left(\frac{48 \text{ women}}{100 \text{ students}} \right) = 120 \text{ women}$$

The term “percent” in chemistry usually implies a mass ratio unless another type of ratio is specified, as in “mole percent” or “percent by volume.”

Quadratic Equations

A quadratic equation is an equation of the form

$$ax^2 + bx + c = 0$$

The solution is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

This equation giving the values of x is known as the quadratic formula. Two answers are given by this equation (depending on whether the plus or minus sign is used), but often, only one of them has any physical significance.

EXAMPLE A.10

Determine the values of a , b , and c in each of the following equations (after it is put in the form $ax^2 + bx + c = 0$). Then calculate two values for x in each case.

$$(a) x^2 + 4 = 5x \quad (b) x^2 - 5x + 6 = 0$$

Solution

(a) First, rearrange the equation into the form

$$ax^2 + bx + c = 0$$

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In this case, subtracting $5x$ from each side yields

$$x^2 - 5x + 4 = 0$$

Thus, $a = 1$, $b = -5$, and $c = 4$. The two values of x are

$$x = \frac{+5 + \sqrt{25 - 16}}{2} = \frac{+5 + 3}{2} = 4$$

and

$$x = \frac{+5 - 3}{2} = 1$$

(b) Here $a = 1$, $b = -5$, and $c = 6$.

$$x = \frac{-(-5) \pm \sqrt{(-5)^2 - 4(1)(6)}}{2(1)}$$

Using the plus sign before the square root yields

$$x = \frac{+5 + \sqrt{25 - 24}}{2} = 3$$

Using the minus sign before the square root yields

$$x = \frac{5 - 1}{2} = 2$$

The two values for x are 3 and 2. Check:

$$(3)^2 - 5(3) + 6 = 0$$

$$(2)^2 - 5(2) + 6 = 0$$

Conversion to Integral Ratios

It is sometimes necessary to convert a ratio of decimal fraction numbers to integral ratios (Sections 3.1 and 7.4). (Note: Do not round off a number more than about 1%.) The steps necessary to perform this operation follow, with an example given at the right:

Steps

Step 1: Divide the larger of the numbers by the smaller to get a new ratio of equal value with a denominator equal to 1.

Step 2: Recognize the *fractional* part of the numerator of the new fraction as a common fraction. (The whole-number part does not matter.) Table A.1 lists decimal fractions and their equivalents.

Step 3: Multiply both numerator and denominator of the calculated ratio in step 1 by the denominator of the common fraction of step 2.

Example

What is the smallest integral ratio equal to 3.224 divided by 2.418?

$$\frac{3.224}{2.418} = \frac{1.333}{1}$$

0.333 is the decimal equivalent of $1/3$

$$\frac{1.333 \times 3}{1 \times 3} = \frac{4}{3}$$

Table A.1 Certain Decimal Fractions and Their Common Fraction Equivalents

Decimal Part of Number	Common Fraction Equivalent	Multiply by	Example
0.5	1/2	2	$\frac{1.5 \times 2}{1 \times 2} = \frac{3}{2}$
0.333	1/3	3	$\frac{1.333 \times 3}{1 \times 3} = \frac{4}{3}$
0.667	2/3	3	$\frac{4.667 \times 3}{1 \times 3} = \frac{14}{3}$
0.25	1/4	4	$\frac{2.25 \times 4}{1 \times 4} = \frac{9}{4}$
0.75	3/4	4	$\frac{1.75 \times 4}{1 \times 4} = \frac{7}{4}$
0.20	1/5	5	$\frac{1.2 \times 5}{1 \times 5} = \frac{6}{5}$

EXAMPLE A.11

Extend Table A.1 by adding 0.4 and 0.8 to the list.

Solution

0.4	2/5	5	$\frac{2.40 \times 5}{1 \times 5} = \frac{12}{5}$
0.8	4/5	5	$\frac{1.80 \times 5}{1 \times 5} = \frac{9}{5}$

Scientific Geometry

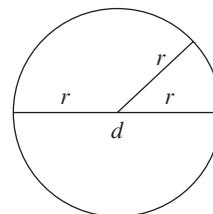
There are only a few simple concepts from geometry that are required in the first courses in chemistry. These include equations for the area of a rectangle, the volume of a rectangular solid, and the volume of a sphere.

$$\text{Rectangle: } A = l \times w$$

$$\text{Rectangular solid: } V = l \times w \times h$$

$$\text{Sphere: } V = \frac{4}{3}\pi r^3$$

The diameter (d) of a circle or a sphere is defined as twice the length of the radius (r):





Snapshot Review

ChemSkill Builder
App 2, 3

- Scientific algebra is very similar to ordinary algebra, except that letters are used that suggest the variables they represent. For example, d is used for density and m is used for mass. We can solve equations for d or m in just the way we can for x or y .
- Be sure to distinguish between an expression and an equation. For example, there is a great difference between $4x = y$ and $4xy$,

$$\text{or } 40 \text{ dollars} \left(\frac{10 \text{ dimes}}{1 \text{ dollar}} \right) \quad \text{and} \quad 40 \text{ dollars} = 400 \text{ dimes.}$$

- In equations and expressions, units can be treated like algebraic variables.

- A. Solve the equation $d = m/V$ for V when $d = 1.25 \text{ g/mL}$ and $m = 22.5 \text{ g}$.
- B. Simplify $(40.0 \text{ g})/(2.50 \text{ g/mL})$.

A.2 The Scientific Calculator

A chemistry student needs to have and know how to operate a scientific calculator capable of handling exponential numbers. A huge variety of features is available on calculators, but any calculator with exponential capability should be sufficient for this and other introductory chemistry courses. Practice doing calculations with the calculator. Do not stop to think about how to use the calculator while solving the chemistry problems. Because so many different models of calculator are in use today, only generic advice can be given here. Consult the owner's manual for specific directions for your calculator.

Some of the examples in this section involve very simple calculations. The idea is to learn to use the calculator for operations that can easily be done mentally. After practicing with simple calculations, practice with some of the examples from Chapter 2.

Precedence Rules

In algebra, when more than one operation is indicated in a calculation, the operations are done in a prescribed order. The order in which they are performed is called the *precedence*, or priority, of the operations. The order of the common algebraic operations is given in Table A.2. If operations having the same precedence are used, they are performed as they appear from left to right (except for exponentiation and unary minus, which are done right to left). For example, if a calculation involves a multiplication and a subtraction, the multiplication should be done first because it has a higher precedence. In each of the following calculations, the multiplication should be done before the subtraction:

$$y = 2 - 5 \times 3$$

$$y = 5 \times 3 - 2$$

The answers are -13 and $+13$. Try each of these calculations on the calculator to make sure that it does the operations in the correct order automatically.

Table A.2 Order of Precedence of Common Operations

	Calculator	Algebra
Highest	Parentheses	Parentheses
	Exponentiation (root) or unary minus*	Exponentiation (root) or unary minus*
	Multiplication or division	Multiplication
Lowest	Addition or subtraction	Division
		Addition or subtraction

*Unary minus makes a single value negative, such as in the number -3 .

If parentheses are used in an equation, they indicate that all calculations within the parentheses are to be done *before* the result is used for the rest of the calculations. For example,

$$y = (2 - 5) \times 3$$

means that the subtraction (within the parentheses) is to be done first, before the other operation (multiplication). *The parentheses override the normal precedence rules.* We might say that parentheses have the highest precedence.

When a multistep calculation is being done, some operation may be waiting for its turn. For example, when $2 - 5 \times 3$ is being entered, the subtraction will not be done until the multiplication operation is completed. If a different order is wanted, use parentheses. Algebraically, ab/cd means that the product of a and b is divided by the product of c and d . Be sure not to multiply the quotient ab/c by d .

EXAMPLE A.12

Solve:

$$(a) \left(\frac{38.4}{48.0} \right) \times 6.00 \quad (b) \frac{38.4}{48.0 \times 6.00}$$

Solution

$$(a) 4.80 \quad (b) 0.133$$

Division

In algebra, division is represented in any of the following ways, all of which mean the same thing:

$$\frac{a}{b} \quad a/b \quad a \div b$$

Note that any *operation* in the numerator or in the denominator of a built-up fraction (a fraction written on two lines), no matter what its precedence, is done

In built-up fractions, do the operations in the numerator and then in the denominator, and finally divide.

590**APPENDIX 1 ■ Scientific Calculations**

before the division indicated by the fraction bar. For example, to simplify the expression

$$\frac{a - b}{c + d}$$

the difference ($a - b$) is divided by the sum ($c + d$). The addition and subtraction, despite being lower in precedence, are done before the division. In the other forms of representation, this expression is written as

$$(a - b)/(c + d) \quad \text{or} \quad (a - b) \div (c + d)$$

where the parentheses are required to signify that the addition and subtraction are to be done first. A calculator usually has only one operation key for division, \div . When using the calculator, be careful to indicate what is divided by what when more than two variables are involved.

The Change Sign Key

If we want to enter a negative number, the number is entered first, and then its sign is changed with the change sign key, *not* the subtraction key.

Exponential Numbers

When displaying a number in exponential notation, some calculators show the coefficient followed by a space or a minus sign and then two digits giving the value of the exponent. For example, the following calculator displays represent 1.23×10^4 and 1.23×10^{-4} , respectively:

1.23 04
1.23 –04
Coefficient Exponent

Note that the base (10) is not shown explicitly on these calculators. On other calculators, where it is shown, interpreting the values of numbers in exponential notation is slightly easier.

To enter a number in exponential form, use the special key, **EE** or **EXP**, meaning “ $\times 10$ to the power,” *not* the multiplication key. To enter a negative number, press the change sign key before **EE** or **EXP**; to enter a negative exponent, press the change sign key after **EE** or **EXP**.

Some calculators display answers in decimal notation unless they are programmed to display them in scientific notation. If a number is too large or too small to fit on the display in decimal format, the calculator will use scientific notation automatically. To get a display in scientific notation for a reasonably sized decimal number, see the owner’s manual. If an easy conversion is not available, multiply the decimal value by 1×10^{10} (if the number is greater than 1) or 1×10^{-10} (if the number is less than 1), and mentally subtract or add 10 to the resulting exponent.

Learn how to convert a number in exponential notation to decimal format and vice versa.

The Reciprocal Key

The reciprocal of a number is 1 divided by the number. The reciprocal has the same number of significant digits as the number itself. For example, the reciprocal of 2.00 is 0.500. A number times its reciprocal is equal to 1. The reciprocal key is especially useful if there is a calculated value in the display that is to be used as a denominator. For example, to calculate $a/(b + c)$ with the value of $b + c$ in the display, divide by a , then take the reciprocal to get the answer. Alternatively, with the value of $b + c$ in the display, take its reciprocal and then multiply that value by a .

$$\frac{a}{b+c} = \left(\frac{1}{b+c} \right) a$$

Logarithms and Antilogarithms

The common logarithm of a number is the power to which 10 must be raised to yield the number.

$$x = 10^{\log x}$$

For example:

$$5 = 10^{\log 5} = 10^{0.69897}$$

The log of 5 is 0.69897.

The **natural logarithm** (abbreviated ln) of a number is the power to which e must be raised to yield the number.

$$y = e^{\ln y}$$

For example:

$$2 = e^{\ln 2} = e^{0.69315}$$

The natural log of 2 is 0.69315.

Both types of logarithms follow the same mathematical rules, but we have to be careful as to when to use each. (Common logs are used with pH calculations, for example, in Section 19.3, and natural logs are generally used with half-life problems in Section 21.2.) Common logs may be converted to natural logs if necessary, and vice versa, using the ratio of the two:

$$\ln 10 = 2.3026$$

$$\log 10 = 1.0000$$

$$\frac{\ln 10}{\log 10} = \frac{2.3026}{1.0000}$$

$$\ln 10 = 2.3026 \log 10$$

Be sure to distinguish between common logarithm (log) and natural logarithm (ln).

Significant Figures

An electronic calculator gives its answers with as many digits as are available on the display unless the last digits are zeros to the right of the decimal point. The calculator has no regard for the rules of significant figures (see Section 2.4).

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APPENDIX 1 ■ Scientific Calculations

The calculator does not generally display the proper number of significant digits.

We must apply the rules when reporting the answer. For example, the reciprocal of 9.00 is really 0.111, but the calculator displays something like 0.111111111. Similarly, dividing 5.34 by 1.78 should yield 3.00, but the calculator displays 3. We must report only the three significant digits in the first example and must add the two significant zeros in the second example.

The significant digits in logarithms, such as pH values, are the *decimal place digits*. The integer digit(s) indicate(s) only the magnitude of the argument. For example, if the coefficient of the hydronium ion concentration has two significant digits, two decimal places are used in the corresponding logarithm.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

EXAMPLE A.13

Consider three solutions with the following hydronium ion concentrations:

$$1.99 \times 10^{-2} \text{ M} \quad 1.99 \times 10^{-9} \text{ M} \quad 1.99 \times 10^{-12} \text{ M}$$

- How many significant digits are in each concentration?
- What logarithm value is shown on an electronic calculator for each?
- Which digits are the significant digits in each calculator value?

Solution

- There are three significant digits in each concentration.
- The values obtained on a calculator are -1.701146924 , -8.701146924 , and -11.70114692 , respectively.
- The first three digits *after the decimal point* (701) are the significant digits in each calculator value. The integer digits tell only to which power of 10 the base is raised. The values should be reported as -1.701 , -8.701 , and -11.701 , respectively.

Practice Problem A.13 (a) Calculate the value of ε if $[\text{H}^+] = 5.55 \times 10^{-2}$ and $\varepsilon = 0.000 - 0.0592 \log[\text{H}^+]$

or

(b) Calculate the pH of a solution for which $[\text{H}_3\text{O}^+]$ is $6.9 \times 10^{-6} \text{ M}$.

EXAMPLE A.14

With the calculator, determine the value of each expression to the proper number of significant digits:

- $(3.2 \text{ m})(4.48 \text{ m})(1.77 \text{ m})$
- $(4.50 \text{ cm}^3)/(1.50 \text{ cm})$
- $6.72 \text{ cm}^2 + 3.111 \text{ cm}^2$
- $(2.00 \text{ m})/(9.00 \text{ s})$
- $(1.31 \times 10^{-7} \text{ cm})^3$
- $(5.123 \times 10^4 \text{ g})/(2.52 \times 10^3 \text{ mL})$
- $\log [(6.17 \times 10^4)/(1.33 \times 10^2)]$
- $\ln (9.72 \times 10^5 - 3.4 \times 10^1)$

■ Answers to Snapshot Review

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Solution

- | | | |
|-------------------------|---|-------------------------|
| (a) 25 m^3 | (b) 3.00 cm^2 | (c) 9.83 cm^2 |
| (d) 0.222 m/s | (e) $2.25 \times 10^{-21} \text{ cm}^3$ | (f) 20.3 g/mL |
| (g) 2.666 | (h) 13.787 | |

***Snapshot Review***

- The scientific calculator performs its operations using the same rules of precedence used by algebra.
- The calculator does not keep track of significant digits.
- Learn to use the calculator well with simple numbers to be able to check the procedures easily before trying to do chemical calculations that take concentration.

A. Simplify each of the following expressions to the proper number of significant digits:

- $(10.0 \text{ g} - 7.00 \text{ g})/(3.00 \text{ mL})$
- $(95.0 \text{ cm})(12.7 \text{ cm})(2.33 \text{ cm})$
- $$\frac{(10.0 \text{ g})(6.0 \text{ mL})}{(20.0 \text{ g})}$$
- $$\frac{(20.0 \text{ g})}{(10.0 \text{ g})/(6.0 \text{ mL})}$$
- $$\frac{(20.00 \text{ cm}^3)}{(10.00 \text{ cm})(5.000 \text{ cm})}$$
- $1/(0.0625 \text{ s})$

Items for Special Attention

- Variables, constants, and units are represented with standard symbols in scientific mathematics (for example, V for volume). Be sure to learn and use the standard symbols.
- Be sure to distinguish between similar symbols for variables and units. Variables are often printed in *italics*. For example, mass is symbolized by m , and meter is represented by m . Capitalization can be crucial: v represents velocity, and V stands for volume.
- Units are treated like algebraic quantities.
- Algebraic and calculator operations must be done in the proper order (according to the rules of precedence). Be especially careful when solving problems in the form a/bc .
- Operations of equal precedence are done left to right except for exponentiation and unary minus, which are done right to left.

Answers to Snapshot Review

- A.1 A. $d = m/V$ so $V = m/d$
 $V = (22.5 \text{ g})/(1.25 \text{ g/mL}) = 18.0 \text{ mL}$
 B. 16.0 mL
- A.2 A. $(3.0 \text{ g})/(3.00 \text{ mL}) = 1.0 \text{ g/mL}$
 (two significant digits)

- (b) $2.81 \times 10^3 \text{ cm}^3$ (c) 3.0 mL (d) 12 mL
 (e) 0.4000 cm
 (f) 16.0 s^{-1} or $16.0/\text{s}$ (assuming that the 1 is a defined number)

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APPENDIX 1 ■ Scientific Calculations

Self-Tutorial Problems**A.1** Simplify each of the following:

(a) $5x = 55$ (b) $\frac{84x}{28y}$

(c) $\frac{3.5}{x} = 7.0$ (d) $9.6\left(\frac{x}{12}\right)$

(e) $2.50(x - 16) = 7$ (f) $(x + 7) - (2x + 25)$

A.2 Simplify each of the following, if possible:

(a) $\frac{V_2 P_1}{V_2}$ (b) $\frac{V_1 T_2}{V_2}$ (c) $\frac{V_2}{2T_2} = \frac{V_2}{6T_1}$

A.3 Using an electronic calculator, find the value of x from

$$x = (a + b) - (c + d)$$

where $a = -2$, $b = -4$, $c = -6$, and $d = -8$. Repeat this calculation twice, once using the parentheses keys and once without using them.

A.4 Using an electronic calculator, find the value of x from

$$x = (a + b) - (c + d)$$

where $a = -2$, $b = -12$, $c = 6$, and $d = 8$.

A.5 Find the value of each of the following:

(a) $\frac{7 + 5}{10}$ (b) $7 + 5/10$ (c) $(7 + 5)/10$

A.6 What is the difference between (3.0 cm^3) and $(3.0 \text{ cm})^3$?**A.7** Simplify each of the following:

(a) $22.75 \text{ dollars} \left(\frac{1 \text{ lb}}{1.75 \text{ dollars}} \right)$

(b) $1626 \text{ miles} \left(\frac{1 \text{ gal}}{29.3 \text{ miles}} \right)$

A.8 What units are obtained when a volume in milliliters is divided into a mass in (a) grams, (b) kilograms, and (c) milligrams?**A.9** In each of the following sets, are the expressions equal?

(a) $\frac{a}{b} \times \frac{1}{c}$ $\frac{1}{b} \times \frac{a}{c}$ $\frac{a}{bc}$

(b) $\frac{a}{b+c}$ $\left(\frac{1}{b+c}\right)a$ $\left(\frac{a}{b+c}\right) + \left(\frac{1}{b+c}\right)$

(c) $\frac{a}{b} + \frac{1}{c}$ $\frac{a}{b} + \frac{a}{c}$ $\frac{a}{b+c}$

A.10 Determine the value of (a) $(3.0)^2$ and (b) 3.0×10^2 .**A.11** Perform the following calculations on an electronic calculator. Check the results mentally:

(a) $6 - 4 \times 3$ (b) $2 \times (3 - 4)$ (c) $\frac{1 - 4}{3 + 3}$

A.12 Perform the following calculations on an electronic calculator. Check the results mentally:

(a) $2 \times (-5)$ (b) $3 \times 5 + (-6)$ (c) $-4 \times (2 - 3)$

A.13 Evaluate each of the following pairs of expressions, using $a = 10$ and $b = 5$. In each case, determine if the two expressions are equal.

(a) $\frac{1}{ab}$ $\frac{1}{a} \times \frac{1}{b}$

(b) $\frac{1}{a+b}$ $\frac{1}{a} + \frac{1}{b}$

(c) $\frac{1}{a-b}$ $\frac{1}{a} - \frac{1}{b}$

A.14 Calculate the percentage of sulfur in sulfur trioxide if a certain sample contains 8.66 g of oxygen and 5.78 g of sulfur.**A.15** Calculate the mass of a sample of carbon monoxide (which is 42.9% carbon) containing 13.7 g of carbon.**A.16** Are the following expressions equal to each other?

(a) $a(b + c) - d(e - f)$ $ab + ac - de - df$
 (b) $ac - bc - ad + bd - eg + eh + fg - fh$

$$(a - b)(c - d) - (e - f)(g - h)$$

A.17 Calculate the reciprocal of $5.0 \times 10^{-4} \text{ m}$.**A.18** What value will be obtained if 3 is entered on a calculator and then the square key is pressed twice?**A.19** What units are obtained when a mass in kilograms is divided by a volume in (a) cubic centimeters (cm^3), (b) liters (L), and (c) cubic meters (m^3)?**A.20** Calculate the volume of a rectangular solid 7.00 cm long, 1.80 cm wide, and 0.750 cm thick.**A.21** Write the exponential number corresponding to each of the following displays on a scientific calculator:

(a) 4.11 05 (b) 4.11-05
 (c) -4.11 05 (d) -4.11-05
 (e) 2.3 09

A.22 Write the display on your scientific calculator corresponding to each of the following exponential numbers:

(a) 6.26×10^4 (b) 6.26×10^{-4}
 (c) -6.26×10^4 (d) -6.26×10^{-4}
 (e) 6.02×10^{23}

A.23 Determine the value of each of the following expressions using your calculator:

(a) $\frac{3.0 \times 10^{10}}{1.0 \times 10^{10}}$ (b) $\frac{-3.0 \times 10^{10}}{1.0 \times 10^{10}}$
 (c) $\frac{3.0 \times 10^{-10}}{1.0 \times 10^{-10}}$ (d) $\frac{-3.0 \times 10^{-10}}{1.0 \times 10^{10}}$
 (e) $\frac{3.0 \times 10^{10}}{1.0 \times 10^{-10}}$

■ Problems

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Problems**A.1 Scientific Algebra**

A.24 What *unit* does the answer have in each of the following?

- 3.0 g is divided by 1 mL
- 42 g is divided by 6.4 cm and by 4.2 cm²
- 4.0 kg is divided by 1.8 L
- 1.0×10^3 kg is divided by 0.800 m³

A.25 What *unit* does the result have when each of the following expressions is simplified?

- $73.2 \text{ ft} \left(\frac{12 \text{ in.}}{1 \text{ ft}} \right) \left(\frac{0.95 \text{ dollar}}{1 \text{ in.}} \right)$
- (6.12 cm)(21.3 cm)
- $(52.4 \text{ cm}^3)/(4.00 \text{ cm}^2)$
- $(7.133 \text{ cm}^3)/(3.37 \text{ cm})$

A.26 What *unit* does the answer have in each of the following?

- 3 cm is added to 16 cm
- 9 cm³ is divided by 7 cm
- 6 cm² is multiplied by 7 cm
- 4.0 cm is multiplied by 25 cm

A.27 Assuming that the units of density are g/mL, what are the units of the reciprocal of density?

A.28 Calculate the mass of a sample of carbon monoxide (which is 57.1% oxygen and the rest carbon) containing 14.7 g of oxygen.

A.29 Calculate the percentage of children at a picnic if there are 15 men, 14 women, 7 boys, and 14 girls.

A.30 Solve

$$213 \text{ dollars} \left(\frac{10 \text{ pair of socks}}{35.50 \text{ dollars}} \right) \left(\frac{2 \text{ socks}}{1 \text{ pair of socks}} \right) =$$

A.31 The specific gravity of a solid or liquid is defined as the density of the substance divided by the density of water at 4°C. What can be said about the unit used with specific gravity?

A.32 (a) Solve $P_1V_1/T_1 = P_2V_2/T_2$ for T_1 .

(b) Solve $E = hv$ for v .

(c) Solve $\Delta t = k_f m$ for k_f .

(d) Solve $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ for P_2 .

(e) Solve $\pi V = nRT$ for V .

(f) Solve $PV = nRT$ for V .

(g) Solve $M = n/V$ for V .

(h) Solve $d = m/V$ for m .

A.33 Solve each of the following equations for the indicated variable, given the other values listed.

Equation	Solve for	Given
$PV = nRT$	n	$R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$ $P = 1.25 \text{ atm}$ $V = 15.0 \text{ L}$ $T = 315 \text{ K}$
$M = n/V$	V	$M = 1.25 \text{ mol/L}$ $n = 0.750 \text{ mol}$
$d = m/V$	m	$d = 2.20 \text{ g/mL}$ $V = 2.75 \text{ mL}$
$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	T_1	$T_2 = 273 \text{ K}$ $P_1 = 836 \text{ torr}$ $P_2 = 760 \text{ torr}$
$\pi V = nRT$	n	$\pi = 1.05 \text{ atm}$ $V = 6.27 \text{ L}$ $T = 298 \text{ K}$ $R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$
$P_1V_1 = P_2V_2$	V_2	$V_1 = 6.10 \text{ L}$ $P_1 = 1.11 \text{ atm}$ $P_2 = 2.34 \text{ atm}$
$E = hv$	v	$E = 8.00 \times 10^{-18} \text{ J}$ $h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$
$\Delta t = k_f m$	k_f	$\Delta t = 0.484^\circ\text{C}$ $m = 0.903 \text{ m}$

A.34 (a) Solve $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ for T_1 .

(b) Solve $\pi V = nRT$ for n .

(c) Solve $PV = nRT$ for R .

(d) Solve $M = n/V$ for n .

(e) Solve $d = m/V$ for V .

A.2 The Scientific Calculator

A.35 Determine the value of each of the following expressions:

$$(a) \frac{(400)(1/800)(2.00)}{(0.100)(300)}$$

$$(b) \frac{(403)(1/760)(2.22)}{(0.0821)(298)}$$

$$(c) \frac{(4.00 \times 10^9)(6.50 \times 10^{-34})}{6.00 \times 10^{-10}}$$

$$(d) \frac{(4.11 \times 10^9)(6.63 \times 10^{-34})}{6.07 \times 10^{-10}}$$

$$(e) \frac{(0.100)(300)}{(2.00)(5.00)}$$

$$(f) \frac{(0.0821)(293)}{(2.20)(4.99)}$$

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- (g) $\frac{(2.00)(4.00 \times 10^2)/(8.00 \times 10^2)}{(1.00 \times 10^{-1})(3.00 \times 10^2)}$
 (h) $\frac{(2.22)(4.03 \times 10^2)/(7.60 \times 10^2)}{(8.21 \times 10^{-2})(2.98 \times 10^2)}$
- (i) Explain why each pair of answers [(a) with (b), etc.] are approximately equal. Of each pair, which can be done mentally as a check on the process?
- A.36 Report the value of each of the following expressions to the proper number of significant digits:
- (a) $(19.7)^3$
 (b) $(-17.9)(-6.07)(-0.7070)$
 (c) $3.00^3/2.00^2$
 (d) $62.8/(-2.7 + 28.1)$
 (e) $6.171/4.202 - 2.11$
 (f) $1.77 - 6.99 \times 7.17$
 (g) $61.1/(2.28)(7.49)$
 (h) $12.7/(4.121 - 3.20)$
- A.37 Perform each of the following calculations, and report each answer to the proper number of significant digits:
- (a) $2.95/273$ (b) 8.11×6.87
 (c) $(12.4)^2$ (d) $6.92/29.13$
 (e) $-43.7 + (-6.22)$ (f) $(-177)(33.8)$
 (g) 4.50^4 (h) $-9.2 \times (-33.4)$
 (i) $103.9 - (98.22)$ (j) $27.5/(-28.9)$
- A.38 Report the value of each of the following expressions to the proper number of significant digits:
- (a) $(6.97 \times 10^5)^4$
 (b) $(-1.22 \times 10^{-1})(143.3)$
 (c) $(4.00 \times 10^{17}) - (4.00 \times 10^{15})$
 (d) $(5.15 \times 10^4) \times (2.44 \times 10^{-3})$
 (e) $(3.94 \times 10^2)/(6.14 \times 10^{-7})$
 (f) $(3.87 \times 10^6)/(2.46 \times 10^{-5})$
- A.39 Determine the value of each of the following expressions:
- (a) 2×3^2 (b) $(2 \times 3)^2$ (c) -3^2 (d) 3^4
- A.40 Report the result for each of the following expressions to the proper number of significant digits:
- (a) $16.1 + 1.44$
 (b) $1.36/4.6123$
 (c) -9.13×4.441
 (d) $(6.16 \times 10^1) - (5.54 \times 10^0)$
 (e) $(6.16 \times 10^{11}) - (5.54 \times 10^{10})$
- A.41 Perform each of the following calculations, and report each answer to the proper number of significant digits:
- (a) $(4.00 \times 10^4) + (5.00 \times 10^3)$
 (b) $(4.00)/(5.00)$

APPENDIX 1 ■ Scientific Calculations

- A.42 Solve each of the following equations for x :
- (a) $\log x = 0.617$ (b) $\log(x/4.00) = 2.110$
 (c) $\log(4.00/x) = 1.61$ (d) $\ln(1.73/x) = 0.555$
 (e) $\ln(x/2.50) = -3.05$ (f) $\ln(4.00 - x) = 3.103$
- A.43 Determine the value of y in each of the following cases:
- (a) $y = \ln 4.17$ (b) $y = \ln 104$
 (c) $y = \ln(4.44 \times 10^4)$ (d) $y = \ln(1.72 \times 10^{-3})$
 (e) $\ln y = 6.132$ (f) $\ln y = (4.618 \times 10^{-2})$
- A.44 Determine the value of x in each of the following cases:
- (a) $x = \log 3.189$ (b) $x = \log 7.468$
 (c) $x = \log(8.90 \times 10^5)$ (d) $x = \log(3.75 \times 10^{-4})$
 (e) $\log x = 1.717$ (f) $\log x = (5.89 \times 10^{-4})$
- A.45 Calculate the result for each of the following expressions to the proper number of significant digits:
- (a) $(96,490)/(1.602 \times 10^{-19})$
 (b) $(6.023 \times 10^{23})(1.602 \times 10^{-19})$
- A.46 Report the result for each of the following expressions to the proper number of significant digits:
- (a) $-14.6 + (-1.76) \times 3.38$
 (b) $-9.11 \times (-20.61)/4.82$
 (c) $7.131 \times 10^2 + 0.94909$
 (d) $-6.322 + (-4.8)$
 (e) $47.4931 - 47.4911$
 (f) $10.02/3.34$
 (g) $(0.250)^{-1}$
- A.47 Report the result for each of the following expressions in scientific notation:
- (a) $(5.0 \times 10^3)(7.0 \times 10^8)$ (b) $\frac{9 \times 10^{-2}}{3 \times 10^6}$
 (c) $(2.5 \times 10^6)(1.2 \times 10^{-3})$ (d) $\frac{5.5 \times 10^{-3}}{2.2 \times 10^{-6}}$
 (e) $\frac{(4.0 \times 10^{13})(9.0 \times 10^4)}{6.0 \times 10^7}$ (f) $\frac{3.0 \times 10^{-7}}{-6.0 \times 10^{-4}}$
 (g) $\frac{-3.0 \times 10^9}{6.0 \times 10^{-4}}$
- A.48 Put parentheses around two successive variables in each expression so that the value of the expression is not changed. Use the precedence rules for algebra. For example, $a \times b + c$ is the same as $(a \times b) + c$.
- (a) $a - b - c - d$ (b) $a/b - c$
 (c) ab/c (d) a/bc

■ General Problems

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General Problems

- A.49** Report the result for each of the following to the proper number of significant digits:

 - $d = 2r = 2(6.28 \text{ cm})$
 - $V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(2.02 \times 10^{-10} \text{ m})^3$

A.50 Report the result for each of the following expressions to the proper number of significant digits:

 - $3.63 \times 10^3 - 5.171 \times 10^4$
 - $$\frac{6.17 \times 10^{13}}{4.23 \times 10^{11} - 9.14 \times 10^9}$$

A.51 A sphere of what radius would hold the contents of a cube with 4.00-cm edges?

A.52 What length would the edge of a cube have to be for the cube to be able to hold the contents of a sphere with a 4.00-cm diameter?

A.53 Calculate the volume of a sphere of radius $6.12 \times 10^{-10} \text{ m}$.

A.54 Calculate the volume of a sphere of diameter $3.88 \times 10^{-10} \text{ m}$.

A.55 Evaluate the expression 4^x , given that $x = 3$.

A.56 Calculate the value of (a) $10^{0.6667}$ and (b) $e^{0.30103}$.

A.57 Determine the value of x in each of the following:

 - $\log x = 0.6667$
 - $\ln x = 0.30103$

A.58 Determine the value of x in each of the following:

 - $x = \log 6.15$
 - $\log x = 4.13$
 - $x = \sqrt[3]{6.98}$
 - $x = (2.81)^4$
 - $x = \sqrt{2.72 \times 10^{18}}$

A.59 Calculate the result for each of the following expressions to the proper number of significant digits:

 - $(71.71 \times 22.7)/(3.00 \times 10^{-2})$
 - $(6.28 \times 10^{12})(7.107 \times 10^{-13})$
 - $6.21 \times 10^3 + 1.61 \times 10^{-2}$
 - $6.21 \times 10^{-7} + 1.61 \times 10^2$
 - $(4.184(922)(93.0 - 92.1))$

A.60 Determine the values of a , b , and c in each of the following quadratic equations after putting the equation in the form $ax^2 + bx + c = 0$. Then calculate two values for each x .

 - $x^2 + x - 6 = 0$
 - $x^2 - 5x + 6 = 0$
 - $x^2 + 4x + 4 = 0$
 - $x^2 - 8x + 16 = 0$
 - $2x^2 + x - 21 = 0$
 - $x^2 = -x + 6$
 - $x^2 - 5x = -6$
 - $x^2 = -(4x + 4)$
 - $x^2 = 8x - 16$
 - $2x^2 = 21 - x$

A.61 Solve for t :

$$t = \left(\frac{6.77 \text{ years}}{0.693} \right) \ln \left(\frac{3.71 \text{ g}}{2.18 \text{ g}} \right)$$

A.62 Solve for m :

$$\ln \left(\frac{12.3 \text{ g}}{m} \right) = \frac{(0.693)(14.1 \text{ years})}{2.98 \text{ years}}$$

A.63 Determine the values of a , b , and c in each of the following quadratic equations after putting the equation in the form $ax^2 + bx + c = 0$. Then calculate two values for each x .

 - $2x^2 = 1.46 \times 10^{-6} - (1.76 \times 10^{-3})x$
 - $4x^2 = 1.53 \times 10^{-7} - (1.46 \times 10^{-3})x$
 - $3x^2 + 3.0 \times 10^{-8} = (8.70 \times 10^{-4})x$

A.64 Determine the values of a , b , and c in each of the following quadratic equations after putting the equation in the form $ax^2 + bx + c = 0$. Then calculate two values for each x .

 - $x^2 = (8.00 \times 10^{-7}) + (2.40 \times 10^{-3})x$
 - $$\frac{4x^2}{0.400 - 4x} = 6.06 \times 10^{-4}$$

Appendix 2

Tables of Symbols, Abbreviations, and Prefixes and Suffixes

Symbols for Variables and Constants

Symbol	Meaning	Unit(s)	Chapter Reference
A	Area	m^2	2
c	Specific heat capacity	$\text{J/g}\cdot\text{°C}$	14
d	Density	kg/m^3	2
e	Charge on the electron	C	3
E	Energy	J	1
ΔE	Change in energy	J	14
ϵ	Potential	V	17
F	Faraday	1 mol e^-	17
H	Enthalpy	J	14
ΔH	Change in enthalpy	J	14
ΔH_f	Enthalpy of formation	J	14
K	Equilibrium constant	Varies	18
K_a	Acid equilibrium constant	mol/L	19
K_b	Base equilibrium constant	mol/L	19
K_w	Water equilibrium constant	mol^2/L^2	19
k	Proportionality constant	Varies	2
k_b	Boiling-point constant	$^\circ\text{C}/\text{m}$	15
k_f	Freezing-point constant	$^\circ\text{C}/\text{m}$	15
KE	Kinetic energy	J	12
l	Length	m	2
m	Mass	g	2
m	Molality	mol/kg	15
M	Molarity	mol/L	11
MM	Molar mass	g/mol	7
n	Number of moles	mol	12
N	Avogadro's number	None	7
N	Number of atoms	None	21
N_o	Original number of atoms	None	21
P	Pressure	atm or torr	12
π	Osmotic pressure	atm or torr	15
pH	$-\log [\text{H}_3\text{O}^+]$	None	19
q	Heat	J	14
r	Radius	m	2
R	Gas constant	$\text{L}\cdot\text{atm}/\text{mol}\cdot\text{K}$	12
STP	Standard temperature and pressure	0°C and 1 atm	12

continued

APPENDIX 2 ■ Tables of Symbols, Abbreviations, and Prefixes and Suffixes**599****Symbols for Variables and Constants—cont'd**

Symbol	Meaning	Unit(s)	Chapter Reference
<i>t</i>	Temperature, in Celsius	°C	2, 12
<i>t_F</i>	Temperature, in Fahrenheit	°F	2
<i>T</i>	Absolute temperature	K	2, 12
Δt	Change in temperature	°C	14
<i>v</i>	Velocity	m/s	12
<i>V</i>	Volume	m ³ or L	2
<i>w</i>	Work	J	14
<i>X_A</i>	Mole fraction of A	None	15

Symbols or Abbreviations for Units*

Symbol or Abbreviation	Unit	Use	Chapter Reference
A	Ampere	Current	17
amu	Atomic mass unit	Mass of atoms etc.	3
atm	Atmosphere	Pressure	12
C	Coulomb	Electric charge	3
°C	Degree Celsius	Temperature	2
°F	Degree Fahrenheit	Temperature	2
g	Gram	Mass	2
h	Hour	Time	2
J	Joule	Energy	2
K	Kelvin	Temperature	2, 12
L	Liter	Volume	2
lb	Pound	Weight	2
m	Meter	Distance (length)	2
m	Molal	Molality	15
M	Molar	Molarity	11
mol	Mole	Quantity of matter	7
oz	Ounce	Weight	2
s	Second	Time	2
torr	Torr	Pressure	12
V	Volt	Potential	17

*See Table 2.2 for metric prefixes.

Symbols for Subatomic Particles

Symbol	Name of Particle	Chapter Reference
α	Alpha (helium nucleus)	21
$-\beta$	Beta (electron)	21
d	Deuteron	21
e	Electron	3
γ	Gamma (photon)	21
n	Neutron	3
$+\beta$	Positron	21
p	Proton	3

600**APPENDIX 2 ■ Tables of Symbols, Abbreviations, and Prefixes and Suffixes****Other Greek Letter Symbols**

Symbol	Name	Meaning	Chapter Reference
δ	Delta	Partial charge	13
Δ	Delta	Change in	14
μ	Mu	Micro	2
π	Pi	Osmotic pressure	15

Prefixes and Suffixes

Prefix	Meaning	Chapter Reference
bi-	A half-neutralized acid salt of an acid with two ionizable hydrogen atoms	6
centi-	One-hundredth	2
di-	Two	6
hexa-	Six	6
hydro-	No oxygen (in an acid)	6
hypo-	Fewer oxygen atoms (in oxoanion or oxoacid)	6
kilo-	One thousand	2
micro-	One-millionth	2
milli-	One-thousandth	2
mono-	One	6
penta-	Five	6
per-	More oxygen atoms	6
tetra-	Four	6
tri-	Three	6

Suffix	Use	Chapter Reference
-al	Name ending for aldehydes	20
-ane	Name ending for alkanes	20
-ate	Name ending for anions with certain numbers of oxygen atoms	6
-ate	Name ending for esters	20
-ene	Name ending for alkenes	20
-ic	Name ending for cation having the larger positive charge	6
-ic acid	Name ending for oxoacid with more oxygen atoms than corresponding acid named with -ous	6
-ide	Name ending for monatomic anions and also cyanide and hydroxide	5, 6
-ide	Name ending for binary nonmetal-nonmetal compounds	6
-ite	Name ending for oxoanions with fewer oxygen atoms than corresponding ions named with -ate	6
-oic acid	Name ending for organic acids	20
-ol	Name ending for alcohols	20
-one	Name ending for ketones	20
-ous	Name ending for cation having the lower positive charge	6
-ous acid	Name ending for oxoacid with fewer oxygen atoms than the corresponding acid named with -ic	6
-yl	Name ending for hydrocarbon radical	20
-yne	Name ending for alkynes	20

Appendix 3**Table of Basic
Mathematical
Equations**

Equation	Name	Chapter Reference
$V = l \times h \times w$	Volume of a rectangular solid	2
$d = m/V$	Density	2
$t = \frac{5}{9}(t_F - 32)$	Temperature conversion, Celsius and Fahrenheit	2
$T = t + 273$	Temperature conversion, Kelvin and Celsius	2
$A = p + n$	Mass number	3
$Z = p$	Atomic number	3
$M = \frac{\text{moles of solute}}{\text{liter of solution}}$	Molarity	11
$P_1V_1 = P_2V_2$	Boyle's law	12
$V_1/T_1 = V_2/T_2$	Charles' law	12
$P_1V_1/T_1 = P_2V_2/T_2$	Combined gas law	12
$PV = nRT$	Ideal gas law	12
$P_{\text{total}} = P_1 + P_2 + \dots$	Dalton's law	12
$\text{Heat} = mc\Delta t$	Heat capacity equation	14
$\Delta E = q + w$	Change in energy	14
$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$	Enthalpy change from enthalpies of formation	14
Concentration = kP_i	Henry's law	15
$m = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$	Molality	15
$X_A = \frac{\text{moles of A}}{\text{total moles in solution}}$	Mole fraction of A	15
$P_Z = X_Z P^\circ$	Vapor pressure of Z	15
$\Delta P = P^\circ - P$	Vapor-pressure lowering	15
$\Delta t_f = k_f m$	Freezing-point depression	15
$\Delta t_b = k_b m$	Boiling-point elevation	15
$\pi = nRT/V$	Osmotic pressure	15
$\varepsilon = \varepsilon^\circ - \frac{0.0592}{n} \log \frac{[\text{products}]^p}{[\text{reactants}]^r}$	Nernst equation	17
$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$	Equilibrium constant expression	18
$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$	Acid dissociation constant expression	19
$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$	Base dissociation constant expression	19
$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$	Water ionization constant expression	19
$\text{pH} = -\log[\text{H}_3\text{O}^+]$	Definition of pH	19
$\ln\left(\frac{N_o}{N}\right) = \left(\frac{0.693}{t_{1/2}}\right)t$	Half-life equation	21
$E = mc^2$	Einstein's equation	21

Appendix 4**Answers to
Practice Problems****1 Basic Concepts****PP1.2** Homogeneous**PP1.3** (a) True. (However, the elements may be combined into compounds.)

(b) False.

(c) False. (Elements are also substances.)

(d) False. (Substances are also homogeneous.)

PP1.4 (a) Bricks. (b) Two packages. (c) “Heavier” means either denser (an intensive property), as in part (a), or more massive (an extensive property), as in part (b).**PP1.5** A chemical reaction takes place, creating a new substance with definite properties of its own. The powder is not an element; it is a compound (a chemical combination of the shiny substance—a metal—and something else).**PP1.6** (a) Kinetic energy is being converted to electrical energy and then to chemical energy.
(b) Kinetic energy is being converted to heat.**PP1.8** Lithium (Li) begins the second period, neon (Ne) ends it, and eight elements are in the period.**PP1.9** Sulfur is more likely to be similar to selenium (Se), because they are in the same group.**PP1.10** Period 6**PP1.11** 28**PP1.12** (a) Carbon is a nonmetal in any of its forms.
(b) Silver is a metal.**PP1.13** Neon (Ne) is the second noble gas.**2 Measurement**

PP2.1 $5445 \text{ min} \left(\frac{60 \text{ s}}{1 \text{ min}} \right) = 326,700 \text{ s}$

PP2.2 $15.0 \text{ miles} \left(\frac{1 \text{ h}}{60.0 \text{ miles}} \right) = 0.250 \text{ h} = 15.0 \text{ min}$

PP2.4 (a) Since both are measured in avoirdupois, the weights are the same.

(b) Since gold is measured in troy, and there are fewer ounces in troy than in avoirdupois, the gold weighs less and the lead weighs more. (The small difference in the definition of ounces in the two systems does not affect this result). This example emphasizes the relative simplicity of the metric system.

PP2.5 $7 \text{ weeks} \left(\frac{7 \text{ days}}{1 \text{ week}} \right) \left(\frac{24 \text{ h}}{1 \text{ day}} \right) \left(\frac{60 \text{ min}}{1 \text{ h}} \right) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) = 4,233,600 \text{ s}$

PP2.6 $7.34 \text{ yd}^3 \left(\frac{27 \text{ ft}^3}{1 \text{ yd}^3} \right) = 198 \text{ ft}^3$

PP2.7 $\frac{100.0 \text{ yd}}{8.53 \text{ s}} \left(\frac{1 \text{ mile}}{1760 \text{ yd}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) = \frac{24.0 \text{ miles}}{1 \text{ h}}$
 $= 24.0 \text{ miles per hour}$

PP2.8 $\left(\frac{1.00 \times 10^{10} \text{ dollars}}{100 \text{ years}} \right) \left(\frac{1 \text{ year}}{365 \text{ days}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right)$
 $= 3.17 \text{ dollars/s}$

PP2.9 Only the number in part (c) is given in scientific notation.

PP2.11 (a) 1.10×10^5 (b) 2.40×10^5 (c) 1.23×10^{-3}

PP2.12 (a) 1.8×10^{15} (b) 2.1×10^8 (c) 5.4×10^{15}

PP2.13 2.5×10^1

PP2.14 6.13

PP2.15 (a) 1.01×10^{-7} (b) 2×10^2
(c) 3.00×10^{-3}

PP2.16 4.0×10^{-3}

PP2.17 (a) -2.11×10^4 (b) 5.92×10^4

PP2.18 9.0×10^{-6}

PP2.19 $\sqrt[3]{8.00 \times 10^6} = \sqrt[3]{8.00} \times \sqrt[3]{10^6} = 2.00 \times 10^2$

PP2.21 (a) $2.370 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 237.0 \text{ cm}$

(b) $2.370 \text{ ft} \left(\frac{12 \text{ in.}}{1 \text{ ft}} \right) = 28.44 \text{ in.}$

(c) The English system conversion requires a calculator (or pencil and paper).

PP2.22 (a) $6.66 \text{ km} \left(\frac{1000 \text{ m}}{1 \text{ km}} \right) = 6660 \text{ m}$

(b) $6.66 \text{ kL} \left(\frac{1000 \text{ L}}{1 \text{ kL}} \right) = 6660 \text{ L}$

(c) $6.66 \text{ kg} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) = 6660 \text{ g}$

(d) The units are changed, but nothing else. The metric system is easy because the same prefixes are used for any unit, and they signify multiples of 10.

PP2.23 (a) $179x + 22x = 201x$

(b) $33.00y \left(\frac{x}{0.10y} \right) = 330.0x$
 $179x + 330.0x = 509x$

PP2.24 $(108x)(6.50x) = 7.02x^2$

The x here and the unit in the example are treated the same algebraically.

PP2.25 $(195x)/(15y^3) = 13x/y^3$

PP2.26 $3.00 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 3000 \text{ mm}$

$10.00 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 10,000 \text{ mm}$

APPENDIX 4 ■ Answers to Practice Problems

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PP2.27 $1.04 \text{ cm} \left(\frac{0.01 \text{ m}}{1 \text{ cm}} \right) \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 10.4 \text{ mm}$

PP2.28 $1 \text{ mg} \left(\frac{0.001 \text{ g}}{1 \text{ mg}} \right) = 0.001 \text{ g}$

PP2.29 $207 \text{ lb} \left(\frac{1 \text{ kg}}{2.20 \text{ lb}} \right) = 94.1 \text{ kg}$

PP2.30 (a) Since both bricks and lead are measured in avoirdupois, the weights are the same. (b) Since gold is measured in troy weight, and there is only 12 ounces per pound, the lead is heavier.

(c) $1 \text{ lb troy} \left(\frac{12 \text{ oz troy}}{1 \text{ lb troy}} \right) \left(\frac{31.103 \text{ g}}{1 \text{ troy oz}} \right) = 373.24 \text{ g gold}$

$1 \text{ lb avoir} \left(\frac{16 \text{ oz avoir}}{1 \text{ lb avoir}} \right) \left(\frac{28.35 \text{ g}}{1 \text{ avoir oz}} \right) = 453.6 \text{ g lead}$

PP2.31 1000 cm^3

PP2.32 $1.77 \times 10^3 \text{ mg} \left(\frac{0.001 \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 1.77 \times 10^{-3} \text{ kg}$

PP2.33 $623 \text{ L} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) = 0.623 \text{ m}^3$

PP2.35 (a) Yes (b) No (c) It is more precise.

PP2.37 Two significant digits, in meters or in centimeters:

($2.4 \text{ m} = 240 \text{ cm}$ The zero is not significant.)

PP2.38 (a) 35.00 cm (b) 23.050 cm (c) 30.20 cm
(d) 30 cm

PP2.41 83.0 cm

PP2.42 (a) 32.4 cm^3 (b) 0.283 g/cm^3

PP2.43 $8.011 \text{ g} \left(\frac{1 \text{ mg}}{0.001 \text{ g}} \right) = 8011 \text{ mg}$

PP2.44 (a) 1.18 m (b) 1.17 m (c) 1.18 m

PP2.45 $2.77 \times 10^5 \text{ km}^2$

PP2.46 $180.9 \text{ cm}^3 + 3.12 \text{ cm}^3 = 184 \text{ cm}^3$

PP2.47 (a) $1.2 \times 10^3 \text{ g}$ (b) $1.20 \times 10^3 \text{ g}$
(c) $1.200 \times 10^3 \text{ g}$

PP2.48 (a) $3.2 \times 10^4 \text{ cm}$ (b) $2.1 \times 10^8 \text{ cm}^2$
(c) $-5.17 \times 10^{-3} \text{ cm}$

PP2.49 $\frac{352 \text{ g}}{(7.00 \text{ cm})(4.00 \text{ cm})(1.00 \text{ cm})} = 12.6 \text{ g/cm}^3$

PP2.51 $12.7 \text{ g Hg} \left(\frac{1 \text{ mL}}{13.6 \text{ g Hg}} \right) = 0.934 \text{ mL}$

PP2.52 $1.000 \text{ L} \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{1.74 \text{ g}}{1 \text{ mL}} \right) = 1740 \text{ g} = 1.74 \text{ kg}$

PP2.53 The density of the solid is

$$\frac{51.5 \text{ g}}{(5.03 \text{ cm})(3.11 \text{ cm})(1.22 \text{ cm})} = 2.70 \text{ g/cm}^3$$

Because the density of the object is less than that of mercury, it will float.

PP2.54 Aluminum (See Table 2.5.)

3 Atoms and Atomic Masses

PP3.1 Anywhere between 63.65% and 46.68% N, depending on how much of each compound is in the mixture.

PP3.2 $100.0 \text{ g N} \left(\frac{100.0 \text{ g NO}}{46.68 \text{ g N}} \right) = 214.2 \text{ g NO}$

PP3.3 Per gram of oxygen, there are

$$\frac{77.73 \text{ g Fe}}{22.27 \text{ g O}} = \frac{3.490 \text{ g Fe}}{1 \text{ g O}} \quad \frac{69.94 \text{ g Fe}}{30.06 \text{ g O}} = \frac{2.327 \text{ g Fe}}{1 \text{ g O}}$$

The ratio of grams of iron in the two compounds per gram of oxygen is

$$\frac{3.490 \text{ g}}{2.327 \text{ g}} = \frac{1.500 \text{ g}}{1 \text{ g}} = \frac{3}{2}$$

Multiplying numerator and denominator by 2 yields a whole-number ratio:

$$\frac{1.500 \text{ g} \times 2}{1 \text{ g} \times 2} = \frac{3 \text{ g}}{2 \text{ g}}$$

PP3.4 They are not isotopes of the same element. Because p + n is the same for both, if n is different, p must also be different. The atoms are $^{119}_{50}\text{Sn}$ and $^{119}_{49}\text{In}$.

PP3.5 $^{119}_{50}\text{Sn}$ has 50 electrons and $^{119}_{49}\text{In}$ has 49.

PP3.6 Let $2x$ = number of bottles of first size and x = number of bottles of second size

Then the ratio of volumes is

$$\frac{(6.50 \text{ L})/2x}{(13.0 \text{ L})/x} = 0.250$$

The ratio is 1 : 4.

PP3.7 Let $2x$ = number of O atoms

and x = number of Se atoms

The ratio of masses of one atom of Se to one atom of O is then:

$$\frac{2.47/x}{1.00/2x} = \frac{4.94}{1.00}$$

The atomic mass of Se is $(16.0 \text{ amu})(4.94) = 79.0 \text{ amu}$.

PP3.10 $(0.60108)(68.9256 \text{ amu}) + (0.39892)(70.9247 \text{ amu})$

$$= 69.723 \text{ amu}$$

PP3.11 No elements are out of order according to atomic number.

4 Electronic Configuration of the Atom

PP4.1 $E = hv = hc/\lambda$
 $= (6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(5.00 \times 10^{-7} \text{ m})$
 $= 3.98 \times 10^{-19} \text{ J}$

PP4.2 The energy difference between the third orbit and the first is the same whether the electron falls there in two steps or directly. The two photons of part (b) have a total energy equal to the energy of the photon of part (a). (See Figure 4.6 for quantitative values.)

PP4.3 The change in energy is the energy of the final state minus the energy of the initial state. Because the electron is falling to a lower energy state, light is emitted.

$$\begin{aligned} \text{(a)} \quad & (-2.178 \times 10^{-18} \text{ J}) - (-2.420 \times 10^{-19} \text{ J}) \\ & = -1.936 \times 10^{-18} \text{ J} \\ \text{(b)} \quad & (-5.445 \times 10^{-19} \text{ J}) - (-2.420 \times 10^{-19} \text{ J}) \\ & = -3.025 \times 10^{-19} \text{ J} \end{aligned}$$

PP4.4 The number is equal to n . (a) Four (b) Two
(The values are listed in Example 4.4.)

PP4.5 The number is $2\ell + 1$. (a) Five (b) One
(The values are listed in Example 4.5.)

PP4.6 With $n = 4$, the maximum possible value for ℓ is 3. The lowest m_ℓ value is therefore -3 .

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PP4.8 Four: $n = 1 \quad 1 \quad 2 \quad 2$
 $\ell = 0 \quad 0 \quad 0 \quad 0$
 $m_\ell = 0 \quad 0 \quad 0 \quad 0$
 $m_s = -\frac{1}{2} \quad +\frac{1}{2} \quad -\frac{1}{2} \quad +\frac{1}{2}$

PP4.10 (a) < (c) < (e) < (d) < (b)

(The $n + \ell$ values are 5, 5, 6, 6, and 7, respectively.)

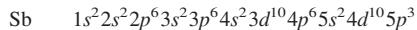
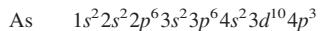
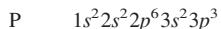
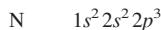
PP4.11 Two. (There is a maximum of two in any $\ell = 0$ subshell.)

PP4.13 Nitrogen (atomic number 7 = sum of superscripts)

PP4.14 Iron (atomic number 26 = sum of superscripts)

PP4.15 (a) None (b) two

PP4.16 They all have ns^2np^3 outermost electronic configurations:



PP4.17 (a) V $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
 (b) Br $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
 (c) Ge $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

PP4.18 [Rn] $7s^2 6d^1 5f^3$

5 Chemical Bonding

PP5.1 (a) 2 Hg, 2 Cl (b) 1 N, 6 H, 1 P, 4 O

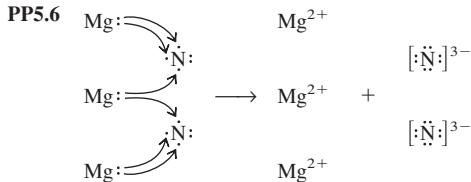
PP5.2 (a) $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$ (b) $\text{C}_4\text{H}_8\text{O}_2$

PP5.3 $1s^2 2s^2 2p^6$

PP5.4 (a) Bi^{3+} [Xe] $6s^2 5d^{10} 4f^{14} 6p^0$ or [Xe] $6s^2 5d^{10} 4f^{14}$
 (b) Pb^{4+} [Xe] $6s^0 5d^{10} 4f^{14} 6p^0$ or [Xe] $5d^{10} 4f^{14}$

PP5.5 $\text{Fe}^{2+} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6$

$\text{Fe}^{3+} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$



PP5.7 Mg_3N_2

PP5.8 (a) CuF_2 (b) Cr_3P_2

PP5.9 Mg^{2+} and P^{3-}

PP5.10 (a) Ag^+ (b) Pb^{4+}

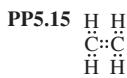
PP5.11 Single bond



PP5.12 (a) Molecules (b) Uncombined atoms (c) Molecules
 (d) Ions

PP5.13 $\text{H}:\ddot{\text{N}}:\text{N}:\ddot{\text{N}}:$

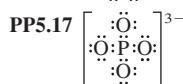
PP5.14 $\text{H}:\ddot{\text{O}}:\ddot{\text{O}}:\text{H}$



The carbon atoms must be the central atoms because hydrogen atoms can have only two electrons each.

APPENDIX 4 ■ Answers to Practice Problems

PP5.16 $\begin{array}{c} \text{H} \\ | \\ \text{H}:\ddot{\text{N}}:\ddot{\text{O}}:\text{H} \end{array}$



PP5.18 $[\ddot{\text{O}}:\ddot{\text{N}}:\ddot{\text{O}}]^-$ and $[\ddot{\text{O}}:\ddot{\text{N}}:\ddot{\text{O}}]^-$

PP5.19 $\text{H}:\ddot{\text{O}}:\ddot{\text{N}}:\ddot{\text{O}}:$

PP5.20 K^+ and $\text{P}_2\text{O}_7^{4-}$

6 Nomenclature

PP6.1 (a) Xe (b) O (c) N

PP6.2 (a) Dichlorine trioxide

(b) Tetrasulfur tetranitride

(c) Diphosphorus pentasulfide

(d) Sulfur difluoride

PP6.3 (a) Tetraphosphorus hexoxide (b) Boron trioxide

(c) Dinitrogen monoxide

(d) Iodine pentachloride

(e) Iodine heptafluoride (f) Phosphorus trichloride

PP6.4 (a) S_2F_{10} (b) IO_3^-

PP6.6 The anion is VO_4^{3-} . We know that the charge is 3- because it takes three (1+) ammonium ions to balance each anion.

PP6.8 (a) Iodine monobromide (b) Sodium bromide

(c) Copper(I) bromide

PP6.9 (a) PtO (b) PtO_2

PP6.10 Titanium(III) ion

PP6.11 The hydrogen atom has a single electron and requires two valence electrons to fill its first shell. Therefore it adds one electron to form the hydride ion.

PP6.12 (a) IO_2^- (b) IO^-

PP6.13 (a) SO_3^{2-} (b) ClO_3^- (c) NO_3^-
 (d) NO_2^-

PP6.14 Arsenate ion (analogous to phosphate ion)

PP6.15 Barium sulfate

PP6.16 (a) Aluminum acetate (b) Cobalt(III) chlorate

PP6.17 (a) $\text{Pb}(\text{SO}_4)_2$ (b) Al_2S_3

PP6.18 The two hydrogen atoms represented first in the formula are the only ionizable ones.

PP6.19 (a) Iodic acid (b) Sulfuric acid (c) Chlorous acid

PP6.20 (a) HNO_2 (b) H_2SO_4

PP6.21 (a) Na_2HPO_4 (b) $\text{Mg}(\text{H}_2\text{PO}_4)_2$

7 Formula Calculations

PP7.2 Cl_2O and NH_3 have molecular masses; they are composed of molecules because they consist of nonmetals only, but have no ammonium ion. (The others are ionic.)

PP7.3 (a) $65.4 \text{ amu} + 4(12.0 \text{ amu}) + 6(1.0 \text{ amu}) + 4(16.0 \text{ amu})$
 $65.4 \text{ amu} + 48.0 \text{ amu} + 6.0 \text{ amu} + 64.0 \text{ amu}$
 $= 183.4 \text{ amu}$

(b) $2(23.0 \text{ amu}) + 2(52.0 \text{ amu}) + 7(16.00 \text{ amu}) = 262 \text{ amu}$

PP7.4 $3 \text{ N} \quad 3 \times 14.01 \text{ amu} = 42.03 \text{ amu}$

$12 \text{ H} \quad 12 \times 1.008 \text{ amu} = 12.10 \text{ amu}$

$\text{P} \quad 1 \times 30.97 \text{ amu} = 30.97 \text{ amu}$

$4 \text{ O} \quad 4 \times 16.00 \text{ amu} = 64.00 \text{ amu}$

Total $= 149.10 \text{ amu}$

APPENDIX 4 ■ Answers to Practice Problems

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$$\%N = \left(\frac{42.03 \text{ amu}}{149.10 \text{ amu}} \right) \times 100\% = 28.19\% \text{ N}$$

$$\%H = \left(\frac{12.10 \text{ amu}}{149.10 \text{ amu}} \right) \times 100\% = 8.12\% \text{ H}$$

$$\%P = \left(\frac{30.97 \text{ amu}}{149.10 \text{ amu}} \right) \times 100\% = 20.77\% \text{ P}$$

$$\%O = \left(\frac{64.00 \text{ amu}}{149.10 \text{ amu}} \right) \times 100\% = 42.92\% \text{ O}$$

$$\text{Total} = 100.00\%$$

$$\text{PP7.5 } \left(\frac{4.00 \text{ in.}}{1 \text{ box}} \right) \left(\frac{12 \text{ boxes}}{1 \text{ dozen}} \right) \left(\frac{1 \text{ dozen}}{4.00 \text{ ft}} \right) = \frac{12.0 \text{ in.}}{1 \text{ ft}}$$

$$\text{PP7.6 } 98.0 \text{ g/mol}$$

$$\text{PP7.7 (a) } 41.9 \text{ g C}_5\text{H}_{12} \left(\frac{1 \text{ mol C}_5\text{H}_{12}}{72.0 \text{ g C}_5\text{H}_{12}} \right) = 0.582 \text{ mol C}_5\text{H}_{12}$$

$$\text{(b) } 7.15 \times 10^{23} \text{ molecules C}_5\text{H}_{12} \times \left(\frac{1 \text{ mol C}_5\text{H}_{12}}{6.02 \times 10^{23} \text{ molecules C}_5\text{H}_{12}} \right) = 1.19 \text{ mol C}_5\text{H}_{12}$$

$$\text{PP7.8 } (6.63 \times 10^{24} \text{ molecules C}_4\text{H}_{10}\text{O}) \times \left(\frac{1 \text{ mol C}_4\text{H}_{10}\text{O}}{6.02 \times 10^{23} \text{ molecules C}_4\text{H}_{10}\text{O}} \right) \left(\frac{74.0 \text{ g C}_4\text{H}_{10}\text{O}}{1 \text{ mol C}_4\text{H}_{10}\text{O}} \right) = 815 \text{ g C}_4\text{H}_{10}\text{O}$$

$$\text{PP7.9 } 4.21 \times 10^{23} \text{ atoms O} \left(\frac{1 \text{ mol O}}{6.02 \times 10^{23} \text{ atoms O}} \right) \times \left(\frac{1 \text{ mol C}_9\text{H}_8\text{O}_4}{4 \text{ mol O}} \right) = 0.175 \text{ mol C}_9\text{H}_8\text{O}_4$$

PP7.10 (a)

$$1500 \text{ g (NH}_4)_3\text{PO}_4 \left(\frac{1 \text{ mol (NH}_4)_3\text{PO}_4}{149 \text{ g(NH}_4)_3\text{PO}_4} \right) \left(\frac{1 \text{ mol P}}{1 \text{ mol (NH}_4)_3\text{PO}_4} \right) \times \left(\frac{31.0 \text{ g P}}{1 \text{ mol P}} \right) = 312 \text{ g P}$$

$$\text{(b) } 1500 \text{ g P} \left(\frac{1 \text{ mol P}}{31.0 \text{ g P}} \right) \left(\frac{1 \text{ mol (NH}_4)_3\text{PO}_4}{1 \text{ mol P}} \right) \times \left(\frac{149 \text{ g (NH}_4)_3\text{PO}_4}{1 \text{ mol (NH}_4)_3\text{PO}_4} \right) = 7210 \text{ g (NH}_4)_3\text{PO}_4$$

$$\text{PP7.11 } 7 \text{ C} = 84.07 \text{ g C}$$

$$5 \text{ H} = 5.04 \text{ g H}$$

$$3 \text{ N} = 42.03 \text{ g N}$$

$$6 \text{ O} = 96.00 \text{ g O}$$

$$\text{Total} = 227.14 \text{ g}$$

$$\left(\frac{84.07 \text{ g C}}{227.14 \text{ g total}} \right) \times 100\% = 37.01\% \text{ C}$$

$$\left(\frac{5.04 \text{ g H}}{227.14 \text{ g total}} \right) \times 100\% = 2.22\% \text{ H}$$

$$\left(\frac{42.03 \text{ g N}}{227.14 \text{ g total}} \right) \times 100\% = 18.50\% \text{ N}$$

$$\left(\frac{96.00 \text{ g O}}{227.14 \text{ g total}} \right) \times 100\% = 42.26\% \text{ O}$$

$$\text{Total} = 99.99\%$$

PP7.12 (a) AB

(b) A₂B₃ (multiply the given ratio by 2)

(c) A₃B₄ (multiply the given ratio by 3)

(d) A₃B₅ (multiply the given ratio by 3)

(e) A₄B₅ (multiply the given ratio by 4)

(f) A₄B₇ (multiply the given ratio by 4)

(g) A₅B₆ (multiply the given ratio by 5)

(h) A₅B₇ (multiply the given ratio by 5)

$$\text{PP7.13 } 38.71 \text{ g Mn} \left(\frac{1 \text{ mol Mn}}{54.94 \text{ g Mn}} \right) = 0.7046 \text{ mol Mn}$$

$$21.82 \text{ g P} \left(\frac{1 \text{ mol P}}{30.97 \text{ g P}} \right) = 0.7046 \text{ mol P}$$

$$39.46 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 2.466 \text{ mol O}$$

$$\frac{0.7046 \text{ mol Mn}}{0.7046} = 1.000 \text{ mol Mn}$$

$$\frac{0.7046 \text{ mol P}}{0.7046} = 1.000 \text{ mol P}$$

$$\frac{2.466 \text{ mol O}}{0.7046} = 3.500 \text{ mol O}$$

Multiplying each of these numbers of moles by 2 yields the empirical formula Mn₂P₂O₇.

$$\text{PP7.14 } 2.453 \text{ g Na} \left(\frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \right) = 0.1067 \text{ mol Na}$$

$$3.422 \text{ g S} \left(\frac{1 \text{ mol S}}{32.06 \text{ g S}} \right) = 0.1067 \text{ mol S}$$

$$2.561 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 0.1601 \text{ mol O}$$

$$\frac{0.1067 \text{ mol Na}}{0.1067} = 1.000 \text{ mol Na}$$

$$\frac{0.1067 \text{ mol S}}{0.1067} = 1.000 \text{ mol S}$$

$$\frac{0.1601 \text{ mol O}}{0.1067} = 1.500 \text{ mol O}$$

The empirical formula is Na₂S₂O₃.

PP7.15 Because a hydrocarbon contains hydrogen and carbon only, the percentage of hydrogen is

$$100.00\% \text{ total} - 89.94\% \text{ C} = 10.06\% \text{ H}$$

The numbers of moles in 100.0 g are

$$89.94 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.489 \text{ mol C}$$

$$10.06 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 9.980 \text{ mol H}$$

The mole ratio is

$$\frac{9.980 \text{ mol H}}{7.489 \text{ mol C}} = \frac{1.333 \text{ mol H}}{1 \text{ mol C}} = \frac{4 \text{ mol H}}{3 \text{ mol C}}$$

The empirical formula is C₃H₄. The empirical formula mass is 40.06 g/mol of empirical formula units:

$$3(12.01 \text{ g/mol}) + 4(1.008 \text{ g/mol}) = 40.06 \text{ g/mol}$$

The number of moles of empirical formula units per mole is

$$\frac{80.2 \text{ g/mol}}{40.06 \text{ g/mol empirical formula units}} = \frac{2 \text{ mol empirical formula units}}{1 \text{ mol}}$$

The molecular formula is therefore C₆H₈.

606**8 Chemical Reactions**

- PP8.1** ? NH₄I + 1 Pb(NO₃)₂ → ? NH₄NO₃ + ? PbI₂
? NH₄I + 1 Pb(NO₃)₂ → 2 NH₄NO₃ + 1 PbI₂
2 NH₄I + 1 Pb(NO₃)₂ → 2 NH₄NO₃ + 1 PbI₂
2 NH₄I + Pb(NO₃)₂ → 2 NH₄NO₃ + PbI₂
- PP8.2** 1 C₈H₁₈ + ? O₂ → ? CO₂ + ? H₂O
1 C₈H₁₈ + ? O₂ → 8 CO₂ + 9 H₂O
1 C₈H₁₈ + $\frac{25}{2}$ O₂ → 8 CO₂ + 9 H₂O
2 C₈H₁₈ + 25 O₂ → 16 CO₂ + 18 H₂O
- PP8.3** ? H₂O + 1 N₂O₅ → ? HNO₃
? H₂O + 1 N₂O₅ → 2 HNO₃
1 H₂O + 1 N₂O₅ → 2 HNO₃
H₂O + N₂O₅ → 2 HNO₃
- PP8.4** (NH₄)₂S + CuCl₂ → CuS + 2 NH₄Cl
- PP8.5** 2 (NH₄)₃PO₄ + 3 Mg(NO₃)₂ → 6 NH₄NO₃ + Mg₃(PO₄)₂
- PP8.6** Al(s) + O₂(g) → Al₂O₃(s) (Unbalanced)
4 Al(s) + 3 O₂(g) → 2 Al₂O₃(s) (Balanced)
- PP8.7** No reaction (Two metals do not combine chemically.)
- PP8.8** (a) 6 Ba(s) + 2 Al₂O₃(s) $\xrightarrow{\text{heat}}$ 6 BaO(s) + 4 Al(s)
(b) 2 NaF(aq) + Cl₂(g) → N.R.
- PP8.9** (a) Ba(OH)₂(aq) + 2 HC₂H₃O₂(aq) → Ba(C₂H₃O₂)₂(aq) + 2 H₂O(ℓ)
(b) AlCl₃(aq) + 3 AgNO₃(aq) → 3 AgCl(s) + Al(NO₃)₃(aq)
- PP8.10** (a) (NH₄)₂CO₃(aq) + 2 HClO₄(aq) → 2 NH₄ClO₄(aq) + H₂O(ℓ) + CO₂(g)
(b) (NH₄)₂CO₃(aq) + 2 NaOH(aq) → 2 NH₃(aq) + 2 H₂O(ℓ) + Na₂CO₃(aq)
- PP8.11** Covalent compounds are formed in each case:
(a) Li₂O(s) + H₂SO₄(aq) → Li₂SO₄(aq) + H₂O(ℓ)
(b) LiHCO₃(aq) + HBr(aq) → LiBr(aq) + H₂O(ℓ) + CO₂(g)
- PP8.12** (a) NH₄NO₃(aq) + NaOH(aq) → NaNO₃(aq) + NH₃(aq) + H₂O(ℓ)
(b) 2 NH₄I(aq) + Ba(OH)₂(aq) → BaI₂(aq) + 2 NH₃(aq) + 2 H₂O(ℓ)
- PP8.15** A mixture of CO and CO₂ will be produced, along with water.
- PP8.17** C₁₂H₂₂O₁₁(s) + 12 O₂(g) → 12 CO₂(g) + 11 H₂O(ℓ)
- PP8.19** NaC₂H₃O₂(aq) + HCl(aq) → HC₂H₃O₂(aq) + NaCl(aq)
(The formation of HC₂H₃O₂, a weak acid, causes the reaction to go.)
- PP8.20** (a) Double substitution (d) Combination
- PP8.21** (a) N₂O₃ + 2 NaOH → 2 NaNO₂ + H₂O
(b) Na₂O + 2 HNO₃ → 2 NaNO₃ + H₂O
- PP8.22** 2-

9 Net Ionic Equations

- PP9.1** (a) BaSO₄(s) (insoluble)
(b) HNO₂(aq) (weak)
(c) Na⁺(aq) + OH⁻(aq)
- PP9.2** Ag⁺(aq) + Cl⁻(aq) → AgCl(s)
- PP9.3** (a)-(d) H⁺(aq) + OH⁻(aq) → H₂O(ℓ)
- PP9.4** NH₃(aq) + H⁺(aq) → NH₄⁺(aq)

APPENDIX 4 ■ Answers to Practice Problems

- PP9.5** HC₂H₃O₂ is a *weak* acid, so the net ionic equation is different:
HC₂H₃O₂(aq) + OH⁻(aq) → C₂H₃O₂⁻(aq) + H₂O(ℓ)
- PP9.7** PbCl₂ is a solid and does not provide Cl⁻ ions to the solution like a soluble ionic chloride does.
- PP9.8** Of many possible examples, two are
Cl₂(aq) + 2 KI(aq) → I₂(aq) + 2 KCl(aq)
Cl₂(aq) + 2 NaI(aq) → I₂(aq) + 2 NaCl(aq)
- PP9.9** Cu(s) + Cu²⁺(aq) + 2 Cl⁻(aq) → 2 CuCl(s)
(There are no spectator ions in this reaction.)
- PP9.10** 1 mol Al(NO₃)₃ $\left(\frac{3 \text{ mol NO}_3^-}{1 \text{ mol Al(NO}_3)_3}\right)$ = 3 mol NO₃⁻

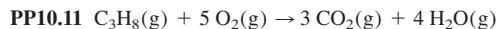
10 Stoichiometry

- | | | | |
|---------------|-------------------------|-------------------------|-------------------------|
| PP10.1 | 1 mol TiCl ₄ | 1 mol TiCl ₄ | 1 mol TiCl ₄ |
| | 2 mol H ₂ O | 1 mol TiO ₂ | 4 mol HCl |
| | 2 mol H ₂ O | 1 mol TiO ₂ | 4 mol HCl |
| | 1 mol TiCl ₄ | 1 mol TiCl ₄ | 1 mol TiCl ₄ |
| | 2 mol H ₂ O | 2 mol H ₂ O | 1 mol TiO ₂ |
| | 1 mol TiO ₂ | 4 mol HCl | 4 mol HCl |
| | 1 mol TiO ₂ | 4 mol HCl | 4 mol HCl |
| | 2 mol H ₂ O | 2 mol H ₂ O | 1 mol TiO ₂ |
- PP10.2** 3.18 mol O₂ $\left(\frac{2 \text{ mol Al}_2\text{O}_3}{3 \text{ mol O}_2}\right)$ = 2.12 mol Al₂O₃
- PP10.3** H₂SO₄(aq) + 2 NaOH(aq) → Na₂SO₄(aq) + 2 H₂O(ℓ)
1.24 mol Na₂SO₄ $\left(\frac{2 \text{ mol NaOH}}{1 \text{ mol Na}_2\text{SO}_4}\right)$ = 2.48 mol NaOH
- PP10.4** 3 H₂(g) + N₂(g) → 2 NH₃(g)
Notice the difference in wording between this problem and Example 10.4. Here, the number of moles of reactant *remaining* is given. The number of moles of hydrogen that reacted is 0.225 mol H₂ present - 0.033 mol H₂ left
= 0.192 mol H₂ reacted
- The number of moles of nitrogen used up is
0.192 mol H₂ $\left(\frac{1 \text{ mol N}_2}{3 \text{ mol H}_2}\right)$ = 0.0640 mol N₂
- PP10.6** 0.0929 mol P $\left(\frac{2 \text{ mol PCl}_5}{2 \text{ mol P}}\right) \left(\frac{208.5 \text{ g PCl}_5}{1 \text{ mol PCl}_5}\right)$ = 19.4 g PCl₅
- PP10.7** 207 × 10³ g NaCl $\left(\frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}}\right) \left(\frac{2 \text{ mol Na}}{2 \text{ mol NaCl}}\right) \left(\frac{23.0 \text{ g Na}}{1 \text{ mol Na}}\right)$ = 8.14 × 10⁴ g Na = 81.4 kg Na
- PP10.8** 3 Cl₂(g) + 2 Cr(s) → 2 CrCl₃(s)
17.6 g CrCl₃ $\left(\frac{1 \text{ mol CrCl}_3}{158.5 \text{ g CrCl}_3}\right) \left(\frac{3 \text{ mol Cl}_2}{2 \text{ mol CrCl}_3}\right) \left(\frac{70.9 \text{ g Cl}_2}{1 \text{ mol Cl}_2}\right)$
= 11.8 g Cl₂

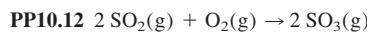
- PP10.9** CuS(s) + O₂(g) $\xrightarrow{\text{Heat}}$ Cu(s) + SO₂(g)
70.0 × 10⁶ g Cu $\left(\frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}}\right) \left(\frac{1 \text{ mol CuS}}{1 \text{ mol Cu}}\right) \left(\frac{95.56 \text{ g CuS}}{1 \text{ mol CuS}}\right)$
= 105 × 10⁶ g CuS = 105 metric tons CuS
- PP10.10** 2 HCl(aq) + BaCO₃(s) → BaCl₂(aq) + H₂O(ℓ) + CO₂(g)
BaCl₂ is the only solid.
1.47 g BaCO₃ $\left(\frac{1 \text{ mol BaCO}_3}{197 \text{ g BaCO}_3}\right) \left(\frac{1 \text{ mol BaCl}_2}{1 \text{ mol BaCO}_3}\right) \times \left(\frac{208 \text{ g BaCl}_2}{1 \text{ mol BaCl}_2}\right)$
= 1.55 g BaCl₂

APPENDIX 4 ■ Answers to Practice Problems

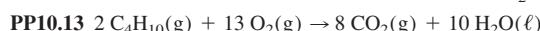
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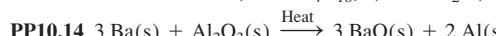
$$48.4 \text{ g C}_3\text{H}_8 \left(\frac{1 \text{ mol C}_3\text{H}_8}{44.0 \text{ g C}_3\text{H}_8} \right) \left(\frac{4 \text{ mol H}_2\text{O}}{1 \text{ mol C}_3\text{H}_8} \right) \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) \times \left(\frac{1 \text{ mL H}_2\text{O}}{1.00 \text{ g H}_2\text{O}} \right) = 79.2 \text{ mL H}_2\text{O}$$



$$0.751 \text{ mol SO}_3 \left(\frac{2 \text{ mol SO}_2}{2 \text{ mol SO}_3} \right) \left(\frac{6.02 \times 10^{23} \text{ SO}_2 \text{ molecules}}{1 \text{ mol SO}_2} \right) = 4.52 \times 10^{23} \text{ SO}_2 \text{ molecules}$$



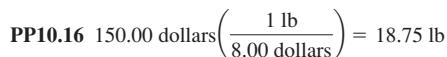
$$4.57 \times 10^{22} \text{ molecules C}_4\text{H}_{10} \left(\frac{1 \text{ mol C}_4\text{H}_{10}}{6.02 \times 10^{23} \text{ molecules C}_4\text{H}_{10}} \right) \times \left(\frac{10 \text{ mol H}_2\text{O}}{2 \text{ mol C}_4\text{H}_{10}} \right) \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 6.83 \text{ g H}_2\text{O}$$



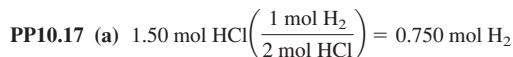
$$7.33 \text{ g Al} \left(\frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right) \left(\frac{3 \text{ mol Ba}}{2 \text{ mol Al}} \right) \left(\frac{6.02 \times 10^{23} \text{ atoms Ba}}{1 \text{ mol Ba}} \right) = 2.45 \times 10^{23} \text{ atoms Ba}$$



$$6.15 \times 10^6 \text{ g H}_3\text{PO}_4 \left(\frac{1 \text{ mol H}_3\text{PO}_4}{98.0 \text{ g H}_3\text{PO}_4} \right) \left(\frac{1 \text{ mol} (\text{NH}_4)_3\text{PO}_4}{1 \text{ mol H}_3\text{PO}_4} \right) \times \left(\frac{3 \text{ mol N}}{1 \text{ mol} (\text{NH}_4)_3\text{PO}_4} \right) \left(\frac{14.0 \text{ g N}}{1 \text{ mol N}} \right) = 2.64 \times 10^6 \text{ g N}$$



The dollars are in limiting quantity, so only 18.75 lb of nuts can be purchased.



$$(b) \frac{1.00 \text{ mol Ca}}{1} = 1.00 \text{ mol Ca}$$

$$\frac{1.50 \text{ mol HCl}}{2} = 0.750 \text{ mol HCl}$$

HCl is in limiting quantity, so the answer is the same as in part (a).

$$(c) \frac{0.500 \text{ mol Ca}}{1} = 0.500 \text{ mol Ca}$$

$$\frac{1.50 \text{ mol HCl}}{2} = 0.750 \text{ mol HCl}$$

Ca is in limiting quantity:

$$0.500 \text{ mol Ca} \left(\frac{1 \text{ mol H}_2}{1 \text{ mol Ca}} \right) = 0.500 \text{ mol H}_2$$



Initial:	0.100 mol	0.0250 mol	0.000 mol
Change:	-0.0500 mol	-0.0250 mol	+0.0250 mol
Final:	0.0500 mol	0.0000 mol	0.0250 mol

Note that the ratio of magnitudes of HCl to Ba(OH)_2 to BaCl_2 to H_2O in the "change" row is 2:1:1:2, just as in the balanced chemical equation.



Initial:	1.00 mol	1.75 mol	0.000 mol
Change:	-1.00 mol	-1.50 mol	+0.500 mol
Final:	0.00 mol	0.25 mol	0.500 mol

Sulfur is in excess, aluminium is in limiting quantity; and 0.500 mol of Al_2S_3 is produced.

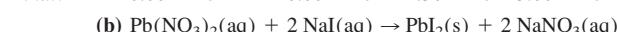


Initial:	4.25 mol	1.95 mol	0.00 mol
Change:	-3.90 mol	-1.95 mol	+1.95 mol
Final:	0.35 mol	0.00 mol	1.95 mol

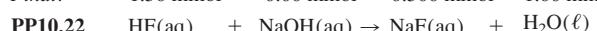
Thus 3.90 mol of water is produced. (We don't know how much is present at the end, because we did not know how much was present initially.)



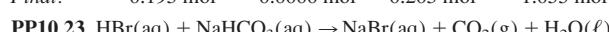
Initial:	2.50 mmol	5.00 mmol	0.00 mmol	0.00 mmol
Change:	-2.50 mmol	-5.00 mmol	+2.50 mmol	+5.00 mmol
Final:	0.00 mmol	0.00 mmol	2.50 mmol	5.00 mmol



Initial:	2.00 mmol	1.00 mmol	0.00 mmol	0.00 mmol
Change:	-0.500 mmol	-1.00 mmol	+0.500 mmol	+1.00 mmol
Final:	1.50 mmol	0.00 mmol	0.500 mmol	1.00 mmol



Initial:	0.250 mol	0.0550 mol	0.150 mol	1.000 mol
Change:	-0.0550 mol	-0.0550 mol	+0.0550 mol	+0.0550 mol
Final:	0.195 mol	0.0000 mol	0.205 mol	1.055 mol



$$12.3 \text{ g NaHCO}_3 \left(\frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g NaHCO}_3} \right) = 0.1464 \text{ mol NaHCO}_3$$

$$25.0 \text{ g HBr} \left(\frac{1 \text{ mol HBr}}{80.9 \text{ g HBr}} \right) = 0.3090 \text{ mol HBr}$$

All in moles:

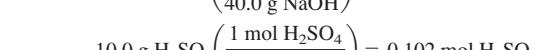
$$\text{NaHCO}_3 + \text{HBr} \rightarrow \text{NaBr} + \text{CO}_2 + \text{H}_2\text{O}$$

$$\text{Initial: } 0.1464 \quad 0.3090 \quad 0.000 \quad 0.000$$

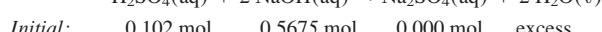
$$\text{Change: } -0.1464 \quad -0.1464 \quad +0.1464 \quad +0.1464$$

$$\text{Final: } 0.0000 \quad 0.1626 \quad 0.1464 \quad 0.1464$$

$$0.1464 \text{ mol NaBr} \left(\frac{102.9 \text{ g NaBr}}{1 \text{ mol NaBr}} \right) = 15.1 \text{ g NaBr}$$



$$10.0 \text{ g H}_2\text{SO}_4 \left(\frac{1 \text{ mol H}_2\text{SO}_4}{98.0 \text{ g H}_2\text{SO}_4} \right) = 0.102 \text{ mol H}_2\text{SO}_4$$



$$\text{Initial: } 0.102 \text{ mol} \quad 0.5675 \text{ mol} \quad 0.000 \text{ mol} \quad \text{excess}$$

$$\text{Change: } -0.102 \text{ mol} \quad -0.204 \text{ mol} \quad +0.102 \text{ mol} \quad +0.204 \text{ mol}$$

$$\text{Final: } 0.000 \text{ mol} \quad 0.3635 \text{ mol} \quad 0.102 \text{ mol} \quad \text{excess}$$

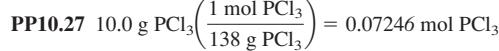
$$0.102 \text{ mol Na}_2\text{SO}_4 \left(\frac{142 \text{ g Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4} \right) = 14.5 \text{ g Na}_2\text{SO}_4$$



$$\text{Initial: } 0.400 \text{ mol} \quad 0.300 \text{ mol} \quad 0.100 \text{ mol} \quad 10.00 \text{ mol}$$

$$\text{Change: } -0.300 \text{ mol} \quad -0.300 \text{ mol} \quad +0.300 \text{ mol} \quad +0.300 \text{ mol}$$

$$\text{Final: } 0.100 \text{ mol} \quad 0.000 \text{ mol} \quad 0.400 \text{ mol} \quad 10.30 \text{ mol}$$



$$6.00 \text{ g Cl}_2 \left(\frac{1 \text{ mol Cl}_2}{70.9 \text{ g Cl}_2} \right) = 0.08463 \text{ mol Cl}_2$$

PCl_3 is present in limiting quantity, so the answer is based on the PCl_3 present, just as in Example 10.27. The answer is again 93.1%.

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$$6.11 \text{ g BaSO}_4 \left(\frac{1 \text{ mol BaSO}_4}{233 \text{ g BaSO}_4} \right) \left(\frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaSO}_4} \right) = 0.02622 \text{ mol Ba}^{2+}$$

$$0.02622 \text{ mol BaCl}_2 \left(\frac{208 \text{ g BaCl}_2}{1 \text{ mol BaCl}_2} \right) = 5.45 \text{ g BaCl}_2$$

11 Molarity

PP11.3 Be sure to choose the correct values to calculate the molarity, which is moles of solute divided by liters of solution:

$$\frac{2.10 \text{ mol solute}}{3.75 \text{ L solution}} = 0.560 \text{ M}$$

PP11.4 $\frac{4.50 \text{ mmol NaCl}}{3.80 \text{ mL}} = 1.18 \text{ M NaCl}$

PP11.5 $0.750 \text{ g CaCl}_2 \left(\frac{1 \text{ mol CaCl}_2}{111 \text{ g CaCl}_2} \right) = 0.006757 \text{ mol CaCl}_2$
 $= 6.757 \text{ mmol CaCl}_2$
 $\frac{6.757 \text{ mmol CaCl}_2}{11.6 \text{ mL}} = 0.582 \text{ M CaCl}_2$

PP11.6 $29.21 \text{ mL} \left(\frac{6.013 \text{ mmol}}{1 \text{ mL}} \right) = 175.6 \text{ mmol CH}_2\text{O}$

PP11.7 $4.00 \text{ L} \left(\frac{0.250 \text{ mol}}{1 \text{ L}} \right) = 1.00 \text{ mol solute}$
 $1.00 \text{ mol solute} \left(\frac{1 \text{ L}}{6.00 \text{ mol solute}} \right) = 0.167 \text{ L}$

PP11.8 $2.00 \text{ L} \left(\frac{3.00 \text{ mol}}{1 \text{ L}} \right) = 6.00 \text{ mol}$
 $4.00 \text{ L} \left(\frac{3.00 \text{ mol}}{1 \text{ L}} \right) = 12.0 \text{ mol}$

Total number of moles = 18.0 mol

Total volume = 6.00 L

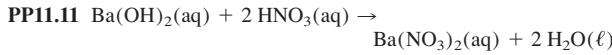
$$\text{Molarity} = \frac{18.0 \text{ mol}}{6.00 \text{ L}} = 3.00 \text{ M}$$

PP11.9 $87.3 \text{ mL} \left(\frac{1.71 \text{ mmol}}{1 \text{ mL}} \right) = 149.3 \text{ mmol}$

$$71.7 \text{ mL} \left(\frac{3.11 \text{ mmol}}{1 \text{ mL}} \right) = 223.0 \text{ mmol}$$

Total = 372.3 mmol

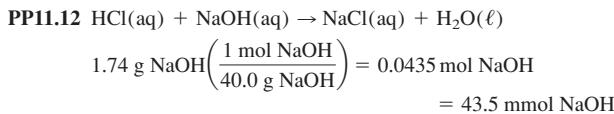
$$\frac{372.3 \text{ mmol}}{275 \text{ mL}} = 1.35 \text{ M}$$



$$41.74 \text{ mL HNO}_3 \left(\frac{0.2500 \text{ mmol HNO}_3}{1 \text{ mL HNO}_3} \right) = 10.435 \text{ mmol HNO}_3$$

$$10.435 \text{ mmol HNO}_3 \left(\frac{1 \text{ mmol Ba(OH)}_2}{2 \text{ mmol HNO}_3} \right) = 5.2175 \text{ mmol Ba(OH)}_2$$

$$5.2175 \text{ mmol Ba(OH)}_2 \left(\frac{1 \text{ mL}}{0.1212 \text{ mmol Ba(OH)}_2} \right) = 43.05 \text{ mL}$$



$$22.4 \text{ mL HCl} \left(\frac{2.00 \text{ mmol HCl}}{1 \text{ mL HCl}} \right) = 44.8 \text{ mmol HCl}$$

APPENDIX 4 ■ Answers to Practice Problems

NaOH is in limiting quantity.

$$43.5 \text{ mmol NaOH} \left(\frac{1 \text{ mmol NaCl}}{1 \text{ mmol NaOH}} \right) \left(\frac{58.5 \text{ mg NaCl}}{1 \text{ mmol NaCl}} \right) = 2540 \text{ mg NaCl}$$

PP11.13 The concentration of A must be very small because the concentration of B cannot be greater than about 10^1 M .

PP11.14 (a) $\frac{0.150 \text{ mol Al}_2(\text{SO}_4)_3}{2.70 \text{ L}} = 0.0556 \text{ M Al}_2(\text{SO}_4)_3$

(b) $0.150 \text{ mol Al}_2(\text{SO}_4)_3 \left(\frac{2 \text{ mol Al}^{3+}}{1 \text{ mol Al}_2(\text{SO}_4)_3} \right) = 0.300 \text{ mol Al}^{3+}$

$$0.150 \text{ mol Al}_2(\text{SO}_4)_3 \left(\frac{3 \text{ mol SO}_4^{2-}}{1 \text{ mol Al}_2(\text{SO}_4)_3} \right) = 0.450 \text{ mol SO}_4^{2-}$$

$$\frac{0.300 \text{ mol Al}^{3+}}{2.70 \text{ L}} = 0.111 \text{ M Al}^{3+}$$

$$\frac{0.450 \text{ mol SO}_4^{2-}}{2.70 \text{ L}} = 0.167 \text{ M SO}_4^{2-}$$

PP11.15 $10.0 \text{ mL} \left(\frac{0.800 \text{ mmol (NH}_4)_3\text{PO}_4}{1 \text{ mL}} \right) = 8.00 \text{ mmol (NH}_4)_3\text{PO}_4$

$$14.9 \text{ mL} \left(\frac{1.44 \text{ mmol NH}_4\text{Cl}}{1 \text{ mL}} \right) = 21.46 \text{ mmol NH}_4\text{Cl}$$

8.00 mmol $(\text{NH}_4)_3\text{PO}_4$ consists of
 24.0 mmol NH_4^+ and $8.00 \text{ mmol PO}_4^{3-}$

21.46 mmol NH_4Cl consists of

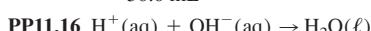
21.46 mmol NH_4^+ and 21.46 mmol Cl^-

The total number of millimoles of NH_4^+ is 45.46 mmol, and the concentrations are

$$\frac{45.46 \text{ mmol NH}_4^+}{50.0 \text{ mL}} = 0.909 \text{ M NH}_4^+$$

$$\frac{8.00 \text{ mmol PO}_4^{3-}}{50.0 \text{ mL}} = 0.160 \text{ M PO}_4^{3-}$$

$$\frac{21.46 \text{ mmol Cl}^-}{50.0 \text{ mL}} = 0.429 \text{ M Cl}^-$$



$$15.5 \text{ mL} \left(\frac{2.50 \text{ mmol H}^+}{1 \text{ mL}} \right) = 38.75 \text{ mmol H}^+$$

$$12.6 \text{ mL} \left(\frac{3.13 \text{ mmol OH}^-}{1 \text{ mL}} \right) = 39.44 \text{ mmol OH}^-$$

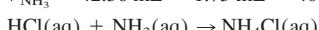
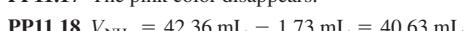
The H^+ is in limiting quantity, so 38.75 mmol H^+ reacts with 38.75 mmol OH^- , leaving no H^+ and 39.44 mmol $\text{OH}^- - 38.75 \text{ mmol} = 0.69 \text{ mmol OH}^-$. The concentrations are

$$\frac{38.75 \text{ mmol Cl}^-}{50.0 \text{ mL}} = 0.775 \text{ M Cl}^-$$

$$\frac{0.69 \text{ mmol OH}^-}{50.0 \text{ mL}} = 0.01 \text{ M OH}^-$$

$$\frac{39.44 \text{ mmol Na}^+}{50.0 \text{ mL}} = 0.789 \text{ M Na}^+$$

PP11.17 The pink color disappears.



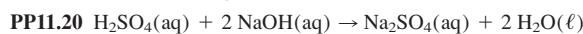
$$25.00 \text{ mL HCl} \left(\frac{1.500 \text{ mmol HCl}}{1 \text{ mL HCl}} \right) = 37.50 \text{ mmol HCl}$$

APPENDIX 4 ■ Answers to Practice Problems

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$$37.50 \text{ mmol HCl} \left(\frac{1 \text{ mmol NH}_3}{1 \text{ mmol HCl}} \right) = 37.50 \text{ mmol NH}_3$$

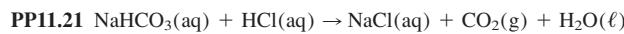
$$\frac{37.50 \text{ mmol NH}_3}{40.63 \text{ mL NH}_3} = 0.9230 \text{ M NH}_3$$



$$25.00 \text{ mL} \left(\frac{4.176 \text{ mmol H}_2\text{SO}_4}{1 \text{ mL}} \right) = 104.4 \text{ mmol H}_2\text{SO}_4$$

$$104.4 \text{ mmol H}_2\text{SO}_4 \left(\frac{2 \text{ mmol NaOH}}{1 \text{ mmol H}_2\text{SO}_4} \right) = 208.8 \text{ mmol NaOH}$$

$$208.8 \text{ mmol NaOH} \left(\frac{1 \text{ mL NaOH}}{1.500 \text{ mmol NaOH}} \right) = 139.2 \text{ mL NaOH}$$



$$27.17 \text{ mL HCl} \left(\frac{2.500 \text{ mmol HCl}}{1 \text{ mL HCl}} \right) = 67.925 \text{ mmol HCl}$$

$$67.925 \text{ mmol HCl} \left(\frac{1 \text{ mmol NaHCO}_3}{1 \text{ mmol HCl}} \right) = 67.93 \text{ mmol NaHCO}_3$$

12 Gases

PP12.2 $P_1V_1 = P_2V_2$

$$(1.50 \text{ atm})(35.0 \text{ mL}) = P_2(20.5 \text{ mL})$$

$$P_2 = 2.56 \text{ atm}$$

PP12.3 $P \quad V$

$$\begin{array}{lll} 1 & 1.20 \text{ atm} & V_1 \\ 2 & 744 \text{ torr} & 70.4 \text{ mL} \end{array}$$

$$P_1V_1 = P_2V_2$$

$$(1.20 \text{ atm})V_1 = (744 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) (70.4 \text{ mL})$$

$$V_1 = 57.4 \text{ mL}$$

PP12.4 $P_1V_1 = P_2V_2$

$$P_1(485 \text{ mL}) = (1.18 \text{ atm})(1.16 \text{ L}) \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right)$$

$$P_1 = 2.82 \text{ atm}$$

PP12.5 $t = \frac{5}{9}(t_F - 32.0) = \frac{5}{9}(98.6 - 32.0) = \frac{5}{9}(66.6) = 37.0^\circ\text{C}$

$$T = 37.0 + 273 = 310 \text{ K}$$

PP12.6 The effect of lowering the temperature is a lowering of the volume. (Note that doubling the Celsius temperature does *not* double the volume.)

PP12.7 $\frac{T_1}{V_1} = \frac{T_2}{V_2}$

$$\frac{T_1}{0.456 \text{ L}} = \frac{(273 + 55) \text{ K}}{1.75 \text{ L}}$$

$$T_1 = 85.5 \text{ K}$$

PP12.8 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{(717 \text{ torr})[(1 \text{ atm})/(760 \text{ torr})]V_1}{(293 \text{ K})} = \frac{(1.07 \text{ atm})(908 \text{ mL})}{(345 \text{ K})}$$

$$V_1 = 875 \text{ mL}$$

PP12.9 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{(811 \text{ torr})(49.7 \text{ mL})}{(325 \text{ K})} = \frac{(760 \text{ torr})V_2}{(273 \text{ K})}$$

$$V_2 = 44.5 \text{ mL}$$

PP12.11 $V = \frac{nRT}{P} = \frac{(0.898 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(292 \text{ K})}{1.06 \text{ atm}}$

$$= 20.3 \text{ L}$$

PP12.12 $7.11 \text{ g N}_2 \left(\frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} \right) = 0.2539 \text{ mol N}_2$

$$799 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.051 \text{ atm}$$

$$16 + 273 = 289 \text{ K}$$

$$V = \frac{nRT}{P} = \frac{(0.2539 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(289 \text{ K})}{1.051 \text{ atm}}$$

$$= 5.73 \text{ L}$$

PP12.15 $P = \frac{nRT}{V} = \frac{(0.0855 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})}{0.0661 \text{ L}}$

$$= 31.6 \text{ atm}$$

PP12.17 $P_{\text{Ne}} = P_{\text{total}} - P_{\text{O}_2} = 1.031 \text{ atm} - 0.922 \text{ atm} = 0.109 \text{ atm}$

PP12.21 $48.3 \text{ g CO}_2 \left(\frac{1 \text{ mol CO}_2}{44.0 \text{ g CO}_2} \right) = 1.098 \text{ mol CO}_2$

$$V = \frac{nRT}{P} = \frac{(1.098 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}}$$

$$= 24.6 \text{ L}$$

Although the masses of the gases are the same, the numbers of moles are different because the gases have different molar masses. Because the numbers of moles are different, the volumes are different.

PP12.22 $n = \frac{PV}{RT} = \frac{(1.043 \text{ atm})(2.76 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(295 \text{ K})} = 0.1189 \text{ mol}$

$$\text{Molar mass} = \frac{3.38 \text{ g}}{0.1189 \text{ mol}} = 28.4 \text{ g/mol}$$

PP12.23 $n = \frac{PV}{RT} = \frac{(0.9855 \text{ atm})(2.90 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(297 \text{ K})} = 0.1172 \text{ mol}$

$$\text{Molar mass} = \frac{3.53 \text{ g}}{0.1172 \text{ mol}} = 30.1 \text{ g/mol}$$

$$79.89 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 6.652 \text{ mol C}$$

$$20.11 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 19.95 \text{ mol H}$$

$$\frac{19.95 \text{ mol H}}{6.652 \text{ mol C}} = \frac{2.999 \text{ mol H}}{1 \text{ mol C}}$$

The empirical formula is CH_3 , with an empirical formula mass of 15.0 g/mol of empirical formula units:

$$\frac{30.1 \text{ g/mol}}{15.0 \text{ g/mol empirical formula units}} = \frac{2 \text{ mol empirical formula units}}{1 \text{ mol}}$$

The molecular formula is C_2H_6 .

PP12.24 $n = \frac{P}{RT} = \frac{(789 \text{ torr})(1 \text{ atm}/760 \text{ torr})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} = 0.04243 \text{ mol/L}$

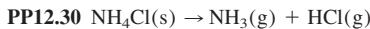
$$\frac{0.04243 \text{ mol}}{\text{L}} = \frac{80.1 \text{ g}}{1 \text{ mol}} = 3.40 \text{ g/L}$$

PP12.25 $\frac{3.00 \text{ g O}_2}{1 \text{ L}} \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 0.09375 \text{ mol/L}$

$$T = \frac{P(V)}{R \cdot n} = \left(\frac{1.50 \text{ atm}}{0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}} \right) \left(\frac{1 \text{ L}}{0.09375 \text{ mol}} \right) = 195 \text{ K}$$

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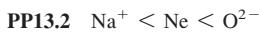
PP12.27 $V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}} = 22.4 \text{ L}$



4.29 L of NH_3 is also expected. Because the mole ratio is 1:1 and the separate gases are at the same temperature and pressure, the volume ratio is also 1:1. Nothing can be said about the volume of the solid.

13 Atomic and Molecular Properties

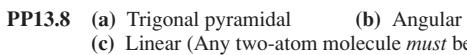
PP13.1 Cl^- is much bigger because it has added an electron, but the nucleus has not changed. The greater interelectronic repulsion causes an increase in size (from $0.99 \times 10^{-10} \text{ m}$ to $1.81 \times 10^{-10} \text{ m}$).



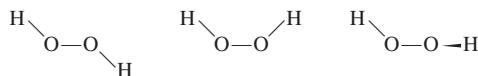
All three species have 10 electrons. Na^+ has the most positive nucleus (11 protons) and, therefore, the smallest size; O^{2-} has the least positive nucleus (8 protons) and, therefore, the largest size.



PP13.5 The third ionization, which breaks the octet of electrons in the third shell.



PP13.10 The hydrogen-oxygen-oxygen angle is about 108° , nearly the tetrahedral angle. The hydrogen atoms can rotate about the oxygen-oxygen bond to form different conformations, for example:



(a) Cl_2	Nonpolar	No dipole
(b) NF_3	Polar	Dipole
(c) BrF	Polar	Dipole
(d) BCl_3	Polar	No dipole
(e) BeH_2	Polar	No dipole

The molecules of BCl_3 and BeH_2 are symmetric, so the effects of the polar bonds cancel out. In NF_3 , the polar bonds do not balance one another. In diatomic molecules, such as Cl_2 and BrF , a polar bond always results in a polar molecule, and a nonpolar bond yields a nonpolar molecule.

PP13.12 Hydrogen, which has the least mass and the fewest electrons

PP13.14 (a) through (c) All three form hydrogen bonds.

14 Solids and Liquids, Energies of Physical and Chemical Changes

PP14.1 (a) Molecular (b) Ionic (c) Macromolecular

PP14.3 $(2.5 \times 10^5)^3 = 1.6 \times 10^{16} \text{ I}_2 \text{ molecules}$

This number of molecules contains $3.2 \times 10^{16} \text{ I atoms}$.

PP14.4 Because molecular solids have relatively weak intermolecular forces, the molecular solid must be the one with the melting point of 90°C .

APPENDIX 4 ■ Answers to Practice Problems

PP14.5 Heat = $mc\Delta t$

$$128 \text{ J} = (4.00 \text{ g})(c)(15.3^\circ\text{C})$$

$$c = \frac{128 \text{ J}}{(4.00 \text{ g})(15.3^\circ\text{C})} = 2.09 \text{ J/g}\cdot^\circ\text{C}$$

PP14.7 Heat = $(123 \text{ g})(0.442 \text{ J/g}\cdot^\circ\text{C})(16.4^\circ\text{C}) = 892 \text{ J}$

Heating the iron takes much less energy because its heat capacity is so much lower.

PP14.10 $0 = m_{\text{metal}}c_{\text{metal}}\Delta t_{\text{metal}} + m_{\text{water}}c_{\text{water}}\Delta t_{\text{water}}$

$$(186 \text{ g})(c_{\text{metal}})(26.4^\circ\text{C} - 74.0^\circ\text{C}) = -(251 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(26.4^\circ\text{C} - 18.0^\circ\text{C})$$

$$c_{\text{metal}}(186 \text{ g})(-47.6^\circ\text{C}) = -8.82 \times 10^3 \text{ J}$$

$$c_{\text{metal}} = 1.0 \text{ J/g}\cdot^\circ\text{C}$$

The metal is magnesium.

PP14.11 $0 = m_{\text{metal}}c_{\text{metal}}\Delta t_{\text{metal}} + m_{\text{water}}c_{\text{water}}\Delta t_{\text{water}}$

$$0 = (11.3 \text{ g})(0.44 \text{ J/g}\cdot^\circ\text{C})(t_f - 60.0^\circ\text{C}) + (97.2 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(t_f - 19.0^\circ\text{C})$$

$$4.97t_f - 298^\circ\text{C} + 406.7t_f - 7727^\circ\text{C} = 0$$

$$411.7t_f = 8025^\circ\text{C}$$

$$t_f = 19.5^\circ\text{C}$$

PP14.12 $16.4 \text{ g}(2260 \text{ J/g}) = 3.71 \times 10^4 \text{ J} = 37.1 \text{ kJ}$

The heat required to vaporize water is much greater than that required to melt the same mass of ice.

PP14.13 For cooling the liquid water to 0°C :

$$\text{Heat} = (40.0 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(0.0^\circ\text{C} - 14.4^\circ\text{C}) = -2410 \text{ J}$$

To freeze the water:

$$\text{Heat} = 40.0 \text{ g}(-335 \text{ J/g}) = -13,400 \text{ J}$$

For cooling the ice:

$$\text{Heat} = (40.0 \text{ g})(2.089 \text{ J/g}\cdot^\circ\text{C})(-16.3^\circ\text{C} - 0.0^\circ\text{C}) = -1362 \text{ J}$$

$$\text{Total heat} = -2410 \text{ J} + (-13,400 \text{ J}) + (-1362 \text{ J}) = -17,200 \text{ J}$$

In each process, the minus sign indicates that heat is being removed.

PP14.15 Heat = $(5650 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(16.5^\circ\text{C}) = 390,000 \text{ J} = 390.0 \text{ kJ}$

Because 390.0 kJ was added to the water, the heat of the reaction is -390 kJ .

PP14.16 $\text{C}_7\text{H}_{16}(\ell) + 11 \text{ O}_2(g) \rightarrow 7 \text{ CO}_2(g) + 8 \text{ H}_2\text{O}(\ell)$

$$\Delta H = 7 \Delta H_f(\text{CO}_2) + 8 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_7\text{H}_{16}) = 7(-393.5 \text{ kJ}) + 8(-285.9 \text{ kJ}) - (-187 \text{ kJ}) = -4855 \text{ kJ}$$

PP14.17 For the products:

$$\Delta H_f = 4 \text{ mol CO} \left(\frac{-110 \text{ kJ}}{1 \text{ mol CO}} \right) + 5 \text{ mol H}_2\text{O} \left(\frac{-286 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \right) = -1870 \text{ kJ}$$

For the reactants:

$$\Delta H_f = 1 \text{ mol C}_4\text{H}_{10} \left(\frac{-126 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} \right) = -126 \text{ kJ}$$

$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

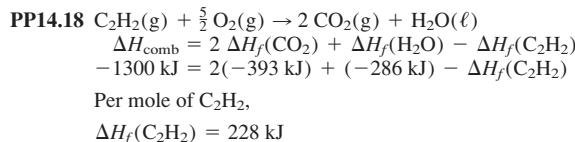
$$= (-1870 \text{ kJ}) - (-126 \text{ kJ})$$

$$= -1740 \text{ kJ}$$

For 1.00 mol, the answer is the same within limits of significant digits.

APPENDIX 4 ■ Answers to Practice Problems

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PP14.19 Adding the three equations given yields the desired equation, so we merely add the three ΔH values, yielding -13.4 kJ .

15 Solutions

PP15.1 A hydrogen-bonding solvent. (Hydrogen-bonding solvents are also polar.)

PP15.2 (a) The solution would be unsaturated in that case because it would be holding less solute (161 g) than is stable at 100°C (170 g).

(b) Not all of the solute would dissolve in 90.0 g of water, and a heterogeneous mixture would still be present.

PP15.3 $46.6 \text{ g H}_2\text{O} \left(\frac{3.00 \text{ g NaCl}}{97.00 \text{ g H}_2\text{O}} \right) = 1.44 \text{ g NaCl}$

PP15.5 $25.0 \text{ g stock} \left(\frac{3.00 \text{ g solute}}{100.0 \text{ g stock}} \right) = 0.750 \text{ g solute}$

$$0.750 \text{ g solute} \left(\frac{100.0 \text{ g solution}}{0.650 \text{ g solute}} \right) = 115 \text{ g solution}$$

PP15.7 $28.2 \text{ g C}_3\text{H}_7\text{OH} \left(\frac{1.00 \text{ mol C}_3\text{H}_7\text{OH}}{60.0 \text{ g C}_3\text{H}_7\text{OH}} \right) = 0.470 \text{ mol C}_3\text{H}_7\text{OH}$

$$207 \text{ mL H}_2\text{O} \left(\frac{1.00 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.207 \text{ kg H}_2\text{O}$$

$$\frac{0.470 \text{ mol}}{0.207 \text{ kg}} = 2.27 \text{ m}$$

PP15.9 $239 \text{ g H}_2\text{O} \left(\frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}} \right) \left(\frac{5.13 \text{ mol HClO}_4}{1 \text{ kg H}_2\text{O}} \right) \times \left(\frac{100.5 \text{ g HClO}_4}{1 \text{ mol HClO}_4} \right) = 123 \text{ g HClO}_4$

PP15.10 $14.7 \text{ g C}_2\text{H}_4\text{O} \left(\frac{1 \text{ mol C}_2\text{H}_4\text{O}}{44.0 \text{ g C}_2\text{H}_4\text{O}} \right) \left(\frac{1 \text{ kg H}_2\text{O}}{1.68 \text{ mol C}_2\text{H}_4\text{O}} \right) \times \left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) = 199 \text{ g H}_2\text{O}$

PP15.11 $1.34 \text{ kg} \left(\frac{0.512 \text{ mol}}{1 \text{ kg}} \right) = 0.686 \text{ mol solute}$

$$2.13 \text{ kg} \left(\frac{0.216 \text{ mol}}{1 \text{ kg}} \right) = 0.460 \text{ mol solute}$$

$$\text{Total} = 1.1462 \text{ mol solute}$$

$$\text{Total mass of solvent} = 1.34 \text{ kg} + 2.13 \text{ kg} = 3.47 \text{ kg}$$

$$\text{Molality} = \frac{1.1462 \text{ mol}}{3.47 \text{ kg}} = 0.330 \text{ m}$$

PP15.12 $10.00 \text{ g CH}_2\text{O} \left(\frac{1 \text{ mol CH}_2\text{O}}{30.0 \text{ g CH}_2\text{O}} \right) = 0.3333 \text{ mol CH}_2\text{O}$

$$10.00 \text{ g C}_3\text{H}_7\text{OH} \left(\frac{1 \text{ mol C}_3\text{H}_7\text{OH}}{60.0 \text{ g C}_3\text{H}_7\text{OH}} \right) = 0.1667 \text{ mol C}_3\text{H}_7\text{OH}$$

$$X_{\text{CH}_2\text{O}} = \frac{0.3333 \text{ mol}}{0.3333 \text{ mol} + 0.1667 \text{ mol}} = 0.667$$

$$X_{\text{C}_3\text{H}_7\text{OH}} = \frac{0.1667 \text{ mol}}{0.3333 \text{ mol} + 0.1667 \text{ mol}} = 0.333$$

$$\text{Check: } 0.667 + 0.333 = 1.000$$

PP15.13 Neither substance is necessarily regarded as the solute or the solvent.

PP15.14 Assume 1.00 kg of water. Then we have $1.27 \text{ mol CH}_3\text{OH}$ and

$$1000 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 55.56 \text{ mol H}_2\text{O}$$

$$X_{\text{CH}_3\text{OH}} = \frac{1.27}{1.27 + 55.56} = 0.0223$$

PP15.15 $P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^{\circ} = (0.820)(123 \text{ torr}) = 101 \text{ torr}$

PP15.17 $P_{\text{CHCl}_3} = P_{\text{CHCl}_3}^{\circ} X_{\text{CHCl}_3} = (160 \text{ torr})(0.402) = 64.32 \text{ torr}$

$$P_{\text{CCl}_4} = 111 \text{ torr} - 64.32 \text{ torr} = 46.7 \text{ torr} = 0.598 P_{\text{CCl}_4}^{\circ}$$

$$P_{\text{CCl}_4}^{\circ} = 78 \text{ torr}$$

PP15.18 The mole fraction of CHCl_3 in the vapor phase is 0.800 , so that of CCl_4 is 0.200 . Their numbers of moles of vapor must be in the same ratio, and thus their pressures also.

$$P_{\text{CHCl}_3} = 0.800(215 \text{ torr}) = 172 \text{ torr}$$

$$P_{\text{CCl}_4} = 0.200(215 \text{ torr}) = 43.0 \text{ torr}$$

The vapor pressures are calculated using these pressures plus the mole fractions in the liquid phase:

$$P_{\text{CHCl}_3} = P_{\text{CHCl}_3}^{\circ} X_{\text{CHCl}_3} = 172 \text{ torr} = P_{\text{CHCl}_3}^{\circ}(0.700)$$

$$P_{\text{CCl}_4} = P_{\text{CCl}_4}^{\circ} X_{\text{CCl}_4} = 43.0 \text{ torr} = P_{\text{CCl}_4}^{\circ}(0.300)$$

$$P_{\text{CHCl}_3}^{\circ} = 246 \text{ torr}$$

$$P_{\text{CCl}_4}^{\circ} = 143 \text{ torr}$$

PP15.19 We get the value of k_f for *naphthalene* from Table 15.2:

$$\Delta t_f = k_f m = (6.85^\circ\text{C/m})(0.250 \text{ m}) = 1.713^\circ\text{C}$$

The freezing point is lowered from 80.22°C by 1.713°C , so the freezing point of the solution is

$$80.22^\circ\text{C} - 1.713^\circ\text{C} = 78.51^\circ\text{C}$$

PP15.21 Ethylene glycol is nonvolatile and nonionic. We get the value of k_b for water from Table 15.3:

$$\Delta t_b = k_b m = (0.512^\circ\text{C/m})(0.650 \text{ m}) = 0.333^\circ\text{C}$$

PP15.22 $\Delta t_b = k_b m = (2.53^\circ\text{C/m})(0.650 \text{ m}) = 1.645^\circ\text{C}$

$$t_b = 80.1^\circ\text{C} + 1.645^\circ\text{C} = 81.7^\circ\text{C}$$

PP15.23 $\pi V = nRT$

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{(68.3 \text{ torr})(1 \text{ atm}/760 \text{ torr})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} = 0.00367 \text{ mol/L}$$

16 Oxidation Numbers

PP16.1 Let x represent the oxidation number of carbon:

$$x + (-2) = 0$$

$$x = +2$$

PP16.3 $x + 3(-2) = -2$

$$x = +4$$

PP16.4 $2x + 7(-2) = -2$

$$x = +6$$

PP16.5 (a and c) +1 (as in all hydrogen compounds except metallic hydrides)

(b) -1 (This compound is a metallic hydride.)

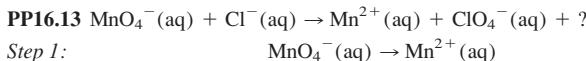
PP16.7 Zero (Metals do not normally have negative oxidation numbers.)

PP16.8 +2, +1, 0

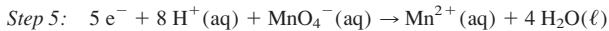
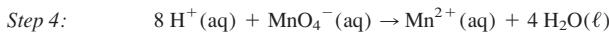
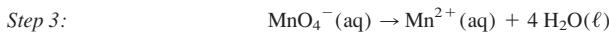
PP16.9 +7, +5, +3, +1 (in steps of 2)

PP16.12 I^- is a good enough reducing agent to reduce Cu^{2+} to copper(I); Cl^- is not.

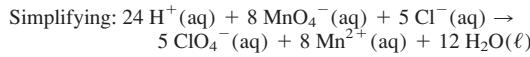
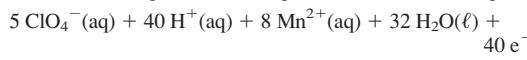
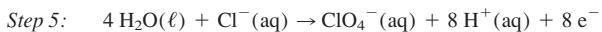
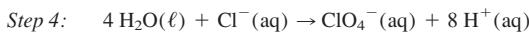
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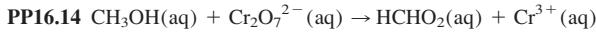
Step 2: No change.



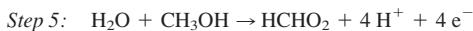
Step 2: No change.



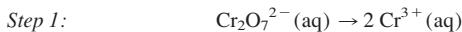
Step 8: 24 H, 8 Mn, 32 O, 5 Cl, 11 net positive charges on each side



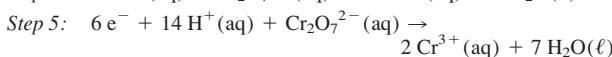
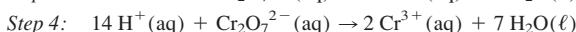
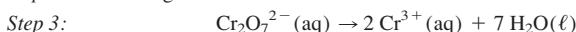
Step 2: No change.



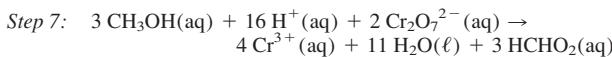
Step 6: 1 C, 6 H, 2 O, zero net charge, change in oxidation number 4 (C from -2 to +2).



Step 2: No change.



Step 6: 14 H, 2 Cr, 7 O, net charge 6+, change in oxidation number -6.



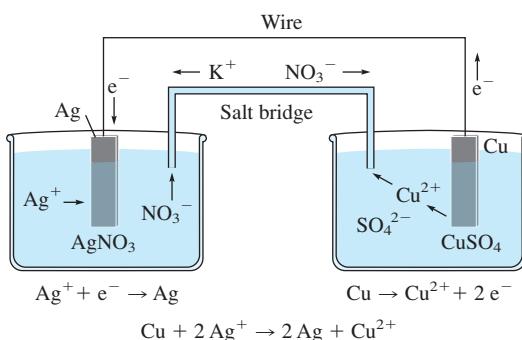
Step 8: 3 C, 28 H, 4 Cr, 17 O, 12 positive net charge on each side.

PP16.15 Both the oxidizing agent and the reducing agent are H_2O_2 . The H_2O_2 disproportionates according to the equation



17 Electrochemistry

PP17.1

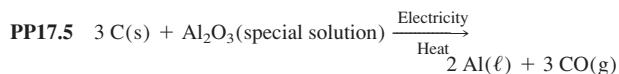


APPENDIX 4 ■ Answers to Practice Problems

$$\text{PP17.3} \quad \varepsilon = \varepsilon^\circ - \frac{0.0592}{n} \log \frac{1}{[\text{Ag}^+]} \\ = 0.80 - 0.0592 \log \frac{1}{(0.100)} = 0.74 \text{ V}$$

$$\text{PP17.4} \quad \varepsilon^\circ = +0.34 \text{ V} + (+0.13 \text{ V}) = 0.47 \text{ V} \\ \varepsilon = \varepsilon^\circ - \frac{0.0592}{n} \log \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]} \\ = 0.47 - \frac{0.0592}{2} \log \frac{(0.100)}{(0.200)} = 0.48 \text{ V}$$

Since ε is positive, Cu is reduced.



$$\text{PP17.6} \quad 3.00 \text{ h} \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \left(\frac{10.0 \text{ C}}{1 \text{ s}} \right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \times \\ \left(\frac{1 \text{ mol Ag}}{1 \text{ mol e}^-} \right) \left(\frac{108 \text{ g Ag}}{1 \text{ mol Ag}} \right) = 121 \text{ g Ag}$$

$$\text{PP17.7} \quad 1.00 \times 10^6 \text{ g Al} \left(\frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \right) \left(\frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1 \text{ s}}{500 \text{ C}} \right) \\ = 2.14 \times 10^7 \text{ s} = 248 \text{ days}$$

18 Chemical Equilibrium

PP18.1 The equilibrium will shift to the right to use up some of the added H_2O .

PP18.3 The equilibrium will shift to the left to use up some nitrogen.

$$\text{PP18.10} \quad K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

$$\text{PP18.11} \quad (\text{a}) \quad K = \frac{[\text{N}_2\text{O}]^2}{[\text{N}_2]^2 [\text{O}_2]} \quad (\text{b}) \quad K = \frac{[\text{N}_2\text{O}]}{[\text{N}_2][\text{O}_2]^{1/2}}$$

The constant in part (b) is the square root of the one in part (a).

PP18.14



Initial: 0.0150 0.00750 0.00000

Change: -0.00760 -0.00380 +0.00760

Equilibrium: 0.0074 0.00370 0.00760

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(0.00760)^2}{(0.0074)^2 (0.0037)} = 2.85 \times 10^2$$

The equilibrium concentrations are the same as in Example 18.14, and the value of K is the reciprocal of that in the example because the equation is written in the opposite direction.

PP18.17



Initial: 0.200 0.200 0.000

Change: $-2x$ $+2x$ $+x$

Equilibrium: $0.200 - 2x$ $0.200 + 2x$ x

$$K = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = 9.3 \times 10^{-8}$$

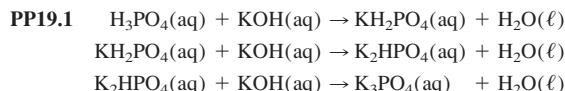
$$= \frac{(0.200)^2 (x)}{(0.200)^2} = 9.3 \times 10^{-8} = x$$

The initial concentration of H_2 has affected the equilibrium concentration of S_2 markedly.

APPENDIX 4 ■ Answers to Practice Problems

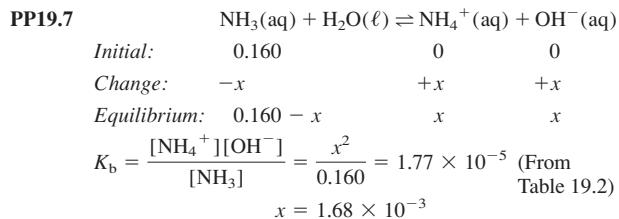
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19 Acid-Base Theory



The acid salts are acids, but hydrogen is written first only in the formula of the anion, not in that of the compound as a whole.

- PP19.2** (a) The perchlorate ion, the conjugate of a strong acid, is a feeble base; it does not react with water at all. (b) The carbonate ion is the conjugate of a weak acid and is weak.



The hydroxide ion concentration is 1.68×10^{-3} M.

- PP19.9** (a) HCl is a strong acid, so $[\text{H}_3\text{O}^+]$ is 0.0050 M. To find the hydroxide ion concentration, use the K_w expression:
 $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (0.0050)[\text{OH}^-] = 1.0 \times 10^{-14}$
Thus, $[\text{OH}^-] = 2.0 \times 10^{-12}$ M.
(b) NaOH is a strong, soluble base, so 0.0050 M NaOH is actually 0.0050 M Na^+ and 0.0050 M OH^- .

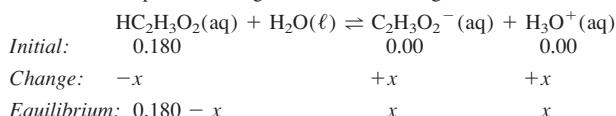
PP19.10 9.68×10^{-13} M

PP19.12 $\text{pH} = 9.44 = -\log[\text{H}_3\text{O}^-]$

Changing the sign of 9.44 and taking the antilogarithm yields the hydronium ion concentration, 3.6×10^{-10} M.

PP19.13 The pH is 7.00 because the solution is neutral.

- PP19.14** The initial concentration of acetic acid (before reaction) is 0.180 M. After it reacts with water, its concentration and those of its products are given in the following table:



The equilibrium constant expression and the value of K_a can be used to solve for x:

$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.180 - x} = 1.76 \times 10^{-5}$$

Ignoring x when it is subtracted from 0.180 yields

$$x^2 = 3.168 \times 10^{-6}$$

Taking the square root of both sides yields

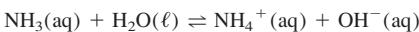
$$x = 1.78 \times 10^{-3}$$

Because $[\text{H}_3\text{O}^+] = 1.78 \times 10^{-3}$ M,

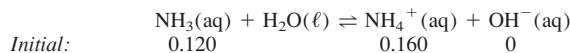
$$\text{pH} = 2.750$$

- PP19.16** A strong base is completely ionized, and its cation has no tendency to react. Any additional hydroxide ion added to this solution cannot react with the cation and thus have its concentration reduced.

- PP19.17** The base ionizes according to the equation



The ammonium chloride is a salt, so the NH_4^+ is initially 0.160 M. The ammonium ion affects the position of the equilibrium:



Ignoring x when added to or subtracted from larger quantities and using the value of K_b from Table 19.2 yields:

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{(x)(0.160)}{0.120} = 1.77 \times 10^{-5}$$

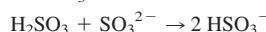
$$x = 1.33 \times 10^{-5}$$

$$[\text{OH}^-] = 1.33 \times 10^{-5}$$
 M

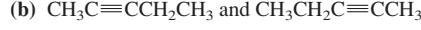
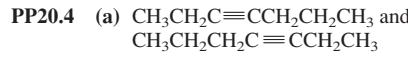
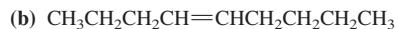
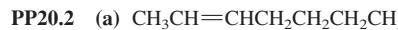
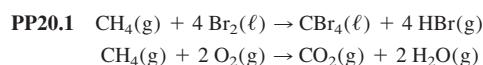
The approximations made by ignoring x when added to 0.160 or subtracted from 0.120 are valid.

- PP19.21** It is the only source of S^{2-} .

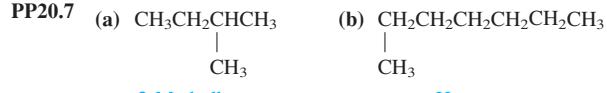
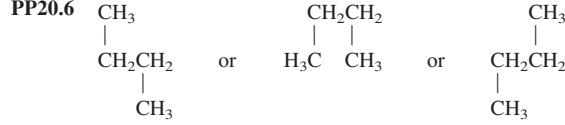
- PP19.23** NaHSO_3



20 Organic Chemistry



- PP20.5** Four. There are two chlorine atoms (as can be seen from the prefix *di-*), leaving four positions on the six carbon atoms of benzene for hydrogen atoms.



2-Methylbutane

Heptane

The methyl group is attached to the carbon atom that is third from the left but *second* from the right. The compound's name is 2-methylbutane.

If the methyl group is attached to the first carbon atom, the longest continuous chain of carbon atoms includes the methyl group. The compound's name is heptane.



1 2 3 4 5 6 7



1-Bromopropane

2-Bromopropane



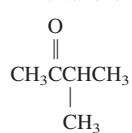
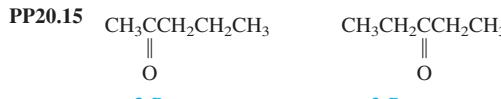
- PP20.12** The nine- and ten-carbon radicals are called nonyl and decyl, respectively.



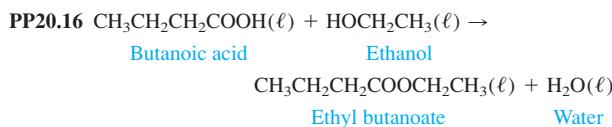
- PP20.14** (a) Ethers, as stated in the problem.

- (b) Ethers and alcohols.

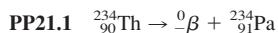
On exams, read the problem carefully.

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3-Methyl-2-butanone



PP20.17 (a) None (b) Polypropylene

21 Nuclear Reactions

PP21.3 $231 = 4(57) + 3 = 4n + 3$

Thus ${}^{231}\text{Th}$ is a member of the $4n + 3$ series.

PP21.4 ${}_{93}^{237}\text{Np}$ loses $237 - 209 = 28$ amu in the change to ${}_{83}^{209}\text{Bi}$. Because emissions of beta and gamma particles do not change the mass number, there must be $28/4 = 7$ alpha particles emitted.

PP21.5 The atomic number changes by ten units, from ${}_{93}^{237}\text{Np}$ to ${}_{83}^{209}\text{Bi}$. The emission of seven alpha particles (Practice Problem 21.4) lowers the atomic number by 14, so four beta particles must be emitted to reduce the atomic number by only 10 units:

$$\text{Change in atomic number} = -7(2) + (-4)(-1) = -10$$

PP21.7 If seven-eighths of the sample disintegrates, one-eighth remains. This is essentially the same problem as Example 21.7, in which one-eighth of the 60.0-g sample remains. The answer is 17,190 years.

PP21.9 $\ln\left(\frac{N_o}{N}\right) = \frac{0.693t}{t_{1/2}}$

$$\ln\left(\frac{N_o}{N_o/5}\right) = \frac{0.693t}{6.79 \text{ y}} = \ln(5)$$

$$1.6094 = \frac{0.693t}{6.79 \text{ y}}$$

$$t = 15.8 \text{ y}$$

PP21.10 (a) $\ln\left(\frac{N_o}{N}\right) = \frac{0.693t}{t_{1/2}}$

$$\ln\left(\frac{1.77 \times 10^{15}}{5.59 \times 10^{14}}\right) = \frac{0.693t}{47.2 \text{ y}}$$

$$1.1526 = \frac{0.693t}{47.2 \text{ y}}$$

$$t = 78.5 \text{ y}$$

(b) $\ln\left(\frac{N_o}{1.77 \times 10^{15}}\right) = \frac{(0.693)(112 \text{ y})}{47.2 \text{ y}}$

$$\left(\frac{N_o}{1.77 \times 10^{15}}\right) = 5.1779$$

$$N_o = 9.16 \times 10^{15} \text{ atoms}$$

PP21.11 0.937 year. The ratio of masses is equal to the ratio of activities, so this is the same problem as Example 21.11.

PP21.13 The total number of atoms at time zero (when the rock solidified) was

$$2.57 \times 10^{17} + 7.71 \times 10^{17} = 1.028 \times 10^{18}$$

$$\frac{2.57 \times 10^{17}}{1.028 \times 10^{18}} = 0.250 = \frac{1}{4}$$

It takes two half-lives, or $2(1.3 \times 10^9 \text{ years}) = 2.6 \times 10^9 \text{ years}$.

PP21.14 Because the mass numbers are the same, the masses of the isotopes are approximately the same, and the mass ratio is nearly equal to the ratio of numbers of atoms. Half of the ${}_{19}^{40}\text{K}$ atoms have therefore disintegrated, and the age of the rock is equal to the half-life of that isotope, which is $1.3 \times 10^9 \text{ years}$.

PP21.15 $\frac{22,900 \text{ years}}{5730 \text{ years}} = 4 \text{ half-lives}$

The sample thus disintegrated to one-sixteenth its original rate.

$$\begin{array}{ccccc} 15.3 \text{ dis/min}\cdot\text{g} & \xrightarrow[1]{>} & 7.65 \text{ dis/min}\cdot\text{g} & \xrightarrow[2]{>} & 3.825 \text{ dis/min}\cdot\text{g} \\ & & & & \\ & & & \xrightarrow[3]{>} & 1.9125 \text{ dis/min}\cdot\text{g} & \xrightarrow[4]{>} & 0.956 \text{ dis/min}\cdot\text{g} \end{array}$$

PP21.16 $2^{20} = 1.05 \times 10^6$ neutrons = 1.05 million neutrons

Appendix 1

PPA.6 (a) dollars/dozen (b) dollars/qt

PPA.9 $\frac{13.5 \text{ m/s}}{0.300 \text{ s}} = 45.0 \text{ m/s}^2$

PPA.13 (a) $\varepsilon = +0.074$

(b) $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(6.9 \times 10^{-6}) = 5.16$

Appendix 5**Answers to Selected
End-of-Chapter
Problems****1 Basic Concepts**

- 1.1** Organic chemistry
- 1.2** No. All chemists use all of the branches of chemistry in their work.
- 1.3** (a) Matter (b) Energy
(c) Matter (d) Energy
- 1.4** Heterogeneous mixtures
- 1.5** Buy the least expensive brand, if it is pure aspirin.
- 1.6** Freezing point (melting point)
- 1.7** The list is extensive. The following is a short sample: Metallic luster, fairly good conductor of heat, fairly good conductor of electricity, strong, somewhat malleable, high melting point, resists rusting. Of these, the resistance to rusting is the chemical property.
- 1.8** Steel does not shatter the way glass does. Glass is more brittle than steel.
- 1.9** (a) 2 and 1. HF has hydrogen and fluorine; Hf is hafnium.
(b) 1 and 2. No is nobelium; NO has nitrogen and oxygen.
(c) 1 and 2. Si is silicon; SI₂ has sulfur and iodine.
(d) 2 and 3. PoCl₂ has polonium and chlorine; POCl₃ has phosphorus, oxygen, and chlorine.
(e) 3
(f) 3
- 1.10** C, Cu, and Cr are already used—for carbon, copper, and chromium, respectively.
- 1.13** (a) IA (b) IIA (c) IB (d) VIIA
(e) 0
- 1.14** Group VIII has nine elements (not counting the artificial elements above 103); the others have three or four each.
- 1.15** Main group elements
- 1.16** Elements in the same group have similar chemical properties.
- 1.17** The main groups have five to seven elements each, and the typical transition group has only three or four.
- 1.18** (a) Group VIA (16) (b) Third period
(c) A main group element
- 1.19** (e)
- 1.21** (a) Physical (b) Chemical
- 1.22** (a) and (b) Physical change
- 1.24** A chemical change, which is more apt to generate heat
- 1.25** (a) Compound (b) Cannot tell
(c) Mixture (d) Mixture
(e) Mixture
- 1.27** It is a compound, which has its own set of properties, as evidenced by the very high melting point.

- 1.28** (a) Element
(b) Compound (a combination with its own set of properties)
(c) Mixture (solution)
- 1.30** (a) Heterogeneous (b) Heterogeneous
(c) Homogeneous (d) Heterogeneous
(e) Homogeneous (f) Homogeneous
(g) Heterogeneous
- 1.31** It is a compound because it can be decomposed into simpler substances. We know that the products are simpler because each is only *part* of the original sample; each has less mass.
- 1.33** (a) Extensive (b) Intensive (c) Intensive
(d) Extensive (e) Extensive (f) Extensive
(g) Intensive (h) Intensive
- 1.36** Iron is heavier (for a given volume), magnetic, rusts more easily, is less easily bent, and is less shiny than aluminum, among many other differences. The rusting is a chemical property.
- 1.38** A solution (Different parts have different properties.)
- 1.40** Striking a match is one example.
- 1.43** 100 kg (Mass does not change with location.)
- 1.44** We use batteries for their portability and convenience and as backups in case of power outages.
- 1.46** None (Energy is changed from chemical to heat.)
- 1.47** Chemical energy to electric energy to light
- 1.48** One example of each is given.
(a) Battery (b) Horn (c) Brakes
(d) Battery (e) Engine (f) Starter
(g) Rear window defogger
- 1.50** $\frac{9}{109} \times 100\% = 8.26\%$
- 1.51** (a) Three (b) Two (c) Two (d) Four
(e) Two (f) One (g) Two
- 1.58** (a) V and As (b) N
- 1.59** Hydrogen
- 1.60** Phosphorus
- 1.61** Vanadium is a typical metal; it is on the left, far from the metal-nonmetal dividing line in the periodic table.
- 1.65** As₂O₅ (P and As are in the same periodic group, so their compounds are expected to have similar formulas.)
- 1.68** (a) Four (Cd, Cr, Co, Cu) (b) Two (Pd, Pt)
- 1.70** Theory
- 1.71** No (It violates the law of conservation of mass.)
- 1.73** (a) Analytical chemistry (b) Physical chemistry
(c) Biochemistry

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1.77 (a) Green (b) No (c) A solution retains the properties of its components, and blue plus yellow yields green. A compound has a set of properties all its own, and its color cannot be predicted from those of its elements.

1.78 (a) The statement implies that oil and water do not form a homogeneous mixture (solution) when mixed. Any substances can be mixed. A drop of oil placed in a cup of water will float on the water surface. The oil from a tanker spilled on an ocean will also float; getting the oil collected or dissolved is a major project that is too often necessary in the modern world.
 (b) The statement means that one should never drive a car after having drunk an alcoholic beverage. People who "mix" gasoline and alcohol imperil their own lives and those of others who use the highways. The statement has nothing to do with the physical mixing of the liquids.

1.79 The minerals required for human health are generally eaten in the form of their compounds, not in elemental form. The patient should eat foods containing compounds of iron but refrain from eating foods containing too much sodium in compounds.

	Total Number	Important	Percent
Main group	44	40	91
Transition	37	17	46
Inner transition	28	1	3.6
Totals	109	58	53

(b) Main groups, then transition groups

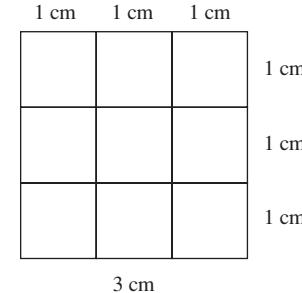
2 Measurement

- 2.1** (a) The cost is a quantity.
 (b) The amount of pay is a quantity.
 (c) The number of hours worked is a quantity.
 (d) The price is a ratio.
 (e) The minimum wage is a rate—a ratio of dollars to hours.
- 2.2** (a) The final answer is the same as the original value.
 (b) The format of the exponential number is changed, but its value is unchanged.
- 2.3** The answer is 2.
- 2.4** (a) 6×10^{-3} (b) 4.2×10^6
 (c) 1.95×10^{11} (d) 1.23×10^7
 (e) 1.1×10^4 (f) 1.7×10^{-5}
- 2.5** The answer is 2. Be sure to *divide* by the 9 in the denominator.
- 2.6** Values less than zero: (a) and (d); magnitudes less than one: (a) and (b); values less than one: (a), (b), and (d)
- 2.7** (a) 10^3 (b) 10^{-2} (c) 10^{-3}
 The appropriate exponential part may replace a metric prefix. For example,
 $3 \text{ mm} = 3 \times 10^{-3} \text{ m}$
 The m- for milli- has been replaced by " $\times 10^{-3}$ ".
- 2.8** (a) The dollar is bigger, so it would take more cents to buy any given purchase.
 (b) The meter is bigger, so it would take more centimeters to measure any given length.
- 2.9** The kilogram is bigger, so there are more milligrams in any given mass.
- 2.10** $7 \text{ mg} = 7 \text{ milligrams} = 0.007 \text{ g}$
 $7 \text{ Mg} = 7 \text{ megagrams} = 7,000,000 \text{ g}$
 Be very careful to use the standard abbreviations for units!
- 2.11** All the units containing the unit *liter* or the *cube* of any *meter* unit are units of volume: L (liter), m^3 (cubic meter), mm^3 (cubic millimeter), and mL (milliliter).
- 2.12** (c) Saint Bernard dog

2.13 The measurements are 171 cm, 64 kg, 4 L.

2.14 $\frac{1 \text{ kg}}{1000 \text{ g}}$ or $\frac{0.001 \text{ kg}}{1 \text{ g}}$

2.15 (a) There are 9 cm^2 in the square, as shown in the accompanying figure.
 $(3.0 \text{ cm})^2 = (3 \text{ cm})(3 \text{ cm}) = 9 \text{ cm}^2$



(b) $(3.0 \text{ cm})^3 = 27 \text{ cm}^3$

2.16 (a) 0.5 km

2.17 There are probably one significant digit in 7 million people and nine in \$7,000,000.00.

2.18 There are 1000 divisions in 1 m, so each division is 1 mm.

2.20 There is no essential difference. (There is not even any difference in the number of significant digits because all the quantities have three significant digits.)

- 2.21** (a) If we add more black coffee (or water or cream), the concentration of the sugar and therefore the sweetness is reduced.
 (b) If the company reduces the mass of the coffee in the can without changing the cost of a can, the price effectively goes up.
 (c) If the time for a trip remains unchanged but less distance is covered, the speed has gone down.

Each of these processes from everyday life shows that the value of a ratio can be changed by changing either its numerator or its denominator (or both).

(d) The density is lowered.

2.22 $5.150 \text{ h} \left(\frac{60 \text{ min}}{1 \text{ h}} \right) = 309.0 \text{ min}$

2.23 (a) $2.50 \text{ dozen} \left(\frac{5.00 \text{ dollars}}{1 \text{ dozen}} \right) = 12.50 \text{ dollars}$

(b) $32.50 \text{ dollars} \left(\frac{1 \text{ dozen}}{5.00 \text{ dollars}} \right) = 6.50 \text{ dozen}$

(c) $6.50 \text{ dozen} \left(\frac{12 \text{ donuts}}{1 \text{ dozen}} \right) = 78 \text{ donuts}$

2.25 $32 \text{ weeks} \left(\frac{18 \text{ h}}{1 \text{ week}} \right) \left(\frac{9.00 \text{ dollars}}{1 \text{ h}} \right) = 5184 \text{ dollars}$

2.27 The percentage of sulfur is $100.0\% - 60.0\% = 40.0\%$. The mass of sulfur is

$$14.6 \text{ g compound} \left(\frac{40.0 \text{ g sulfur}}{100 \text{ g compound}} \right) = 5.84 \text{ g sulfur}$$

2.29 We can change each length to yards first, then multiply:

$$15.3 \text{ ft} \left(\frac{1 \text{ yd}}{3 \text{ ft}} \right) = 5.10 \text{ yd} \quad 18.3 \text{ ft} \left(\frac{1 \text{ yd}}{3 \text{ ft}} \right) = 6.10 \text{ yd}$$

$$5.10 \text{ yd} \times 6.10 \text{ yd} = 31.11 \text{ yd}^2$$

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Alternatively, we can multiply the lengths together first and then change the square feet to square yards:

$$15.3 \text{ ft} \times 18.3 \text{ ft} = 280.0 \text{ ft}^2$$

$$280.0 \text{ ft}^2 \left(\frac{1 \text{ yd}}{3 \text{ ft}} \right)^2 = 31.11 \text{ yd}^2$$

Note that in each method we divide by 3 *twice*.

$$31.11 \text{ yd}^2 \left(\frac{29.00 \text{ dollars}}{1 \text{ yd}^2} \right) = 902 \text{ dollars}$$

- 2.30** (c), (e), and (f) are in standard exponential notation. (a) has a fractional exponent, and (b) and (d) have coefficients above 10 or below 1.

2.31 (a) 6.21×10^2 (b) 1.033×10^{-1}
 (c) 1.00001×10^2 (d) 1.1×10^{-2}

2.34 (a) 1.6×10^0 (b) 4.02×10^3 (c) -1.8×10^{-4}
 (d) 1.8×10^6 (e) 2.5×10^6

2.35 $(0.70 \times 10^{-2}) - (-8.0 \times 10^{-2}) = 8.7 \times 10^{-2}$

2.36 (a) $6.21 \text{ g} \left(\frac{1 \text{ mg}}{0.001 \text{ g}} \right) = 6210 \text{ mg}$
 (b) $6.21 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 621 \text{ cm}$
 (c) $6.21 \text{ g} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.00621 \text{ kg}$

2.38 (a) $6.96 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 6960 \text{ mm}$
 (b) $6.96 \text{ L} \left(\frac{1 \text{ mL}}{0.001 \text{ L}} \right) = 6960 \text{ mL}$
 (c) $6.96 \text{ g} \left(\frac{1 \text{ mg}}{0.001 \text{ g}} \right) = 6960 \text{ mg}$
 (d) $6.96 \text{ W} \left(\frac{1 \text{ mW}}{0.001 \text{ W}} \right) = 6960 \text{ mW}$

(*Milli* means the same thing no matter what the units.)

2.39 (a) $21.3 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 2130 \text{ cm} = 2.13 \times 10^3 \text{ cm}$
 (b) $21.3 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 21,300 \text{ mm} = 2.13 \times 10^4 \text{ mm}$
 (c) $21.3 \text{ m} \left(\frac{1 \text{ km}}{1000 \text{ m}} \right) = 0.0213 \text{ km} = 2.13 \times 10^{-2} \text{ km}$

2.43 $0.0722 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 7.22 \text{ cm}$

$$7.013 \text{ mm} \left(\frac{0.001 \text{ m}}{1 \text{ mm}} \right) \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 0.7013 \text{ cm}$$

$$(7.22 \text{ cm})(3.39 \text{ cm})(0.7013 \text{ cm}) = 17.2 \text{ cm}^3$$

2.44 $l = \sqrt[3]{V} = \sqrt[3]{2.57 \text{ cm}^3} = 1.37 \text{ cm}$

- 2.46** (a) Swimming pool

2.49 $6.11 \times 10^{-2} \text{ m}^3 \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) = 61.1 \text{ L}$

2.51 $(6.22 \text{ cm})(7.15 \text{ cm})(5.60 \text{ cm}) = 249 \text{ cm}^3$

2.53 (a) $6.133 \times 10^2 \text{ cm}$ (b) $1.733 \times 10^2 \text{ cm}$
 (c) $2.02 \times 10^6 \text{ cm}$ (d) $6.191 \times 10^3 \text{ cm}$

2.55 (a) 67.00 km (b) 0.0013 kg
 (c) $\underline{\underline{690 \text{ m}}}$ (d) $\underline{\underline{209 \text{ L}}}$

- 2.56** All digits in the coefficient of a properly reported number in scientific notation are significant:

(a) $5.0 \times 10^2 \text{ cm}$ (b) $5.02 \times 10^2 \text{ cm}$
 (c) $7.00 \times 10^2 \text{ cm}$ (d) $5.000 \times 10^{-2} \text{ m}$

- 2.57** (a) 6000 cm (b) 6000 cm (c) 6000 cm
 (d) 6000 cm

- 2.58** (a) 7.00 mL (b) 7.0 mL (c) 7 mL

- 2.61** (a) 0.0637 cm (b) 0.637 cm (c) 6.37 cm
 (d) 63.7 cm (e) 6370 cm

- 2.63** (a) 23.0 cm^2 (b) -119.6 cm (c) 3.91 g/mL

	Significant digits	Decimal digits
(a) 0.020 kg	2	3
(b) 33.0 cm ³	3	1
(c) 403 mL	3	0
(d) 1.0 m	2	1

2.70 The measurements are 3.8 cm and 3.77 cm.

- 2.71** (a) 236 g (b) 6.12 mL (c) 1.115 mL
 (d) 104.1 km

- 2.72** (a) 111 mL (b) 1110 mL

(c) The answers are not the same. The answer in part (b) has a nonsignificant zero to properly express its magnitude.

- 2.76** (a) $2.0 \times 10^{-1} \text{ cm}$ (b) $7.44 \times 10^2 \text{ g}$

Each answer is the same as the larger of the two quantities added because the smaller value is too small to affect the last significant digit.

2.80 $\frac{2.79 \text{ g}}{37.95 \text{ mL}} = 0.074 \text{ g/mL}$

- 2.81** (a) $1.69 \times 10^5 \text{ cm}^2$ (b) $4.4 \times 10^{-11} \text{ m}^2$
 (c) $9.0 \times 10^{-4} \text{ kg/mL}$ (d) 14.50 g/L
 (e) $1.40 \times 10^8 \text{ cm}^2$ (f) 22.3 g

- 2.85** (a) Mass (b) Volume (c) Density

2.86 $4.415 \text{ kg} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mL}}{11.3 \text{ g}} \right) = 367 \text{ mL}$

2.88 $d = \frac{m}{V} = \frac{52.6 \text{ kg}}{7.05 \text{ L}} = 7.46 \text{ kg/L}$

2.90 Magnesium is less dense. Therefore, a given volume (needed to make the airplane) weighs much less. Aluminum is also useful.

2.92 $1213 \text{ g} \left(\frac{1 \text{ mL}}{13.6 \text{ g}} \right) = 89.2 \text{ mL}$

2.93 Yes, it is less dense.

2.95 $V = (12.2 \text{ cm})(3.05 \text{ cm})(1.43 \text{ cm}) = 53.21 \text{ cm}^3$

$$d = \frac{42.3 \text{ g}}{53.21 \text{ cm}^3} = 0.795 \text{ g/cm}^3$$

2.102 $3.55 \times 10^3 \text{ kg/m}^3$

- 2.104** (a) $(212^\circ\text{F} - 32^\circ\text{F}) \frac{5}{9} = 100^\circ\text{C}$ (b) 0°C
 (c) 16°C (d) 37.0°C (e) -18°C
 (f) -40.0°C (g) 1.7°C

- 2.105** (a) $0^\circ\text{C} \left(\frac{9}{5} \right) = 0^\circ$
 $0^\circ + 32^\circ = 32^\circ\text{F}$

- (b) 212°F (c) 80.6°F (d) 122.0°F
 (e) 5°F (f) 167°F (g) -459°F

- 2.106** (a) $25^\circ\text{C} + 273^\circ = 298 \text{ K}$

- (b) 292 K (c) 0 K (d) 315 K (e) 373 K

- 2.108** (a) $(13.53 \text{ cm}) \times (5.00 \text{ cm}) = 67.7 \text{ cm}^2$

- (b) $(1.37 \text{ cm}) \times (4.268 \text{ cm}) = 5.85 \text{ cm}^2$
 (c) 11.6 cm^2 (d) $3.89 \times 10^3 \text{ cm}^2$
 (e) $2.04 \times 10^4 \text{ cm}^2$ (f) 0.0711 cm^2

- 2.109** (a) 41 cm^2 (b) 94 cm^2 (c) 10.4 cm^2
 (d) $1.47 \times 10^7 \text{ cm}^2$ (e) $1.25 \times 10^6 \text{ cm}^3$
 (f) $1.45 \times 10^{-4} \text{ cm}^2$

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2.110 (a) $4.82 \text{ km} \left(\frac{1000 \text{ m}}{1 \text{ km}} \right) \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 4.82 \times 10^6 \text{ mm}$
 (b) $4.82 \times 10^{-3} \text{ m}^3$ (c) $4.82 \times 10^{-6} \text{ kg}$

2.115 $69.0 \text{ m} + 7.10 \text{ m} = 76.1 \text{ m}$

2.116 $6.90 \times 10^3 \text{ cm}$
 $(6900 \text{ cm} + 0.00710 \text{ cm} = 6900 \text{ cm})$

2.119 $7.440 \text{ kg} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ cm}^3}{19.3 \text{ g}} \right) = 385.5 \text{ cm}^3$
 $l = \sqrt[3]{V} = \sqrt[3]{385.5 \text{ cm}^3} = 7.28 \text{ cm}$

2.120 2.82 g/cm^3

2.122 They are the same. Because the size is the same and the mass is the same, the densities must be the same. That is, $2.82 \times 10^3 \text{ kg/m}^3 = 2.82 \text{ g/cm}^3$.

2.123 The volume of the box is $1.00 \text{ m}^3 = 1.00 \times 10^6 \text{ cm}^3$
 $1.00 \times 10^6 \text{ cm}^3 \left(\frac{1 \text{ particle}}{2.0 \times 10^{-22} \text{ cm}^3} \right) = 5.0 \times 10^{27} \text{ particles}$

2.124 1.75 g/mL

2.127 $8.87 \times 10^3 \text{ cm}^3$

2.129 $4.00 \text{ mL} \left(\frac{1 \text{ m}^3}{1 \times 10^6 \text{ mL}} \right) \left(\frac{1 \text{ particle}}{3.44 \times 10^{-28} \text{ m}^3} \right) = 1.16 \times 10^{22} \text{ particles}$

2.130 Addition and subtraction do not depend on the number of significant digits. Consider the following example:

$$(28.34 \text{ cm})(3.502 \text{ cm}) + (3.2 \text{ cm})(0.25 \text{ cm}) \\ = 99.247 \text{ cm}^2 + 0.80 \text{ cm}^2 = 100.05 \text{ cm}^2$$

2.133 $d = (579 \text{ g})/(3.00 \text{ cm})^3 = 21.4 \text{ g/cm}^3$
 It is Pt.

2.136 (a) 1.21 mm (b) 5.09 mL (c) $3.12 \times 10^3 \text{ mg}$

2.138 $346.0 \mu\text{g} \left(\frac{10^{-6} \text{ g}}{1 \mu\text{g}} \right) \left(\frac{1 \text{ mg}}{0.001 \text{ g}} \right) = 0.3460 \text{ mg}$

Because $346.0 \mu\text{g}$ is equal to 0.3460 mg , the values are the same.

2.139 $0.150 \text{ cg} \left(\frac{1 \text{ g}}{100 \text{ cg}} \right) \left(\frac{1000 \text{ mg}}{1 \text{ g}} \right) = 1.50 \text{ mg}$

The nurse should give a pill with 1.50 mg of active ingredients.

2.142 $1.72 \times 10^8 \text{ cm}$

2.143 $\frac{1.485 \times 10^{-22} \text{ g}}{1.709 \times 10^{-20} \text{ cm}^3} = 8.69 \times 10^{-3} \text{ g/cm}^3$

2.145 2.00 m. The 2.00-m length has more imprecision than 0.200 mm, and they cannot meaningfully be added.

2.146 $253 \text{ g salt} \left(\frac{100 \text{ g solution}}{25.0 \text{ g salt}} \right) = 1012 \text{ g solution}$

$$\frac{1012 \text{ g solution}}{850 \text{ mL}} = 1.19 \text{ g/mL}$$

2.147 The two penalties, by definition, yield exactly 10 yd and a new first down. After a no-gain play, in which an inch or less may have been lost, exactly 10 yd in penalties might not be sufficient for a new first down.

2.149 (a) The box is 3.15 cm and the man is 5.20 cm.
 Let x = actual height of the man

$$\text{Then } \frac{x}{1.00 \text{ m}} = \frac{5.20 \text{ cm}}{3.15 \text{ cm}}$$

and $x = 1.65 \text{ m}$

(b) The box is $1\frac{1}{4}$ in. and the man is $2\frac{1}{8}$ in.
 Let x = actual height of the man

Then $\frac{x}{1.00 \text{ m}} = \frac{2\frac{1}{8} \text{ in.}}{1\frac{1}{4} \text{ in.}} = \frac{17/8 \text{ in.}}{5/4 \text{ in.}}$
 and $x = 1.70 \text{ m}$

(c) Decimal fractions (in the metric system) are easier to use than common fractions (in the English system).

2.151 (a) $72.90 \times 10^3 \text{ s} \left(\frac{1 \text{ min}}{60 \text{ s}} \right) = 1215 \text{ min}$

(b) 20.25 h

2.152 $\frac{835 \text{ corp}}{1 \text{ mm}^3} \left(\frac{10 \text{ mm}}{1 \text{ cm}} \right)^3 = 8.35 \times 10^5 \text{ corp/cm}^3$
 $= 8.35 \times 10^5 \text{ corp/mL}$

2.154 The approximate volume of the Earth is

$$V = \frac{4}{3}(\pi)(6.4 \times 10^3 \text{ km})^3 = 1.1 \times 10^{12} \text{ km}^3$$

To convert that volume to cubic millimeters:

$$1.1 \times 10^{12} \text{ km}^3 \left(\frac{10^3 \text{ m}}{1 \text{ km}} \right)^3 \left(\frac{1 \text{ mm}}{10^{-3} \text{ m}} \right)^3 = 1.1 \times 10^{30} \text{ mm}^3$$

$$1.1 \times 10^{30} \text{ mm}^3 \left(\frac{1 \text{ grain}}{1.0 \text{ mm}^3} \right) = 1.1 \times 10^{30} \text{ grains}$$

2.160 (a) $(98.6^\circ\text{F} - 32.0^\circ\text{F})\frac{5}{9} = 37.0^\circ\text{C}$
 $37.0^\circ\text{C} + 273^\circ = 310 \text{ K}$

(b) 233 K (c) 276 K (d) 373 K

2.162 One (The value is probably closer to 0°F than to 1°F or -1°F .) Two (-18°C) (The value is probably closer to -18°C than to -19°C or -17°C .)

2.164 $512 \text{ g} \left(\frac{1 \text{ cm}^3}{6.12 \text{ g}} \right) = 83.66 \text{ cm}^3$

$V = lwt$ hence $l = V/wt$

$$= \frac{83.66 \text{ cm}^3}{(9.12 \text{ cm})(0.250 \text{ cm})} = 36.7 \text{ cm}$$

2.166 (a) 124 cm^3 (b) $2.30 \times 10^{-22} \text{ cm}^3$

2.167 $V = \frac{4\pi r^3}{3} = \frac{4(3.14)(3.00 \text{ cm})^3}{3} = 113.0 \text{ cm}^3$

$$d = \frac{m}{V} = \frac{177 \text{ g}}{113.0 \text{ cm}^3} = 1.57 \text{ g/cm}^3$$

The substance is sugar.

2.168 $V = \frac{\frac{4}{3}\pi r^3}{3} = \frac{4(3.14)(6.40 \times 10^6 \text{ m})^3}{3} = 1.098 \times 10^{21} \text{ m}^3$

$$d = \frac{m}{V} = \frac{6.1 \times 10^{24} \text{ kg}}{1.098 \times 10^{21} \text{ m}^3} = 5.6 \times 10^3 \text{ kg/m}^3$$

2.169 (a) $250 \text{ K} - 273 = -23^\circ\text{C}$

$$\frac{9}{5}(-23^\circ\text{C}) + 32.0 = -9.4^\circ\text{F}$$

(b) -459°F (c) 32°F (d) 133°F

2.171 (a) $1 \text{ grain} \left(\frac{1 \text{ lb}}{4.1 \times 10^4 \text{ grains}} \right) \left(\frac{2.12 \text{ dollars}}{1 \text{ lb}} \right)$

$$= 5.2 \times 10^{-5} \text{ dollar}$$

(b) Two. Significant figures rules are used for calculations involving very large or very small amounts of money.

2.172 $V = 87.1 \text{ cm}^3$

$$87.1 \text{ cm}^3 \left(\frac{0.382 \text{ g}}{1 \text{ cm}^3} \right) = 33.3 \text{ g}$$

2.174 $V = \frac{4(3.1416)(1.05 \times 10^{-8} \text{ cm})^3}{3} = 4.85 \times 10^{-24} \text{ cm}^3$

$$d = \frac{m}{V} = \frac{5.89 \times 10^{-23} \text{ g}}{4.85 \times 10^{-24} \text{ cm}^3} = 12.1 \text{ g/cm}^3$$

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- 2.175** Volume of water = volume of alcohol = V mL

$$\text{Mass of water} = 1.00V \text{ g}$$

$$\text{Mass of alcohol} = 0.789V \text{ g}$$

$$\text{Total mass} = 1.79V \text{ g}$$

$$\text{Density} = m/V$$

$$V_{\text{solution}} = m/d = (1.79V \text{ g}) \left(\frac{1 \text{ mL}}{0.942 \text{ g}} \right) = 1.90V \text{ mL}$$

The volume of the solution is 1.90 times that of the water (and of the alcohol).

- 2.178** 99.00 g acid $\left(\frac{1 \text{ mL acid}}{1.8305 \text{ g acid}} \right) = 54.084 \text{ mL acid}$

$$1.000 \text{ mL water} + 54.084 \text{ mL acid} = 55.084 \text{ mL total}$$

$$100.00 \text{ g solution} \left(\frac{1 \text{ mL solution}}{1.8342 \text{ g solution}} \right) = 54.5197 \text{ mL solution}$$

The change in volume is

$$55.084 \text{ mL total} - 54.5197 \text{ mL solution} = 0.56 \text{ mL}$$

- 2.179** There is 1.00 g water and

$$54.08 \text{ mL acid} \left(\frac{1.8305 \text{ g acid}}{1 \text{ mL acid}} \right) = 98.993 \text{ g acid}$$

The total mass is 99.993 g, and the density is

$$\frac{99.993 \text{ g}}{54.52 \text{ mL}} = 1.834 \text{ g/mL}$$

- 2.183** $2.55 \times 10^{-2} \text{ m}^3 \left(\frac{10^3 \text{ L}}{1 \text{ m}^3} \right) \left(\frac{1 \mu\text{L}}{10^{-6} \text{ L}} \right) = 2.55 \times 10^7 \mu\text{L}$

3 Atoms and Atomic Masses

3.1 $\frac{5}{2} = \frac{2.50}{1}$

The gambler wins \$2.50 for each dollar bet. Although $2.50/1$ is not an integral ratio, it is equal to the integral ratio $5/2$.

- 3.2** (b) 0.05 g (exactly half of 6.10 g)
(c) 12.2 g (exactly double 6.10 g)

Note that (a) is the *same* compound.

- 3.3** The mass of ^{12}C

- 3.4** Chemists use atomic mass and atomic weight as synonyms. All the other terms have different meanings.

- 3.5** (a) 19 (b) 19 (c) 19

The three parts actually ask the same question in different words.

- 3.6** Atomic number: (a) 65
Atomic mass: (b) 101.07 (the only noninteger)
Mass number: (c) (242) (too high for an atomic number, and in parentheses)

- 3.7** (a) e , the charge on the electron (b) amu

The three parts actually ask the same question in different words.

$$3(4.21 \text{ g}) + 7(5.55 \text{ g}) + 2(6.42 \text{ g}) = 5.36 \text{ g}$$

- 3.9** Mass

- 3.10** The symbol for the isotope has a superscript on its left side, denoting the mass number.

- 3.11** Atomic number and atomic mass

- 3.12** The mass number is an integer—the number of protons plus neutrons. The mass is an actual measured quantity and is not integral.

- 3.13** (a) 84.9 g (b) 13.0 g (c) 23.7 g
(d) The law of conservation of mass for part (a), and the law of definite proportions for parts (b) and (c)

3.14 (a) $9.08 \text{ g total} \left(\frac{85.63 \text{ g C}}{100.0 \text{ g total}} \right) = 7.78 \text{ g C}$

(b) There is 7.78 g of carbon in any 9.08-g portion because of the law of definite proportions.

3.15 $4.73 \text{ g} + 12.11 \text{ g} = 16.84 \text{ g}$

- 3.18** Protons and electrons

- 3.19** (a) V (b) Na
(c) V is in group VB; Na is in group IA.

3.20 (a) 38.0 g

$$(b) \frac{8(30.0 \text{ g}) + 12(46.0 \text{ g})}{20} = 39.6 \text{ g}$$

$$(c) \frac{3(35.0 \text{ amu}) + 37.0 \text{ amu}}{4} = 35.5 \text{ amu}$$

3.21 Atomic numbers had not been developed at the time Mendeleev did his work. Atoms were still thought to be indivisible.

3.22 Elements with atomic numbers 61, 84–87, 89, and 94 and higher have mass numbers given because they do not occur naturally.

3.23 The total mass of the reactants must equal the total mass of the products:

$$31.9 \text{ mg} + x = 87.7 \text{ mg} + 71.8 \text{ mg}$$

$$x = 127.6 \text{ mg oxygen}$$

3.25 (a) $7.33 \text{ g} - 7.05 \text{ g} = 0.28 \text{ g oxygen}$

$$(b) \frac{0.28 \text{ g}}{7.33 \text{ g}} = 0.038 \quad (c) 3.8\%$$

3.27 (a) $15.44 \text{ g Na} \left(\frac{3.454 \text{ g Cl}}{2.241 \text{ g Na}} \right) = 23.80 \text{ g Cl}$

(b) 0.4675 g Na

3.29 (a) For each atom of A present, the mass of B present is $2 \times 127 = 254$ amu, and the mass of A present is 24.3 amu. The ratio is therefore

$$(254 \text{ amu B})/(24.3 \text{ amu A}) = (10.5 \text{ units B})/(\text{unit A})$$

(b) The ratio of atoms (2 : 1) is integral.

3.30 No; the law of multiple proportions involves two compounds containing the same elements (such as SO_2 and SO_3), in which the ratio of masses of one element is a small, whole-number ratio (for a given mass of the other element).

- 3.34** (a) Per gram of element 2 (E2):

First compound	Second compound
$\frac{92.26 \text{ g E1}}{7.74 \text{ g E2}} = \frac{11.92 \text{ g E1}}{1 \text{ g E2}}$	$\frac{85.63 \text{ g E1}}{14.37 \text{ g E2}} = \frac{5.959 \text{ g E1}}{1 \text{ g E2}}$

Per gram of E2, the ratio of E1 is

$$\frac{11.92 \text{ g}}{5.959 \text{ g}} = \frac{2 \text{ g}}{1 \text{ g}}$$

(b) This is exactly the same problem with the data presented in a different order. Be sure to calculate per gram of one of the elements.

- 3.36** (a) 1.234 g or (b) 4.936 g.

Either is a small whole-number ratio, as required by the law of multiple proportions.

[(d) is the same compound.]

- 3.37** (a) It is amended or discarded entirely. (b) The fifth

3.39 (a) $\frac{65.4 \text{ amu}}{32.1 \text{ amu}} = 2.04$

(b) 6540 amu Zn; 3210 amu S

$$(c) \frac{6540 \text{ amu}}{3210 \text{ amu}} = 2.04$$

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- (d) For 1 billion atoms of each:

$$\frac{65.4 \times 10^9 \text{ amu}}{32.1 \times 10^9 \text{ amu}} = 2.04$$

- (e) For equal numbers of atoms, the ratio is always the same.

3.42 They occur in the same ratio in all naturally occurring samples.

3.44 $1.0 : 1.5 = 2:3$

3.45 The weighted average is given by the sum of the fraction of ^{28}Si times its mass, the fraction of ^{29}Si times its mass, and the fraction of ^{30}Si times its mass:

$$(0.9221)(27.97693 \text{ amu}) + (0.0470)(28.97649 \text{ amu}) + (0.0309)(29.97376 \text{ amu}) \\ = 25.798 \text{ amu} + 1.362 \text{ amu} + 0.9262 \text{ amu} \\ = 28.09 \text{ amu}$$

3.48 ^1H

- 3.49** 1. Atoms of an element are the smallest particles with the characteristic composition of the element.
2. Atoms of an element have the same atomic number, which is different from the atomic number of atoms of any other element.
3. Atoms of different elements can combine in certain small whole-number ratios to form compounds.

3.53

Isotopic Symbol	Atomic Number	Mass Number	No. of Protons	No. of Neutrons	No. of Electrons
(a) $^{112}_{48}\text{Cd}$	48	112	48	64	48
(b) $^{115}_{49}\text{In}$	49	115	49	66	49
(c) $^{203}_{81}\text{Tl}$	81	203	81	122	81
(d) $^{80}_{34}\text{Se}$	34	80	34	46	34
(e) $^{128}_{52}\text{Te}$	52	128	52	76	52
(f) $^{96}_{42}\text{Mo}$	42	96	42	54	42
(g) $^{103}_{45}\text{Rh}$	45	103	45	58	45

3.54 (a) ^3H (b) ^2H (c) ^1H (d) ^3He (e) ^3H

- 3.55** (a) The atomic number and mass number are given. The atomic number is implied by the symbol for the element.
(b) Because the atomic number is the number of electrons for a neutral atom, the two numbers are really only one value, which would not yield the mass number or the number of neutrons.
(c) In a neutral atom, the numbers of protons and electrons are the same, and again the number of neutrons and the mass number could not be determined.

3.58 (a) Hydrogen (b) ^2H

3.60 The atomic mass of fluorine is 19.0 amu. The element with atomic mass $10 \times 19.0 \text{ amu} = 190 \text{ amu}$ is osmium (atomic mass 190.2 amu).

3.62 (a) If 37.4% weigh 185.0 lb, then

$$100.00\% - 37.4\% = 62.6\% \text{ weigh } 187.0 \text{ lb.}$$

$$185.0 \text{ lb} \left(\frac{37.4}{100} \right) + 187.0 \text{ lb} \left(\frac{62.6}{100} \right) = 186 \text{ lb}$$

$$(b) (184.953 \text{ amu}) \left(\frac{37.40}{100} \right) + (186.956 \text{ amu}) \left(\frac{62.60}{100} \right) = 186.2 \text{ amu}$$

3.65 The *average* of the masses of lighter and heavier isotopes is 79.909 amu. (The actual composition is 50.54% ^{79}Br and 49.46% ^{81}Br .)

3.67 Atomic mass

$$= (0.7217)(84.9118 \text{ amu}) + (0.2783)(86.9092 \text{ amu}) \\ = 85.47 \text{ amu}$$

- 3.68** (a) Less than 1 amu is too small to be the mass of an atom.
(b) 12.0 g is much too large.
(c) This again is much too large to be the mass of an atom.
(d) More than 2000 amu is too large.
(e) 74.9 amu is the mass of an average arsenic atom.

3.69 Mass of selenium \equiv mass of fluorine $= x$ amu
Number of selenium atoms $= x/79$
Number of fluorine atoms $= x/19 \equiv 4(x/79)$

There are four F atoms for every Se atom.

3.72 That fact was crucial because atomic numbers were as yet unknown. Because atomic mass rises as atomic number rises, and the periodic table is based on atomic numbers, Mendeleev could use atomic mass to build his table.

3.73 Na_2O MgO Al_2O_3 SiO_2 P_2O_3 SO_2 Cl_2O

3.75 Each property of bromine may be expected to be an “average” of those of chlorine and iodine. The actual properties are

Liquid under normal conditions
Dark brown
Reacts with metals
Reacts with oxygen
Does not conduct electricity

3.76 A crude periodic table could be built with the weighted average of the number of neutrons since the number of neutrons rises generally as atomic number rises.

3.79 We can calculate the mass of each of the other elements per gram of any one of them. For example, per gram of hydrogen, the masses of carbon and oxygen are as follows:

$$(a) \frac{62.1 \text{ g C}}{10.3 \text{ g H}} = \frac{6.03 \text{ g C}}{1 \text{ g H}} \quad \frac{27.6 \text{ g O}}{10.3 \text{ g H}} = \frac{2.68 \text{ g O}}{1 \text{ g H}}$$

$$(b) \frac{52.2 \text{ g C}}{13.0 \text{ g H}} = \frac{4.02 \text{ g C}}{1 \text{ g H}} \quad \frac{34.8 \text{ g O}}{13.0 \text{ g H}} = \frac{2.68 \text{ g O}}{1 \text{ g H}}$$

The gram ratios can be simplified by dividing each set by the second value in the set:

Ratios of Masses of Carbon **Ratios of Masses of Oxygen**

$$6.03 \text{ g : } 4.02 \text{ g} \quad 2.68 \text{ g : } 2.68 \text{ g}$$

$$1.50 \text{ g : } 1.00 \text{ g} \quad 1.00 \text{ g : } 1.00 \text{ g}$$

The numbers in the first set can be made integral by multiplying each one by 2. The second set is 1 : 1.

3 : 2 1 : 1

The resulting values are integers within the accuracy of the significant digits reported. If we chose to calculate the masses per gram of carbon or per gram of oxygen, integral ratios would have been obtained.

$$3.80 (a) \frac{V_a}{V_n} = \frac{\frac{4}{3} \pi r_a^3}{\frac{4}{3} \pi r_n^3} = \frac{r_a^3}{r_n^3} = (10^4)^3 = 10^{12}$$

(b) Yes. The atom has a volume 1000 billion times that of the nucleus.

3.83 Per gram of hydrogen:

$$\text{Compound 1: } \frac{39.02 \text{ g S}}{2.44 \text{ g H}} = \frac{16.0 \text{ g S}}{1 \text{ g H}} \quad \frac{58.54 \text{ g O}}{2.44 \text{ g H}} = \frac{24.0 \text{ g O}}{1 \text{ g H}}$$

$$\text{Compound 2: } \frac{94.12 \text{ g S}}{5.88 \text{ g H}} = \frac{16.0 \text{ g S}}{1 \text{ g H}}$$

$$\text{Compound 3: } \frac{32.65 \text{ g S}}{2.04 \text{ g H}} = \frac{16.0 \text{ g S}}{1 \text{ g H}} \quad \frac{65.31 \text{ g O}}{2.04 \text{ g H}} = \frac{32.0 \text{ g O}}{1 \text{ g H}}$$

For a fixed mass of hydrogen (1 g), the ratio of masses of sulfur is 1 : 1 : 1 and that of oxygen is 0.750 : 0 : 1 = 3 : 0 : 4

3.90 (a) The oxygen in the nitrogen monoxide has a mass of $4.75 \text{ g} - 2.22 \text{ g} = 2.53 \text{ g O}$.

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- (b) The oxygen in the sample of nitrogen dioxide has a mass twice that of the oxygen in the 4.75 g of nitrogen monoxide: $2(2.53 \text{ g}) = 5.06 \text{ O}$.

- (c) The total mass of nitrogen dioxide containing 2.22 g of nitrogen is therefore $2.22 \text{ g} + 5.06 \text{ g} = 7.28 \text{ g}$, and the percentage of nitrogen is

$$\left(\frac{2.22 \text{ g N}}{7.28 \text{ g total}}\right) \times 100\% = 30.5\% \text{ N}$$

The percentage of oxygen is

$$100.0\% - 30.5\% = 69.5\%$$

- 3.91** The atomic mass is an average, and no atom of chlorine has that mass. (About 75% of the chlorine atoms have masses about 35 amu and 25% have masses about 37 amu.) The weighted average of these masses is 35.453 amu.

- 3.92** Since the problem implies that fluorine atoms do have a mass equal to the atomic mass, it can be deduced that fluorine is composed 100% of this isotope.

- 3.96** (a) 65.17 g (law of conservation of mass)
(b) 55.17 g (law of definite proportions)
(c) 65.17 g (laws of definite proportions and conservation of mass)

4 Electronic Configuration of the Atom

- 4.1** The frequency (the number of times she passes a given point) is $12/\text{h}$.

- 4.2** $3.00 \times 10^8 \text{ m/s}$. The same value results each time because no matter what the frequency, the following equation is valid for any electromagnetic radiation:

$$c = \lambda\nu$$

- 4.3** None. A definite frequency implies a definite wavelength and a definite energy.

- 4.4** Hydrogen

- 4.5** Ac is in period 7, so it has n values up to 7—1, 2, 3, 4, 5, 6, and 7.

- 4.6** (a) Because the s subshell contains only one orbital, there is no difference.
(b) A p subshell contains three p orbitals.

- 4.7** (a) One (b) All 10 (c) No (d) Yes

- 4.8** The Pauli exclusion principle, the $n + \ell$ rule, and the permitted values of the quantum numbers

- 4.9** (a) No (b) At least one must be different.
(c) No (d) At least one must be different.

- 4.10** (a) Yes; the sign can be either plus or minus, and because both have equal energy, either is correct.
(b) No; once the first electron has a given sign, the second electron must have the opposite sign so as not to violate the Pauli exclusion principle.

(c) Yes

- (d) No; once the other five electrons in the 2p subshell have given signs, the last electron must have the opposite sign to the other electron in its orbital so as not to violate the Pauli exclusion principle.

- 4.11** Helium's outermost shell is complete.

- 4.12** $(-1.6335 \times 10^{-18} \text{ J}) + (-3.025 \times 10^{-19} \text{ J}) = -1.9360 \times 10^{-18} \text{ J}$

The same energy change is accomplished in going from the third shell to the second to the first as in going directly from the third to the first (PP 4.3).

- 4.13** $v = c/\lambda = (3.00 \times 10^8 \text{ m/s})/(6.563 \times 10^{-7} \text{ m}) = 4.57 \times 10^{14}/\text{s}$

4.14 $E = hc/\lambda$
 $= E\lambda/c = (\text{J})(\text{m})/(\text{m/s}) = \text{J}\cdot\text{s}$

4.15 $\lambda = hc/E$
 $= (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})/(4.09 \times 10^{-19} \text{ J}) = 4.86 \times 10^{-7} \text{ m}$

4.18 $E = hc/\lambda$
 $= (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})/(4.340 \times 10^{-7} \text{ m}) = 4.58 \times 10^{-19} \text{ J}$

- 4.20** Electric energy gives some electrons enough energy to move to higher energy levels; when they fall back to their ground states, the added energy is given off in the form of light.

- 4.21** Four paths are possible for an electron descending from the sixth shell (energy level) to the third in a hydrogen atom (see Figure 4.6):

- | | |
|----------------|------------------------|
| One path: | shell 6 to 5 to 4 to 3 |
| Another path: | shell 6 to 5 to 3 |
| A third path: | shell 6 to 4 to 3 |
| A fourth path: | shell 6 to 3 |

- 4.22** Six distinctly different wavelengths of light would be emitted, corresponding to the transitions from shell 6 to 5, 6 to 4, 6 to 3, 5 to 4, 5 to 3, and 4 to 3.

- 4.23** $\ell = 0, 1, 2, \text{ or } 3$

- 4.24** $m_\ell = -3, -2, -1, 0, 1, 2, \text{ or } 3$

- 4.25** $m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$, no matter what the values of the other quantum numbers are.

- 4.26** (a) (m_ℓ must be 0 if ℓ is 0.)
(b) (m_ℓ must be either $+\frac{1}{2}$ or $-\frac{1}{2}$.)
(c) (ℓ must be 0 or positive.)
(d) (ℓ cannot equal n .)

- 4.28** (a) $-5, -4, -3, -2, -1, 0, +1, +2, +3, +4,$ and $+5$
(b) Eleven ($2\ell + 1$)

- 4.29** The lowest $n + \ell$ value is that of (d).

- | |
|-------------------------------------|
| (a) $n = 6, \ell = 3, n + \ell = 9$ |
| (b) $n = 6, \ell = 2, n + \ell = 8$ |
| (c) $n = 5, \ell = 3, n + \ell = 8$ |
| (d) $n = 5, \ell = 2, n + \ell = 7$ |

Because (c) has a lower n value than (b), it is lower in energy. (a) is highest in energy because it has the highest $n + \ell$ value. The order of energies is (d) $<$ (c) $<$ (b) $<$ (a).

- 4.31** All are equal in energy because they all have the same n value and the same ℓ value.

- 4.34** They are the same.

- 4.37** (a) 13, aluminum (b) 21, scandium (c) 36, krypton

- 4.38** (a) In any orbital, there can be a maximum of two electrons.
(b) A d subshell has an ℓ value of 2, so five different m_ℓ values and two different m_s values are possible, for a total of ten combinations. There may be up to ten electrons in a d subshell.

Li	$1s^2 2s^1$
C	$1s^2 2s^2 2p^2$
Mg	$1s^2 2s^2 2p^6 3s^2$

- 4.40** (a) Three (b) Three (c) Three (d) Six

- 4.44** d_{xy} and d_{yz}

- 4.47** (a) All three (b) Two ($d_{x^2-y^2}$ and d_{z^2})

- 4.48** In each case it is the number of orbitals:

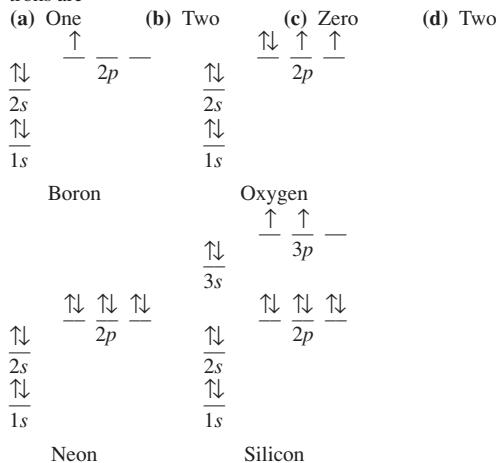
- | | | | |
|-------|-------|-------|-------|
| (a) 1 | (b) 3 | (c) 5 | (d) 7 |
|-------|-------|-------|-------|

- 4.49** (a) None (b) Four (c) Six

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- 4.50** See the accompanying figures. The numbers of unpaired electrons are



- 4.51** (e) (The 15 electrons lie in the lowest energy orbitals possible, with the three electrons in the $3p$ subshell in separate orbitals with parallel spins.)

- 4.55** (a) Two (b) Six (c) Ten (d) Fourteen
In each case, the width of the block in the periodic table gives the number of electrons. For example, the s block is two groups wide.

- 4.56** (a) Two each
(b) Ten each
(c) Eighteen each

- 4.58** (a) Be $1s^2 2s^2$
(b) Mg $1s^2 2s^2 2p^6 3s^2$
(c) Ca $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
(d) Sr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$

- 4.60** (a) Ge $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$
(b) Mn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
(c) N $1s^2 2s^2 2p^3$
(d) Br $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
(e) Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

- 4.62** (a) Tl $[Xe] 6s^2 5d^{10} 4f^4 6p^1$
(b) La $[Xe] 6s^2 5d^1$
(c) Gd $[Xe] 6s^2 5d^1 4f^7$

- 4.67** (a) Mn (b) Te (c) Bi (d) Rb (e) Br (f) Lr

- 4.68** The differences corresponding to the possible transitions are as follows:

From 5 to 4: 4.898×10^{-20} J
From 5 to 3: 1.549×10^{-19} J
From 5 to 2: 4.574×10^{-19} J
From 4 to 3: 1.059×10^{-19} J
From 4 to 2: 4.084×10^{-19} J
From 3 to 2: 3.025×10^{-19} J

- 4.71** No. Every element with an atomic number 4 or greater has this *inner* configuration.

- 4.75** (a) A $1p$ subshell does not exist.
(b) There is only one $1s$ electron.
(c) The $2s$, $3s$, $3p$, etc. subshells are missing.
(d) The $2p$ subshell is not filled.
(e) There are too many electrons in the $4f$ subshell.
(f) There are too many electrons in the $3d$ subshell.
(g) There are too many electrons in the $2s$ subshell.
(h) There is no $2d$ subshell.
(i) The $3d$ subshell, not the $4d$ subshell, follows the $4s$ subshell.

- 4.77** (a) One (b) Five (c) Five

- 4.84** The atom with the most unpaired electrons will be drawn into the magnetic field the most.

- (a) Mn (has 5 unpaired electrons)
(b) Cu (has 1 unpaired electron)
(c) V (has 3 unpaired electrons)
(d) Ti (has 2 unpaired electrons)

- 4.86** The actual configuration has six unpaired electrons, and chromium is drawn into a magnetic field more than would be expected from the $4s^2 3d^4$ configuration, with four unpaired electrons.

5 Chemical Bonding

- 5.1** (a) The valence shell is the outermost shell of an uncombined atom. If all the valence electrons have been removed, the outermost shell of the resulting positive ion will be the shell just below the valence shell.

- (b) *Diatom* means two atoms per molecule; *binary* means two elements per compound.

- 5.2** Diatomic molecules: uncombined elements
Charges on ions: ionic compounds

- 5.3** (a) It has only 1 electron to lose.
(b) The first shell can hold only 1 additional electron.

- 5.4** Ionic: (b) $MgCl_2$
Covalent: (a) Cl_2 and (c) SCl_2

- 5.5** (a) Hydrogen is a group IA element, but it is not a metal.
(b) Because hydrogen can form H^- ions, only the first statement is correct.
(c) No. All group IIA elements are metals.

- 5.6** The first is an ionic chloride of cobalt; the second contains carbon and oxygen as well as chlorine, all covalently bonded.

- 5.7** (a) $ZnBr_2$ (b) Zn^{2+} and F^-
(c) SnO (d) Fe^{2+} and O^{2-}

- 5.8** Eight, five from the outermost shell of nitrogen and three extra transferred from some cation(s).

- 5.9** (a) $2+$ (b) $2+$ (c) 0 (d) $2+$ (e) $2+$
The charge on the zinc ion in each of its compounds is $2+$ (equal to its group number). In the free element, as in all free elements, the charge on the atom is zero.

- 5.10** (a) 0 (b) $2+$
(c) $20+$ (equal to the atomic number)

Note the great difference in the meaning of the questions with only a slight difference in the wording.

- 5.11** (a) The alkali metals, the alkaline earth metals, the group IIIB metals, silver, zinc, cadmium, and aluminum
(b) The group IA and group IB metals

- 5.12** NH_3 and NH_4^+

- 5.13** (a) $(UO_2)_3(AsO_4)_2$ (b) $(MO_y)_3(XO_z)_2$
(c) $(AX_y)_3(BZ_z)_2$ (d) The charges on the ions must be balanced no matter *what* the identity of each ion.

- 5.14** (a) Yes, it has the electronic structure of He.
(b) No; it has no electrons. (This ion is not a stable species, but chemists often use the symbol H^+ to represent H_3O^+ .)

- 5.15** The first is a compound, and the second is an ion—part of a compound.

- 5.16** CdS in all cases. Note the different ways in which the same problem may be presented.

- 5.17** Atoms of the main group elements except for the noble gases have valence electrons equal in number to their (classical) periodic group numbers.

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- 5.18** (a) Li^+ : H^-
 (b) H^- Ca^{2+} H^- or Ca^{2+} 2 : H^-

- 5.19** (a) Ag_2O (b) Ag^+ and S^{2-}

- 5.20** (a) None; the valence electrons of the magnesium atom have been donated to form the ion.
 (b) The magnesium atom does not share electrons; it forms ionic compounds.

- 5.22** (a) H^- (b) He : (c) Li^+ (d) Be^{2+}

All of these species have the same electronic configuration, but because only valence electrons are shown, the electron dot diagram for the lithium and beryllium ions look different from those of H^- and He.

- 5.23** (a) 1+ (b) 2+ (c) 2- (d) 1-

The metals of parts (a) and (b) have charges equal to their classical group numbers. For parts (c) and (d), each monatomic anion has a charge equal to its classical group number minus 8 (or the modern group number minus 18).

- 5.24** The charge on a monatomic anion (except H^-) is equal to the classical group number minus 8. Generally, the charge on a polyatomic anion is even if the central element is in an even periodic group and odd if it is in an odd periodic group.

- 5.25** (a) K^- (b) K^+ (no valence electrons)
 (c) $:\ddot{\text{N}}:$ (d) $[\ddot{\text{N}}]^3-$

- 5.26** (a) Covalent (b) Covalent (c) Ionic

- 5.27** (a) The subscript in N_2 implies that the atoms are bonded; the coefficient in 2 N does not imply either that the atoms are bonded or not bonded.
 (b) The six atoms in N_2O_4 are all bonded together; those in 2 NO_2 are bonded in two molecules of three atoms each.

- 5.29** (a) 3 N, 12 H, 1 P, 4 O
 (b) 3 Li, 1 N
 (c) 1 Al, 6 C, 9 H, 6 O

- 5.31** There are three zinc atoms, two phosphorus atoms, and eight oxygen atoms per formula unit of the compound. Moreover, the four oxygen atoms in each PO_4 group are bonded to the phosphorus atom in some way, and the PO_4 groups are bonded to the zinc atoms in some way.

- 5.32** (a) Sn^{4+} and O^{2-} (b) Cr^{3+} and PO_4^{3-}
 (c) Cr^{2+} and SO_4^{2-} (d) Na^+ and HCO_3^-
 (e) Ca^{2+} and HPO_4^{2-}

- 5.35** (a) The alkali metals and the coinage metals.
 (b) The alkali metals and silver.

Symbol	Atomic Number	No. of Protons	No. of Electrons	Net Charge
(a) Cl^-	17	17	18	1-
(b) S^{2-}	16	16	18	2-
(c) K^+	19	19	18	1+
(d) Fe^{3+}	26	26	23	3+
(e) Pt^{2+}	78	78	76	2+

- (a) Chlorine has an atomic number of 17 (see the periodic table) and therefore has 17 protons in its nucleus. Because the ion is shown with a 1- charge, the number of electrons is 1 greater than the number of protons, so 18 electrons are present.
 (b) The element with atomic number 16 is sulfur. Because the number of protons is equal to the atomic number and there are 2 more electrons than protons, the net charge is 2-. The symbol for this ion is therefore S^{2-} . Do not forget the charge!
 (c) Because the number of protons is always equal to the atomic number, the same reasoning is used here as in part (b).

- (d) The atomic number is 26, so the element is iron and the number of protons is also 26. Because the ion has a 3+ charge, there must be three fewer electrons than protons. The symbol is Fe^{3+} .
 (e) The number of protons is 78, as is the atomic number. The element is platinum, and the symbol is Pt^{2+} .

- 5.38** (a) Na^+ $1s^2 2s^2 2p^6$
 (b) Al^{3+} $1s^2 2s^2 2p^6$
 (c) Zn^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6$

- 5.40** In each case, the outermost s electrons are donated first.

- (a) Co^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$
 (b) Cr^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
 (c) Cu^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

- 5.41** (a) $[\ddot{\text{O}}]^{2-}$ (b) $[\ddot{\text{C}}\text{l}]^-$ (c) $[\ddot{\text{N}}]^{3-}$

- 5.42** (a)-(c) In each of these cases, the metal loses all its valence electrons, and the electron dot symbol consists only of the chemical symbol and charge. (a) Na^+ (b) Ca^{2+} (c) Al^{3+}
 (d) In the case of tin, only two of its four valence electrons are lost, resulting in a diagram : Sn^{2+}

5.43 Atoms Ions

- (a) $\cdot\text{Al}\cdot$ $:\ddot{\text{S}}:$ Al^{3+} $[\ddot{\text{S}}]^{2-}$
 (b) Ca : $:\ddot{\text{Br}}:$ Ca^{2+} $[\ddot{\text{Br}}]^-$
 (c) Mg : $:\ddot{\text{N}}:$ Mg^{2+} $[\ddot{\text{N}}]^{3-}$

- 5.45** (a) Li^+ (b) Ca^{2+} (c) Zn^{2+}
 (d) Al^{3+} (e) Sc^{3+}

- 5.46** (a) CrCl_2 and CrCl_3 (b) CrO and Cr_2O_3

- 5.47** (a) Al_2S_3 (b) Ag_2O
 (c) Mg_3N_2 (Don't forget that the positive ion is written first.)

- 5.48** O^{2-} Br^- N^{3-}
 K^+ K_2O KBr K_3N
 Ca^{2+} CaO CaBr_2 Ca_3N_2
 Al^{3+} Al_2O_3 AlBr_3 AlN

- 5.51** (a) 1 Zn^{2+} and 2 $\text{C}_2\text{H}_3\text{O}_2^-$ (b) 2 Al^{3+} and 3 CO_3^{2-}
 (c) 2 K^+ and 1 SO_4^{2-} (d) 1 NH_4^+ and 1 HCO_3^-

- 5.56** (a) Li^+ H^- (b) Zn^{2+} ClO_3^-
 (c) Rb^+ O_2^{2-} (d) Na^+ ClO_3^-
 (e) Ba^{2+} Cl^- (f) Hg_2^{2+} NO_3^-
 (g) NH_4^+ HPO_4^{2-}

- 5.57** Two; there are 4 valence electrons in the neutral lead atom (group IVA [14]), of which 2 are donated to some other atom(s) in forming a 2+ ion. (The electronic configuration is $[\text{Xe}] 6s^2 5d^{10} 4f^{14} 6p^0$.)

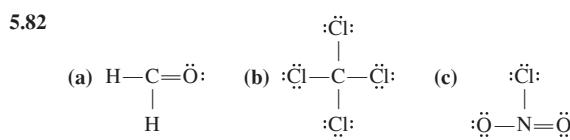
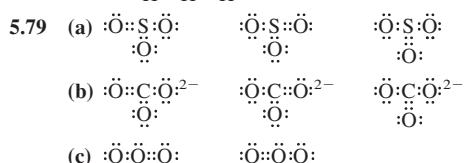
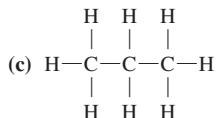
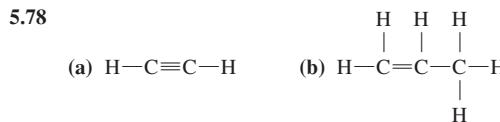
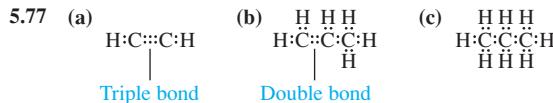
- 5.59** (a) O^{2-} Pt^{2+} and Pt^{4+}
 (b) O^{2-} Fe^{3+} and Fe^{2+}
 (c) SO_4^{2-} Cr^{2+} and Cr^{3+}

- 5.61** ClO_2^- SO_4^{2-} PO_4^{3-} $\text{P}_2\text{O}_7^{4-}$
 NH_4^+ NH_4ClO_2 $(\text{NH}_4)_2\text{SO}_4$ $(\text{NH}_4)_3\text{PO}_4$ $(\text{NH}_4)_4\text{P}_2\text{O}_7$
 Fe^{2+} $\text{Fe}(\text{ClO}_2)_2$ FeSO_4 $\text{Fe}_3(\text{PO}_4)_2$ $\text{Fe}_2\text{P}_2\text{O}_7$
 Al^{3+} $\text{Al}(\text{ClO}_2)_3$ $\text{Al}_2(\text{SO}_4)_3$ AlPO_4 $\text{Al}_4(\text{P}_2\text{O}_7)_3$

- 5.63** (a) FePO_4 (b) $(\text{NH}_4)_2\text{SO}_3$ (c) Ag_2CO_3
 Note that the cation is written first in each compound, no matter which ion is stated first in the problem.

- 5.68** The H atom can hold a maximum of two electrons.

- 5.71** (a) $:\ddot{\text{O}}\text{S}\ddot{\text{O}}^{2-}$ (b) $:\ddot{\text{N}}\text{:N}:\ddot{\text{N}}^-$
 (c) Ca^{2+} $:\ddot{\text{O}}^{2-}$

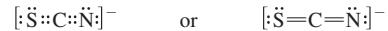
624**APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems**

- 5.84** (a) An ion is a charged atom or group of atoms.
 (b) An anion is a negatively charged ion.
 (c) An octet is a group of 8 electrons in the outermost shell of an atom.
 (d) A lone pair is a pair of valence electrons not shared between atoms.
 (e) Ozone is an allotropic form of oxygen with formula O_3 .
 (f) Monatomic means “one-atom”; a monatomic ion is composed of one charged atom.
 (g) A noble gas configuration has 8 (or 2 for the lightest elements) valence electrons.
 (h) A polyatomic ion is a charged group of atoms covalently bonded together (and ionicly bonded to some other ion).
 (i) A triple bond is a covalent bond formed by 6 shared electrons.

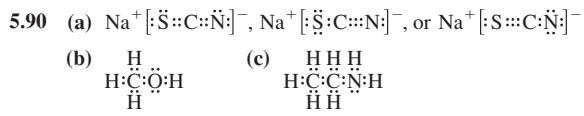
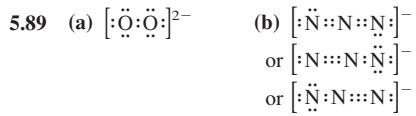
- 5.85** Deduce the number of shared electrons in the usual way:

Atoms	Valence Electrons Available	Valence Electrons Required
S	6	8
C	4	8
N	5	8
Negative charge	1	
Total	16	24

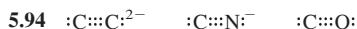
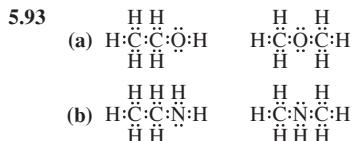
To be shared: $24 - 16 = 8$



- 5.86** (a) Eight; 1 valence electron has been donated to form the ion.
 (b) The ion does not share electrons with other ions; it forms ionic compounds by electron transfer.



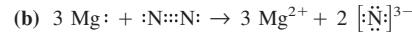
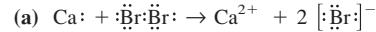
- 5.92** An atom with a total of 8 electrons in its outermost shell (*s* and *p* subshells) is stable.



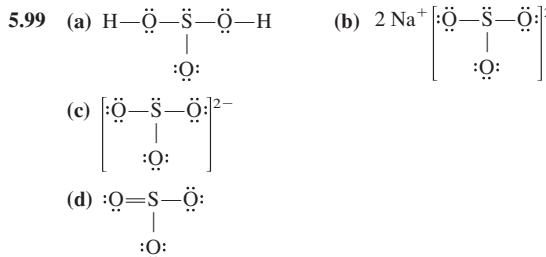
They all have the same number of electrons, and their structures reflect that similarity.

- 5.96** (a) Cr^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$
 (b) Fe^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
 (c) Ni^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

- 5.97** Remember that elemental nitrogen and fluorine occur in diatomic molecules.



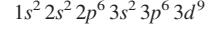
(c) The elements were required in this problem, and the nonmetals occur in diatomic molecules.



- 5.105** An “infinite” number

- 5.106** The charge is $3+$. No monatomic ion can have a charge of $5+$, which might have been expected because bismuth is in periodic group VA (15).

- 5.112** In the “expected” configuration, the atom would lose the two $4s$ electrons. In the actual configuration, the atom loses the one $4s$ electron and one $3d$ electron. In either case, the Cu^{2+} configuration is the same:



- 5.115** (a) Four (b) Two

- 5.117** (a) Nonmetal, VA (b) Metal, IA
 (c) Metal, IIIA (d) Metal, IIA
 (e) Metal, IVA (f) Metal, IIIA

6 Nomenclature

- 6.1** (a) Hafnium
 (b) Hydrogen fluoride (or hydrofluoric acid)
 (c) Nitrogen monoxide (d) Nobelium
- 6.2** The prefix *bi-* represents hydrogen in an acid salt, as in sodium bicarbonate; the prefix *di-* means two atoms of some element.
- 6.3** The Group IA, IIA, and IIIB metals, zinc, cadmium, silver, and aluminum form a single type of ion with charge equal to the metal’s classical periodic group number.
- 6.4** The first is a compound, chlorine dioxide, and the second is an ion, chlorite ion. The ion has one more electron.
- 6.5** (a) Except for the hydride ion, the charge on a monatomic anion is equal to the classical group number minus 8.
 (b) The charge on an oxoanion is generally even if the central element is in an even-numbered periodic group and odd if it is in an odd-numbered group.

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- 6.6** (a) Ionic, calcium chloride
 (b) Covalent, carbon dioxide
 (c) Ionic, chromium(II) oxide
 (d) Covalent, carbon tetrachloride
- 6.7** (a) Sulfate ion
 (b) Nitrate ion
 (c) Phosphate ion
 (d) Sulfide ion
- 6.9** (a) We can tell the numbers of each type of ion in a formula unit of the compound.
 (b) The compound (or ion) is an acid (or acid salt).
 (c) There is oxygen in the compound or ion.
- 6.10** (a) Variable type, chromium(II) sulfate
 (b) Variable type, cobalt(II) sulfate
 (c) Constant type, calcium sulfate
 (d) Constant type, aluminum chloride
 (e) Variable type, iron(II) sulfate
 (f) Constant type, potassium sulfate
- 6.12** (a) Hydrogen ion is H^+ ; hydride ion is H^- .
 (b) Although hydrogen forms ions with two different charges, the ion with the negative charge is distinguished by the ending *-ide*, so the Roman numeral is unnecessary in the name of H^+ .
- 6.13** (a) Cl^- (b) ClO_3^- (c) ClO_2^-
- 6.14** NH_3 is a compound; NH_4^+ is an ion. The compound is ammonia; the ion is the ammonium ion.
- 6.16** H_2SO_4 is not a *binary* nonmetal-nonmetal compound.
- 6.17** (a) *Hypo-* indicates an oxygen-containing ion or acid with two fewer oxygen atoms than the corresponding ion or acid whose name ends in *-ate* or *-ic acid*.
 (b) *Hydro-* indicates an acid that contains no oxygen.
 (c) *Hydrogen* is used in acid salts, but not in covalent acids.
- 6.18** (a) Sodium sulfate (b) Sulfuric acid
- 6.19** Hydrochloric acid refers to the compound in aqueous solution; hydrogen chloride is used for the pure compound.
- 6.21** (a) Sodium chloride and hydrogen chloride
 (b) Sodium sulfide and hydrogen sulfide
 Binary hydrogen compounds that are acids have names in which hydrogen is named as if it were an alkali metal.
- 6.22** (a) Perbromic acid (b) Bromic acid
 (c) Bromous acid (d) Hypobromous acid
 (e) Hydrobromic acid
- 6.23** (a) 1- (HSO_3^-) (b) 1- ($H_2PO_4^-$)
 (c) 2- (HPO_3^{2-})
- 6.24** (a) Dinitrogen pentoxide (b) Carbon tetrafluoride
 (c) Diphosphorus trisulfide (d) Sulfur tetrafluoride
 (e) Bromine trifluoride
- 6.25** (a) CO_2 (b) HBr (c) SiF_4 (d) IF_5
 (e) BrO_2 (f) H_2S (g) N_2O_3
- 6.27** (a) ClF (b) NH_3 (c) AsF_3
 (d) SO_3 (e) PCl_5 (f) H_2O
- 6.28** (a) Sulfur dioxide (b) Silicon tetrafluoride
 (c) Arsenic trifluoride (d) Disulfur dichloride
 (e) Xenon hexafluoride
- 6.33** The word “sulfide” refers only to the ion; the word “potassium” can refer to the atom, the element, or the ion.
- 6.34** (a) Calcium ion (b) Silver ion
 (c) Aluminum ion
- 6.35** (a) Cu^+ (b) Ni^{2+} (c) Li^+
 (d) NH_4^+ (e) Au^+
- 6.37** (a) Chloride ion (b) Phosphide ion
 (c) Oxide ion (d) Nitride ion
- 6.38** (a) NO_2^- (b) ClO_4^- (c) CN^-
 (d) PO_3^{3-} (e) $Cr_2O_7^{2-}$ (f) IO^-
- 6.41** (a) Cobalt(III) sulfate
 (b) Calcium phosphate
 (c) Ammonium sulfite
- 6.42** (a) Co_2O_3 (b) $NiSO_4$ (c) $LiOH$
 (d) $CuCO_3$ (e) $Mg(CN)_2$ (f) NH_4ClO_3
- 6.43** (a) Copper(I) oxide
 (b) Copper(II) sulfide
- 6.46**

Nitrate	Sulfate	Acetate	Phosphate
Ammonium	NH_4NO_3	$(NH_4)_2SO_4$	$NH_4C_2H_3O_2$
Calcium	$Ca(NO_3)_2$	$CaSO_4$	$Ca(C_2H_3O_2)_2$
Vanadium(III)	$V(NO_3)_3$	$V_2(SO_4)_3$	$V(C_2H_3O_2)_3$
Lead(IV)	$Pb(NO_3)_4$	$Pb(SO_4)_2$	$Pb_3(PO_4)_4$
- 6.49** The instructor would say, “The magnesium(I) ion cannot be prepared in a solid.”
- 6.50** (a) Chromium(III) ion or chromic ion
 (b) Cobalt(II) ion or cobaltous ion
 (c) Gold(I) ion or aurous ion
 (d) Platinum(IV) ion or platinic ion
- 6.51** (a) H_3PO_4 (b) HBr (c) $HClO_3$ (d) H_2S
- 6.52** (a) Sulfuric acid
 (b) Perchloric acid
 (c) Phosphorous acid
- 6.56** (a) Hydrobromic acid and hydrogen bromide
 (b) Hydrosulfuric acid and hydrogen sulfide
 (c) Hydrochloric acid and hydrogen chloride
- 6.58**

Monohydrogen Phosphate	Hydrogen Sulfate	Dihydrogen Phosphate
<i>Magnesium</i>	$MgHPO_4$	$Mg(HSO_4)_2$
<i>Chromium(III)</i>	$Cr_2(HPO_4)_3$	$Cr(HSO_4)_3$
<i>Ammonium</i>	$(NH_4)_2HPO_4$	NH_4HSO_4
<i>Copper(II)</i>	$CuHPO_4$	$Cu(HSO_4)_2$
- 6.59** Phosphorus is the name of the element, and phosphorous is the name of the oxoacid with one fewer oxygen atom than phosphoric acid.
- 6.60** (a) Barium hypochlorite dihydrate
 (b) Sodium carbonate heptahydrate
 (c) Iron(III) bromide hexahydrate
- 6.61** (a) $FeSO_4 \cdot H_2O$ (b) $BaBr_2 \cdot 2H_2O$
- 6.62** (a) Sulfur trioxide (b) Sulfite ion
 (c) Sodium sulfite (d) Sulfurous acid
 (e) Potassium sulfite
- 6.66** The binary nonmetal-nonmetal compounds are named with the prefixes; the “variable” cations are named with the Roman numerals; and the “constant” cations are named with neither:
 (a) Carbon tetrachloride (b) Sodium carbonate
 (c) Nitrogen trichloride (d) Cobalt(II) chloride
 (e) Sodium sulfate (f) Sulfur dioxide
- 6.68**

<i>Potassium:</i>	NO_3^-	SO_4^{2-}	PO_4^{3-}
	KNO_3	K_2SO_4	K_3PO_4
	Potassium nitrate	Potassium sulfate	Potassium phosphate
- Iron(II):** $Fe(NO_3)_2$ $FeSO_4$ $Fe_3(PO_4)_2$
- Iron(II)
nitrate** **Iron(II)
sulfate** **Iron(II)
phosphate**
- Titanium(III):** $Ti(NO_3)_3$ $Ti_2(SO_4)_3$ $TiPO_4$
- Titanium(III)
nitrate** **Titanium(III)
sulfate** **Titanium(III)
phosphate**

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- 6.69** (a) Nickel(II) ion (b) Copper(I) ion
 (c) Iron(III) ion (d) Copper(II) ion
 (e) Lead(II) ion

- 6.72** (a) PtHPO_4 (b) $\text{Pt}(\text{H}_2\text{PO}_4)_2$

6.73

Formula	Corresponding Acid	Corresponding Anion
(a) HSO_4^-	H_2SO_4 , sulfuric acid	SO_4^{2-} , sulfate ion
(b) HCO_3^-	H_2CO_3 , carbonic acid	CO_3^{2-} , carbonate ion
(c) HS^-	H_2S , hydrosulfuric acid	S^{2-} , sulfide ion
(d) H_2PO_4^-	H_3PO_4 , phosphoric acid	PO_4^{3-} , phosphate ion

- 6.79** (a) Sulfate ion (b) Selenate ion
 (c) Phosphate ion (d) Arsenate ion

- 6.80** (a) CaO (b) Na_2O_2 (c) PbO_2 (d) K_2O_2

- 6.82** (a) Nickel(II) hydrogen carbonate
 (b) Chromium(III) chloride
 (c) Iron(III) sulfate
 (d) Cobalt(III) oxide

- 6.85** (a) Mg_3N_2 (b) $\text{Al}_2(\text{SO}_4)_3$ (c) PbO_2

- 6.86** H_2S , HS^- , and H_2S^-

Type	Name
(a) IV	Iron(III) fluoride
(b) IV	Nickel(II) oxide
(c) C	Iodine trichloride
(d) IC	Sodium hydride
(e) IV	Gold(I) sulfide
(f) IC	Magnesium hydroxide
(g) A	Nitric acid
(h) IC	Ammonium sulfate
(i) IC	Magnesium sulfite
(j) A	Phosphorous acid
(k) A	Hydrochloric acid
(l) IC	Potassium carbonate
(m) IC	Ammonium dichromate

Type	
(a) IV	CoCO_3
(b) C	PI_3
(c) A	H_2SO_3
(d) IC	NH_4BrO_3
(e) IV	MnO_2
(f) C	SF_6
(g) IC	$\text{Ba}_3(\text{PO}_4)_2$
(h) A	HNO_2
(i) C	CCl_4
(j) IV	FeCl_2
(k) C	P_2S_5

- 6.101** (a) Calcium oxide
 (b) Nitric acid
 (c) Titanium(III) hydroxide
 (d) Manganese(II) chromate
 (e) Nickel(II) nitrate
 (f) Potassium dichromate
 (g) Chromium(III) chloride
 (h) Nitrogen trifluoride
 (i) Sulfur tetrafluoride
 (j) Sulfurous acid

- 6.105** (a) Fe_2O_3 (b) Co_2O_3 (c) BrF_3
 (d) LiH (e) AuBr_3 (f) $\text{Mg}(\text{ClO}_4)_2$
 (g) Li_3N (h) CCl_4 (i) CaH_2

- 6.109** (a) HN_3 (b) Hydrazoic acid

- 6.112** Addition of neutral oxygen atoms to a pair of electrons on the monatomic anion does not change the charge on the resulting oxoanion. [The second-period oxoanions are small

and electronegative, and therefore lose an oxygen atom and two charges (an “oxide ion”) to yield a smaller oxoanion with a negative charge two units lower.]

7 Formula Calculations

- 7.1** (a) Multiply by 2 to get 3/2.
 (b) Multiply by 4 to get 9/4.
 (c) Multiply by 3 to get 10/3.
 (d) Multiply by 3 to get 11/3.
 (e) Multiply by 4 to get 11/4.
 (f) Multiply by 5 to get 6/5.

- 7.3** (a) grams (b) amu (c) amu (d) amu
 (e) g/mol

- 7.4** (a) 18 pairs (b) 18 socks (c) 9 pairs
 (d) 36 socks (e) 0.75 dozen pairs
 (f) 3 dozen socks

7.5 The parts of this problem mirror those of Problem 7.4. Instead of pairs of socks, there are pairs of nitrogen atoms bonded into molecules; instead of dozens, there are moles. Note that each answer is different, although some of the numbers in the answers are the same.

- (a) $9.03 \times 10^{23} \text{ Cl}_2$ molecules
 (b) $9.03 \times 10^{23} \text{ Cl}$ atoms
 (c) $4.52 \times 10^{23} \text{ Cl}_2$ molecules
 (d) $1.81 \times 10^{24} \text{ Cl}$ atoms
 (e) 0.750 mol Cl_2 molecules
 (f) 3.00 mol Cl atoms

7.6 The compound contains 92.3% carbon, no matter what the size of the sample is. Percent composition is an intensive property; that is, compounds have definite compositions. The mass of carbon is

$$29.7 \text{ g sample} \left(\frac{92.3 \text{ g C}}{100 \text{ g sample}} \right) = 27.4 \text{ g C}$$

- 7.7** (a) The socks weigh the same, whether or not they are rolled together.
 (b) Two dozen pairs weigh twice as much because there are twice as many socks.
 (c) The atoms have the same mass, whether or not they are bonded.
 (d) The 2.00 mol of nitrogen molecules has double the mass because there are twice as many atoms as 2.00 mol of nitrogen atoms.

- 7.9** (a) A dozen grapefruit weighs more because each grapefruit weighs more than each cherry. There are the same number of fruits; a dozen is 12 in each case.
 (b) A mole of iodine weighs more because each iodine atom weighs more than each fluorine atom. There are the same number of atoms in each case because a mole of atoms is 6.02×10^{23} atoms.

- 7.10** (a) 1.0 ft
 (b) 4.0 ft
 $1 \text{ dozen boxes} \left(\frac{4.0 \text{ in.}}{1 \text{ box}} \right) \left(\frac{1 \text{ ft}}{12 \text{ in.}} \right) \left(\frac{12 \text{ boxes}}{1 \text{ dozen}} \right) = 4.0 \text{ ft}$

- (c) 7.0 ft
 (d) The factor (12) that converts inches to feet also converts boxes to dozens of boxes, and the factors cancel each other.

- 7.12** (a) The molar mass (formula mass in grams per mole)

- (b) Avogadro’s number

- 7.13** Avogadro’s number is used to convert the number of formula units to moles and then the molar mass is used to convert the number of moles to the mass. (See Figure 7.1.)

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7.14 Rounding First:

- (a) $12(12.01 \text{ amu}) + 26(1.01 \text{ amu}) = 170.38 \text{ amu}$
 (b) $39.10 \text{ amu} + 35.45 \text{ amu} + 4(16.00 \text{ amu}) = 138.55 \text{ amu}$
 (c) $30.97 \text{ amu} + 3(35.45 \text{ amu}) = 137.32 \text{ amu}$

Rounding Last:

- (a) $12(12.011 \text{ amu}) + 26(1.0080 \text{ amu}) = 170.34 \text{ amu}$
 (b) $39.102 \text{ amu} + 35.453 \text{ amu} + 4(15.9994) \text{ amu} = 138.55 \text{ amu}$
 (c) $30.9738 \text{ amu} + 3(35.453 \text{ amu}) = 137.33 \text{ amu}$

The initial rounding can make a small difference.

7.15 CCl_4 , C_2H_4 , and S_8 are substances that exist in the form of molecules and thus have molecular masses. Ne can be considered a monatomic molecule, in which case its molecular mass is equal to its atomic mass. All of the substances have molar masses, whether they exist in the form of molecules or not.

- 7.17** (a) Molecular mass (b) Atomic mass
 (c) Formula mass (d) Molecular mass
 (e) Atomic mass (f) Molar mass

7.18 $1.00 \text{ mol Al}(\text{ClO}_3)_3 \left(\frac{3 \text{ mol Cl}}{1 \text{ mol Al}(\text{ClO}_3)_3} \right) = 3.00 \text{ mol Cl}$

7.20 Intensive

7.21 The molar mass is 17.0 g/mol, no matter what size sample of the compound is considered. Molar mass is an intensive property.

- 7.22** (a) The atomic mass refers to an N atom; the molecular mass refers to an N_2 molecule.
 (b) The phrase might refer to the mass of a mole of nitrogen atoms or the mass of a mole of nitrogen molecules.
 (c) It refers to the molar mass of N_2 molecules because nitrogen gas exists in the form of diatomic molecules.

7.23 Only CH , C_5H_9 and C_9H_{17} are empirical formulas. For each of the other formulas, the subscripts can be evenly divided by a small integer.

- 7.26** (a) C_2H_3 (b) $\text{C}_2\text{H}_3\text{O}$ (c) CH_2O
 (d) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

- 7.27** (a) Molecular formula (b) Empirical formula
 (c) Percent composition

7.28 We can do calculations that lead us to the empirical formula.

7.29 The formula yields the following information:

Sodium, copper, carbon, and nitrogen are present, and all the atoms are bonded together in some way.

The carbon atom and the nitrogen atom of each CN group are covalently bonded together.

The mole ratios of atoms of each element to each other and to formula units of the compound are given.

7.30 Hg_2Cl_2 is ionic—it contains Cl^- ions—but the formula is not an empirical formula. (The cation has an even charge and an even number of mercury atoms.)

- 7.32** (a) 2 mol C, 1 mol N, 7 mol H
 (b) 1 mol In, 6 mol C, 9 mol H, 6 mol O
 (c) 3 mol Na, 1 mol Co, 6 mol F
 (d) 1 mol Co, 6 mol N, 18 mol H, 1 mol P, 4 mol O

- 7.35** (a) 1.008 amu, for a hydrogen atom
 (b) 2.016 amu, for an H_2 molecule
 (If a smaller value is calculated for an atomic mass or molecular mass, there is a mistake somewhere.)

- 7.36** (a) 1 Na $1 \times 23.0 \text{ amu} = 23.0 \text{ amu}$
 1 H $1 \times 1.0 \text{ amu} = 1.0 \text{ amu}$
 1 C $1 \times 12.0 \text{ amu} = 12.0 \text{ amu}$
 3 O $3 \times 16.0 \text{ amu} = 48.0 \text{ amu}$
 Total = 84.0 amu

(b) Ca $= 40.1 \text{ amu}$
 2 C $2 \times 12.0 \text{ amu} = 24.0 \text{ amu}$
 2 N $2 \times 14.0 \text{ amu} = 28.0 \text{ amu}$
 2 S $2 \times 32.1 \text{ amu} = 64.2 \text{ amu}$
 Total = 156.3 amu

(c) 116.1 amu (d) 164 amu
 (e) 114.2 amu (f) 181.3 amu

7.40 12 C $12 \times 12.01 \text{ amu} = 144.12 \text{ amu}$
 17 H $17 \times 1.008 \text{ amu} = 17.136 \text{ amu}$
 4 N $4 \times 14.01 \text{ amu} = 56.04 \text{ amu}$
 O $16.00 \text{ amu} = 16.00 \text{ amu}$
 S $32.06 \text{ amu} = 32.06 \text{ amu}$
 Cl $35.45 \text{ amu} = 35.45 \text{ amu}$
 Total = 300.81 amu

$$\% \text{ C} = \left(\frac{144.12 \text{ amu}}{300.81 \text{ amu}} \right) \times 100.0\% = 47.91\%$$

$$\% \text{ H} = \left(\frac{17.136 \text{ amu}}{300.81 \text{ amu}} \right) \times 100.0\% = 5.70\%$$

$$\% \text{ N} = \left(\frac{56.04 \text{ amu}}{300.81 \text{ amu}} \right) \times 100.0\% = 18.63\%$$

$$\% \text{ O} = \left(\frac{16.00 \text{ amu}}{300.81 \text{ amu}} \right) \times 100.0\% = 5.32\%$$

$$\% \text{ S} = \left(\frac{32.06 \text{ amu}}{300.81 \text{ amu}} \right) \times 100.0\% = 10.66\%$$

$$\% \text{ Cl} = \left(\frac{35.45 \text{ amu}}{300.81 \text{ amu}} \right) \times 100.0\% = 11.78\%$$

Total = $\overline{100.0\%}$

7.44 Each compound consists of 85.63% carbon and 14.37% hydrogen. They have the same mass ratio of carbon to hydrogen because they have the same mole ratio of carbon to hydrogen; that is, they have the same empirical formula (CH_2).

7.47 (a) 2 Na $2 \times 23.0 \text{ amu} = 46.0 \text{ amu}$
 2 Cr $2 \times 52.00 \text{ amu} = 104.0 \text{ amu}$
 7 O $7 \times 16.00 \text{ amu} = 112.0 \text{ amu}$
 Total = 262.0 amu

$$\% \text{ Na} = \frac{46.0 \text{ amu}}{262.0 \text{ amu}} \times 100\% = 17.6\% \text{ Na}$$

$$\% \text{ Cr} = \frac{104.0 \text{ amu}}{262.0 \text{ amu}} \times 100\% = 39.7\% \text{ Cr}$$

$$\% \text{ O} = \frac{112.0 \text{ amu}}{262.0 \text{ amu}} \times 100\% = 42.7\% \text{ O}$$

Total = $\overline{100.0\%}$

(b) 1 K $1 \times 39.1 \text{ amu} = 39.1 \text{ amu}$
 1 Mn $1 \times 54.9 \text{ amu} = 54.9 \text{ amu}$
 4 O $4 \times 16.0 \text{ amu} = 64.0 \text{ amu}$
 Total = 158.0 amu

$$\% \text{ K} = \frac{39.1 \text{ amu}}{158.0 \text{ amu}} \times 100\% = 24.7\% \text{ K}$$

$$\% \text{ Mn} = \frac{54.9 \text{ amu}}{158.0 \text{ amu}} \times 100\% = 34.7\% \text{ Mn}$$

$$\% \text{ O} = \frac{64.0 \text{ amu}}{158.0 \text{ amu}} \times 100\% = 40.5\% \text{ O}$$

Total = $\overline{99.9\%}$

- 7.52** (a) 96.0 amu and 96.0 g/mol

- (b) 304 amu and 304 g/mol

- (c) 128 amu and 128 g/mol

7.53 $1.76 \text{ mol HC}_2\text{H}_3\text{O}_2 \left(\frac{60.0 \text{ g HC}_2\text{H}_3\text{O}_2}{1 \text{ mol HC}_2\text{H}_3\text{O}_2} \right) = 106 \text{ g}$

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7.55 (a) $1.25 \text{ mol O} \left(\frac{16.0 \text{ g O}}{1 \text{ mol O}} \right) = 20.0 \text{ g O}$

(b) Same as part (a)

(c) $1.25 \text{ mol O}_2 \left(\frac{32.0 \text{ g O}}{1 \text{ mol O}_2} \right) = 40.0 \text{ g O}_2$

7.59 $12.9 \text{ g} \left(\frac{1 \text{ mol}}{62.0 \text{ g}} \right) = 0.208 \text{ mol}$

7.61 (a) $1 \text{ atom} \left(\frac{1.00 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} \right) \left(\frac{16.0 \text{ g}}{1 \text{ mol}} \right) = 2.66 \times 10^{-23} \text{ g}$

(b) One molecule has a mass twice that.

7.62 $12.9 \text{ g} \left(\frac{1 \text{ mol}}{64.0 \text{ g}} \right) \left(\frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) = 1.21 \times 10^{23} \text{ molecules}$

7.65 $3.91 \times 10^{24} \text{ molecules CH}_4$

7.66 (a) $9.25 \times 10^{20} \text{ units} \left(\frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ units}} \right) = 1.54 \times 10^{-3} \text{ mol}$

(b) $1.67 \text{ mol} \left(\frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) = 1.01 \times 10^{24} \text{ molecules}$

7.67 $1.91 \times 10^{24} \text{ molecules} \left(\frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}} \right) \left(\frac{342 \text{ g}}{1 \text{ mol}} \right) = 1085 \text{ g} = 1.09 \text{ kg}$

7.69 (a) $44.7 \text{ g C}_2\text{H}_4 \left(\frac{1 \text{ mol C}_2\text{H}_4}{28.05 \text{ g C}_2\text{H}_4} \right) = 1.594 \text{ mol C}_2\text{H}_4$

(b) $1.594 \text{ mol C}_2\text{H}_4 \left(\frac{2 \text{ mol C atoms}}{1 \text{ mol C}_2\text{H}_4} \right) = 3.187 \text{ mol C atoms}$

(c) $3.187 \text{ mol C atoms} \left(\frac{6.02 \times 10^{23} \text{ C atoms}}{1 \text{ mol C atoms}} \right) = 1.92 \times 10^{24} \text{ C atoms}$

7.72 $4.11 \text{ mol NH}_3 \left(\frac{3 \text{ mol H}}{1 \text{ mol NH}_3} \right) \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 12.4 \text{ g H}$

7.76 $6.78 \times 10^{24} \text{ O atoms} \left(\frac{1 \text{ mol O atoms}}{6.02 \times 10^{23} \text{ O atoms}} \right) \times \left(\frac{1 \text{ mol H}_3\text{PO}_4}{4 \text{ mol O atoms}} \right) = 2.82 \text{ mol H}_3\text{PO}_4$

7.80 $125 \text{ g C}_6\text{H}_6 \left(\frac{1 \text{ mol C}_6\text{H}_6}{78.0 \text{ g C}_6\text{H}_6} \right) \left(\frac{6 \text{ mol H}}{1 \text{ mol C}_6\text{H}_6} \right) \times \left(\frac{6.02 \times 10^{23} \text{ H atoms}}{1 \text{ mol H atoms}} \right) = 5.79 \times 10^{24} \text{ H atoms}$

7.82 $1.44 \times 10^{25} \text{ C atoms} \left(\frac{1 \text{ molecule C}_5\text{H}_{12}}{5 \text{ C atoms}} \right) = 2.88 \times 10^{24} \text{ molecules C}_5\text{H}_{12}$

7.85 The only empirical formula: (c) $\text{K}_2\text{Cr}_2\text{O}_7$

7.87 (a) 85.63 g of carbon and 14.37 g of hydrogen

(b) 7.130 mol C and 14.26 mol H

(c) 1:2 (d) CH_2

7.88 $79.12 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 6.588 \text{ mol C}$

$9.79 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 9.71 \text{ mol H}$

$11.10 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 0.6938 \text{ mol O}$

The ratio of moles is

9.496 mol C : 14.0 mol H : 1.000 mol O

In integral numbers 19 mol C, 28 mol H, 2 mol O: $\text{C}_{19}\text{H}_{28}\text{O}_2$

7.91 $82.66 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 6.8826 \text{ mol C}$

$17.34 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 17.202 \text{ mol H}$

$\frac{6.8826 \text{ mol C}}{6.8826} = 1.000 \text{ mol C}$

$\frac{17.202 \text{ mol H}}{6.8826} = 2.4993 \text{ mol H}$

Multiply each of these by 2 to get 2 mol C to 5 mol H. The empirical formula is C_2H_5 .(b) Mn_3O_4 (c) P_2O_5 (d) $\text{C}_2\text{H}_4\text{Cl}$ (e) $\text{C}_2\text{H}_4\text{O}$ 7.96 (a) H_2SO_4 Sulfuric acid (b) Na_2SO_3 Sodium sulfite

7.98 (a) 13.0 amu and 78.0 amu (b) 14.0 amu and 42.0 amu (c) 15.0 amu and 30.0 amu

7.100 Each compound consists of 92.26% carbon and 7.74% hydrogen. They have the same mass ratio of carbon to hydrogen because they have the same mole ratio of carbon to hydrogen; that is, they have the same empirical formula (CH).

7.102 The empirical formula mass is 42.0 amu.

(a) There is one empirical formula unit in each molecule, so the molecular formula is NO_2 .(b) There are $(92.0 \text{ amu})/(46.0 \text{ amu}) = 2$ empirical formula units per molecule, so the molecular formula is N_2O_4 .7.105 Empirical formula: CH_2O ; molecular formula: $\text{C}_6\text{H}_{12}\text{O}_6$ 7.107 (a) $\text{C}_3\text{H}_8\text{O}_3$ (b) $\text{H}_2\text{C}_2\text{O}_4$ (c) $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_6$ (d) $\text{C}_3\text{H}_6\text{O}_2$

7.108 The mass per mole of empirical formula units is 31.0 g/mol. Therefore,

$$\frac{124 \text{ g/mol}}{31.0 \text{ g/mol empirical formula units}} = \frac{4 \text{ mol empirical formula units}}{1 \text{ mol}}$$

The formula is P_4 .7.110 C_2H_6

7.114 (a) The law of conservation of mass enables us to calculate the mass of oxygen used:

$$17.9 \text{ mg} + 11.0 \text{ mg} - 6.09 \text{ mg} = 22.81 \text{ mg}$$

(b) The number of millimoles of carbon in the reactant is the same as that in the CO_2 :

$$17.9 \text{ mg CO}_2 \left(\frac{1 \text{ mmol CO}_2}{44.0 \text{ mg CO}_2} \right) \left(\frac{1 \text{ mmol C}}{1 \text{ mmol CO}_2} \right) = 0.4068 \text{ mmol C}$$

$$(\text{c}) 11.0 \text{ mg H}_2\text{O} \left(\frac{1 \text{ mmol H}_2\text{O}}{18.0 \text{ mg H}_2\text{O}} \right) \left(\frac{2 \text{ mmol H}}{1 \text{ mmol H}_2\text{O}} \right) = 1.222 \text{ mmol H}$$

(d) The millimole ratio is 0.4068 mmol C : 1.222 mmol H or 1.00 mmol C : 3.00 mmol H

The empirical formula is CH_3 .7.116 We treat this problem as an empirical formula problem with H_2O as one of the “elements.”

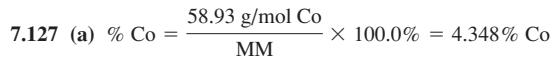
$$40.0 \text{ g C} \left(\frac{1 \text{ mol C}}{12.0 \text{ g C}} \right) = 3.33 \text{ mol C}$$

$$60.0 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 3.33 \text{ mol H}_2\text{O}$$

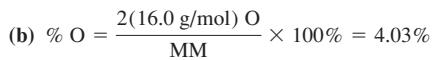
The ratio is 1:1 and the empirical formula is CH_2O .7.118 $4.14 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) \left(\frac{2 \text{ mol C}}{6 \text{ mol H}} \right) = 1.37 \text{ mol C}$

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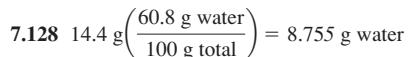
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$$MM = \frac{(58.93 \text{ g/mol})(100\%)}{4.348\%} = 1355 \text{ g/mol}$$



$$MM = \frac{3200 \text{ g/mol}}{4.03} = 794 \text{ g/mol}$$



$$8.755 \text{ g} \left(\frac{1 \text{ mol}}{18.0 \text{ g}} \right) \left(\frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) = 2.93 \times 10^{23} \text{ molecules}$$

- 7.132** Because the total of the percentages must be 100.00%, the percentage of hydrogen must be
 $100.00\% \text{ total} - 87.73\% \text{ C} = 12.27\% \text{ H}$

First, calculate the mass of carbon and the mass of hydrogen in 1.00 mol of compound:

$$1.00 \text{ mol compound} \left(\frac{82.0 \text{ g compound}}{1 \text{ mol compound}} \right) \left(\frac{12.27 \text{ g H}}{100 \text{ g compound}} \right) = 10.06 \text{ g H}$$

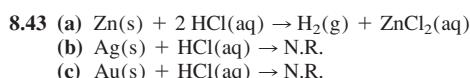
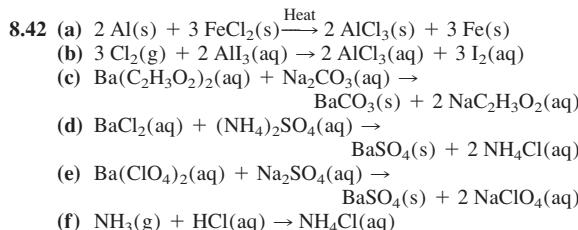
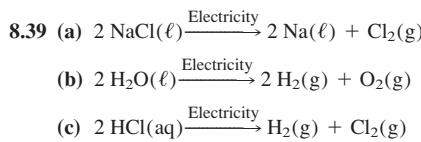
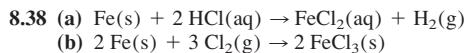
Now convert the number of grams of each element to moles of the element:

$$71.94 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 5.99 \text{ mol C}$$

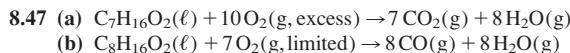
$$10.06 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 9.98 \text{ mol H}$$

The molecular formula is C_6H_{10} . Note that there is no need to try to get integral numbers of moles if an exact molar mass is given; the values come out very nearly integral. (If an approximate molar mass is given, the numbers of moles of each element must be rounded to the nearest integer. Retry Problem 7.110 this way.)

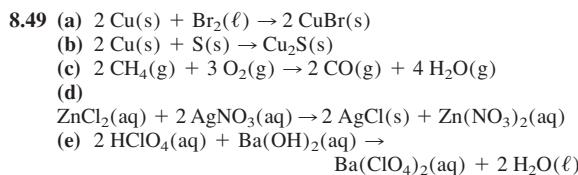
8 Chemical Reactions

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8.44 According to the table, alkali metal sulfides and ammonium sulfide are soluble.



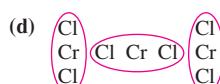
8.48 Double substitution reactions



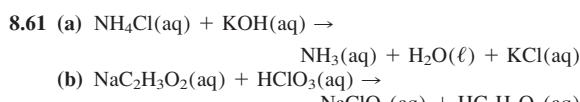
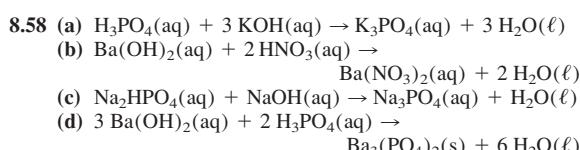
8.51 No reaction is expected in any part.

- (a) Mg is more active than Pb.
- (b) H is more active than Au.
- (c) No substitution reaction is possible, and Cl₂ cannot add to ZnCl₂.
- (d) Ne does not react with anything.

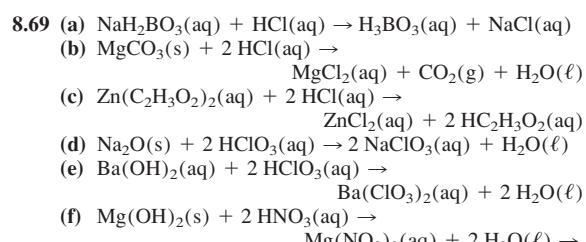
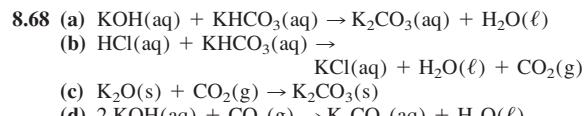
8.52 (a) Reducing the relative amount of chlorine
 (b) CrCl₂



8.53 No. As soon as it is prepared, it will decompose.



8.64 Add HCl to Ca, Ca(OH)₂, Ca(HCO₃)₂, or CaCO₃.

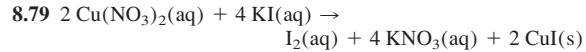


All of the reactions proceed due to formation of covalent compounds.

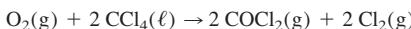
- 8.71** (a) A salt and water
 (b) A salt and water
 (c) A salt, water, and carbon dioxide
 (d) The carbon dioxide

8.72 There is no difference in the chemistry, but the questions get progressively harder to answer as more is left to interpret.

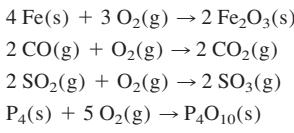
8.76 They are all balanced, but none goes as written: (a) and (b) go in the opposite direction; (c) does not go in either direction.



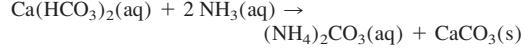
8.80 Oxygen is one of the reactants in a combustion reaction. Carbon and hydrogen are often components of the other reactant. Note that oxygen can be involved in a displacement reaction:



Combustion of substances that do not contain carbon *and* hydrogen can often be regarded as either combustion or combination:



8.81 CaCO₃ The reaction is



8.84 The reaction would produce CaCO₃(s) and NaCl(aq) from CaCl₂(aq) and Na₂CO₃(aq), not the products that are wanted.

- 8.92** (a) $4 \text{Li(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{Li}_2\text{O(s)}$
 (b) $2 \text{Na(s)} + \text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{O}_2(\text{s})$
 (c) $\text{K(s)} + \text{O}_2(\text{g}) \rightarrow \text{KO}_2(\text{s})$

9 Net Ionic Equations

9.1 In PCl₃, the chlorine atoms are covalently bonded to the phosphorus atom. In FeCl₃, the chloride ions are ionically bonded to the iron(III) ion. In Fe(ClO₃)₃, the iron(III) ion is ionically bonded to the chlorate ion, and within the chlorate ion, the oxygen atoms are covalently bonded to the chlorine atom. In Cl₂, the chlorine atoms are covalently bonded to each other.

- 9.2** (a) Mg²⁺ NO₂⁻ (b) Cr²⁺ F⁻
 (c) NH₄⁺ PO₄³⁻ (d) K⁺ SO₄²⁻
 (e) K⁺ MnO₄⁻ (f) Ba²⁺ O₂²⁻

APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems

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- 9.3 Soluble? Ionic? Written As Separate Ions?**
- | | | | |
|--------------------------------------|-----|-----|--|
| (a) H ₂ O ₂ | Yes | No | No, written H ₂ O ₂ (aq) |
| (b) Hg ₂ Cl ₂ | No | Yes | No, written Hg ₂ Cl ₂ |
| (c) HgCl ₂ | Yes | Yes | Yes, written
Hg ²⁺ (aq) + 2 Cl ⁻ (aq) |
| (d) HI | Yes | Yes | Yes, written H ⁺ (aq) + I ⁻ (aq) |
| (e) HClO ₄ | Yes | Yes | Yes, written
H ⁺ (aq) + ClO ₄ ⁻ (aq) |
| (f) C ₄ H ₉ OH | Yes | No | No, written C ₄ H ₉ OH(aq) |
- 9.4** (a) H₃PO₄(aq) (Weak acid)
 (b) BaSO₄(s) (Solid)
 (c) Ag⁺(aq) + C₂H₃O₂⁻(aq)
 (d) Pb²⁺(aq) + 2 ClO₃⁻(aq)
 (e) NH₄⁺(aq) + IO₃⁻(aq)
 (f) PbCl₂(s) (Solid)
 (g) K⁺(aq) + MnO₄⁻(aq)
 (h) 2 K⁺(aq) + Cr₂O₇²⁻(aq)
 (i) H⁺(aq) + NO₃⁻(aq)
 (j) C₃H₆O(aq) (Covalent)
- 9.6** (a) In the pure state, no common acids exist as ions.
 (b) In water solution, the strong acids (Table 9.1) exist in the form of their ions.
- 9.7** (a) H⁺(aq) + Cl⁻(aq) (HCl is a strong acid.)
 (b) HClO(aq) (HClO is a weak acid.)
 (c) HClO₂(aq) (HClO₂ is a weak acid.)
 (d) H⁺(aq) + ClO₃⁻(aq) (HClO₃ is a strong acid.)
 (e) H⁺(aq) + ClO₄⁻(aq) (HClO₄ is a strong acid.)
- 9.8** All salts are ionic, and all potassium salts are soluble.
 (a) K⁺(aq) + Cl⁻(aq) (b) K⁺(aq) + ClO₃⁻(aq)
 (c) K⁺(aq) + ClO₂⁻(aq) (d) K⁺(aq) + ClO₄⁻(aq)
 (e) K⁺(aq) + ClO₄⁻(aq)
- 9.9** (a)-(c) Zn(s) + 2 H⁺(aq) → Zn²⁺(aq) + H₂(g)
- 9.11** (a) HCl(g) is a strong electrolyte because its aqueous *solution* conducts (but the gas does not).
 (b) KCl(s) is a strong electrolyte because its *solution* conducts (but the solid does not).
 (c) H₂SO₃ does not conduct pure, but in aqueous solution it conducts poorly; it is a weak electrolyte.
- 9.13** It contains Cl⁻ ions, water, and some type of cation, such as Na⁺, that forms a soluble compound with chloride ion. No bottle can contain only cations or only anions.
- 9.14** (a) Cu²⁺(aq) + SO₄²⁻(aq)
 (b) H₂S(aq)
 (c) HNO₃(aq)
 (d) UO₂²⁺(aq) + 2 NO₃⁻(aq)
 (e) 2 NH₄⁺(aq) + Cr₂O₇²⁻(aq)
- 9.15** (a) H⁺(aq) + ClO₄⁻(aq)
 (b) Cu²⁺(aq) + 2 Cl⁻(aq)
 (c) HClO₂(aq) (Not ionic)
 (d) Cu₂S(s) (Not soluble)
 (e) AgCl(s) (Not soluble)
 (f) 2 NH₄⁺(aq) + SO₃²⁻(aq)
- 9.17** In each case, a compound that is ionic in solution is required.
 (a) NaF yields Na⁺ and F⁻ ions and is thus better. HF ionizes to only a very limited extent.
 (b) Because HCl is a *strong* acid, both compounds are fully ionic in solution, and either would be suitable.
- 9.19** Not only the *atoms* but also the *net charges* must be balanced.
 (a) Pb(s) + 2 Cr³⁺(aq) → 2 Cr²⁺(aq) + Pb²⁺(aq)
 (b) 2 Br⁻(aq) + 2 Ce⁴⁺(aq) → 2 Ce³⁺(aq) + Br₂(aq)
 (c) 2 Ag⁺(aq) + Cu(s) → Cu²⁺(aq) + 2 Ag(s)
 (d) Cu₂O(s) + 2 H⁺(aq) → Cu(s) + Cu²⁺(aq) + H₂O(ℓ)
 (e) 2 Co³⁺(aq) + Co(s) → 3 Co²⁺(aq)

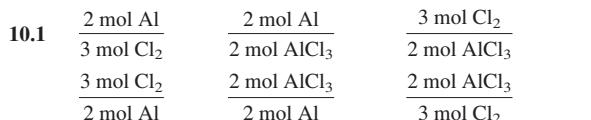
- 9.20** M₂O₃(s) + 6 H⁺(aq) → 2 M³⁺(aq) + 3 H₂O(ℓ)
- 9.22** (a) Ba²⁺(aq) + CO₃²⁻(aq) → BaCO₃(s)
 (b) 2 H⁺(aq) + Ba(OH)₂(s) → Ba²⁺(aq) + 2 H₂O(ℓ)
 Ba(OH)₂ is only slightly soluble; here, it exists as a solid and is written as a compound.
 (c) HCO₃⁻(aq) + OH⁻(aq) → CO₃²⁻(aq) + H₂O(ℓ)
 (d) HCO₃⁻(aq) + H⁺(aq) → H₂O(ℓ) + CO₂(g)
 (e) Br⁻(aq) + Ag⁺(aq) → AgBr(s)
 (f) Pb²⁺(aq) + 2 I⁻(aq) → PbI₂(s)
- 9.23** Obviously it is easier to write the one net ionic equation:
 2 Cl⁻(aq) + Pb²⁺(aq) → PbCl₂(s)
- 9.29** (a) H⁺(aq) + OH⁻(aq) → H₂O(ℓ)
 (b) HClO₂(aq) + OH⁻(aq) → ClO₂⁻(aq) + H₂O(ℓ)
 Note that HClO₃ is a strong acid and is completely ionized in water; HClO₂ is a weak acid and exists mostly in the form of covalent molecules, so it is written as a compound in the net ionic equation.
- 9.30** (a) NH₄⁺(aq) + OH⁻(aq) → NH₃(aq) + H₂O(ℓ)
 (b) NH₃(aq) + H⁺(aq) → NH₄⁺(aq)
- 9.35** Two of the many possible equations are
 2 HCl(aq) + Na₂CO₃(aq) → 2 NaCl(aq) + H₂O(ℓ) + CO₂(g)
 2 HBr(aq) + Na₂CO₃(aq) → 2 NaBr(aq) + H₂O(ℓ) + CO₂(g)
 Using other strong acids and/or other soluble carbonates would give at least 54 additional equations.
- 9.38** (a) H⁺(aq) + OH⁻(aq) → H₂O(ℓ)
 (b) H⁺(aq) + NH₃(aq) → NH₄⁺(aq)
 (c) HA(aq) + OH⁻(aq) → A⁻(aq) + H₂O(ℓ)
- 9.41** (a) Pb²⁺(aq) + SO₄²⁻(aq) → PbSO₄(s)
 (b) Ag⁺(aq) + CN⁻(aq) → AgCN(s)
 (c) H⁺(aq) + NH₃(aq) → NH₄⁺(aq)
 (d) H⁺(aq) + CO₃²⁻(aq) → HCO₃⁻(aq)
 (e) HCO₃⁻(aq) + H⁺(aq) → H₂O(ℓ) + CO₂(g)
 (f) HCO₃⁻(aq) + OH⁻(aq) → H₂O(ℓ) + CO₃²⁻(aq)
- 9.46** See Figure 8.10.
 (a) CO₃²⁻(aq) + 2 H⁺(aq) → CO₂(g) + H₂O(ℓ)
 (b) HCO₃⁻(aq) + H⁺(aq) → CO₂(g) + H₂O(ℓ)
 (c) HCO₃⁻(aq) + OH⁻(aq) → CO₃²⁻(aq) + H₂O(ℓ)
 (d) CO₂(g) + 2 OH⁻(aq) → CO₃²⁻(aq) + H₂O(ℓ)
- 9.47** CHCl₃ is not ionic. The Ag⁺ ion precipitates AgCl in the presence of Cl⁻ ions, but no Cl⁻ ions are present in this case.
- 9.49** The total equation is
 2 Na(s) + 2 H₂O(ℓ) → H₂(g) + 2 NaOH(aq)
 The net ionic equation is
 2 Na(s) + 2 H₂O(ℓ) → H₂(g) + 2 Na⁺(aq) + 2 OH⁻(aq)
 This is one of very few net ionic equations in which an alkali metal ion appears. Most of the time, alkali metal ions are spectator ions because they don't form insoluble salts or covalent compounds and don't often change ionic charges.
- 9.50** 2 CaC₂O₄(s) + 2 HCl(aq) → CaCl₂(aq) + Ca(HC₂O₄)₂(aq)
- 9.51** MgC₂O₄(s) + H⁺(aq) → HC₂O₄⁻(aq) + Mg²⁺(aq)
- 9.53** They yield the same quantity of heat because they are essentially the same reaction:
 H⁺(aq) + OH⁻(aq) → H₂O(ℓ)
 The quantity of heat liberated in this reaction does not depend on the anion and the cation that *do not* react.
- 9.54** The net ionic equations are
 S²⁻(aq) + H⁺(aq) → HS⁻(aq) + 59.4 kJ
 HS⁻(aq) + H⁺(aq) → H₂S(g) + 2.5 kJ
 S²⁻(aq) + 2 H⁺(aq) → H₂S(g)

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The sum of the first two equations is the third, and the same is true for the heats of reaction:

$$59.4 \text{ kJ} + 2.5 \text{ kJ} = 61.9 \text{ kJ}$$

The spectator ions do not contribute to the heat of reaction because they do not react.

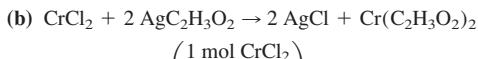
10 Stoichiometry

- 10.3** (a) 36 HCl molecules (b) 72 HCl molecules
 (c) 300 HCl molecules (d) 3 dozen HCl molecules
 (e) 3 mol HCl (f) 9 mol HCl

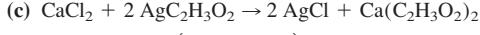
10.5 All of them. (The equation merely gives the *mole ratio*, not any particular number of moles.)



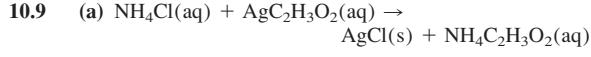
$$2.20 \text{ mol AgCl} \left(\frac{1 \text{ mol CoCl}_2}{2 \text{ mol AgCl}} \right) = 1.10 \text{ mol CoCl}_2$$



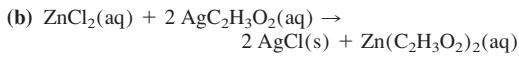
$$2.20 \text{ mol AgCl} \left(\frac{1 \text{ mol CrCl}_2}{2 \text{ mol AgCl}} \right) = 1.10 \text{ mol CrCl}_2$$



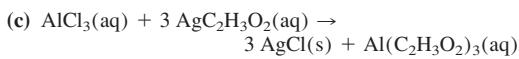
$$2.20 \text{ mol AgCl} \left(\frac{1 \text{ mol CaCl}_2}{2 \text{ mol AgCl}} \right) = 1.10 \text{ mol CaCl}_2$$



$$0.700 \text{ mol AgCl} \left(\frac{1 \text{ mol NH}_4\text{Cl}}{1 \text{ mol AgCl}} \right) = 0.700 \text{ mol NH}_4\text{Cl}$$



$$0.700 \text{ mol AgCl} \left(\frac{1 \text{ mol ZnCl}_2}{2 \text{ mol AgCl}} \right) = 0.350 \text{ mol ZnCl}_2$$



$$0.700 \text{ mol AgCl} \left(\frac{1 \text{ mol AlCl}_3}{3 \text{ mol AgCl}} \right) = 0.233 \text{ mol AlCl}_3$$

10.10 (a) 12 sandwiches

(b) 12 sandwiches (This problem involves a limiting quantity; you cannot make 14 sandwiches with only 24 slices of bread.)

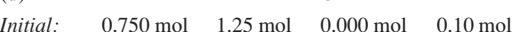
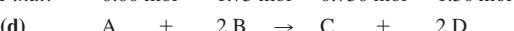
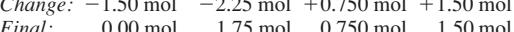
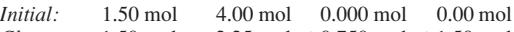
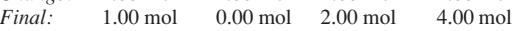
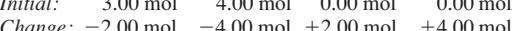
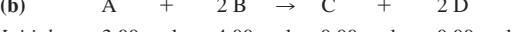
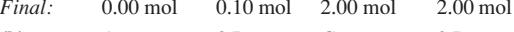
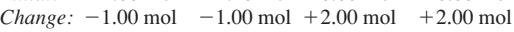
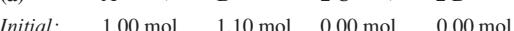
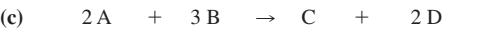
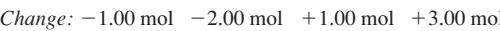
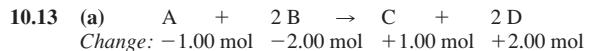
(c) 11 sandwiches (You cannot make 12 sandwiches with only 11 patties.)

(d) The quantities of two (or more) reactants are given in the problem statement.

10.11 (a) No NaBr can be produced without any bromine.

(b) 2 mol of NaBr can be produced. The numbers of moles present are exactly the same as the coefficients in the balanced equation.

(c) 2 mol of NaBr can be produced. The sum of the numbers of moles of reactants in parts (a) and (b) produces the sum of the numbers of moles of products. Put another way, after 1 mol of Br₂ reacts with 2 mol of Na, as in part (b), there is no more Br₂ left, and we are back to the situation in part (a).



10.16 Decomposition reactions have only one reactant.

10.17 (a) 2.00 mol

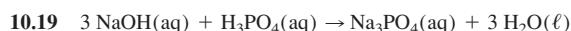
(b) No (There is no assurance that all the H₂ reacts.)

(c) Yes (4.50 mol)

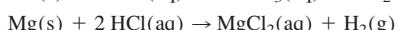
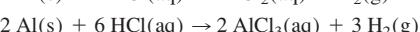
10.18 (a) 3 mol

(b) 3 mol [The number of moles of HCl is the limiting quantity, even though it is greater than the number of moles of La(OH)₃.]

(c) 2 mol [The La(OH)₃ is present in limiting quantity.]

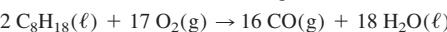


$$1.29 \text{ mol NaOH} \left(\frac{1 \text{ mol H}_3\text{PO}_4}{3 \text{ mol NaOH}} \right) = 0.430 \text{ mol H}_3\text{PO}_4$$

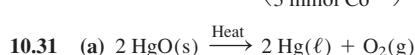
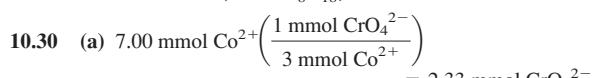


The sample of aluminum can produce the most hydrogen because there is a 3:2 mole ratio of hydrogen to aluminum metal in the balanced equation for that reaction and only a 1:1 mole ratio in the other two equations. That is, each mole of aluminum produces more hydrogen.

10.26 Note that *incomplete combustion* means formation of CO rather than CO₂. The balanced equation is



$$7.80 \text{ mol C}_8\text{H}_{18} \left(\frac{17 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} \right) = 66.3 \text{ mol O}_2$$



(b) The product (Not all of the HgO reacted.)

APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems

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(c) $1.50 \text{ mmol O}_2 \left(\frac{2 \text{ mmol HgO}}{1 \text{ mmol O}_2} \right) = 3.00 \text{ mmol HgO reacted}$
 $\frac{3.00 \text{ mmol HgO reacted}}{8.00 \text{ mmol HgO present}} \times 100\% = 37.5\% \text{ reacted}$

- 10.32** (a) $\text{Zn(s)} + 2 \text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$
 $2.48 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.37 \text{ g Zn}} \right) \left(\frac{1 \text{ mol H}_2}{1 \text{ mol Zn}} \right) = 0.0379 \text{ mol H}_2$
- (b) $\text{Cd(s)} + 2 \text{HCl(aq)} \rightarrow \text{CdCl}_2\text{(aq)} + \text{H}_2\text{(g)}$
 $2.48 \text{ g Cd} \left(\frac{1 \text{ mol Cd}}{112.4 \text{ g Cd}} \right) \left(\frac{1 \text{ mol H}_2}{1 \text{ mol Cd}} \right) = 0.0221 \text{ mol H}_2$
- (c) Although the number of grams of each metal is the same, the numbers of moles are different because of the difference in atomic masses. Therefore, the number of moles of H_2 produced differs.
- 10.33** (a) $2 \text{C}_4\text{H}_{10}\text{(g)} + 13 \text{O}_2\text{(g)} \rightarrow 8 \text{CO}_2\text{(g)} + 10 \text{H}_2\text{O(g)}$
- (b) $14.9 \text{ g CO}_2 \left(\frac{1 \text{ mol CO}_2}{44.0 \text{ g CO}_2} \right) = 0.3386 \text{ mol CO}_2$
- (c) $0.3386 \text{ mol CO}_2 \left(\frac{2 \text{ mol C}_4\text{H}_{10}}{8 \text{ mol CO}_2} \right) = 0.08465 \text{ mol C}_4\text{H}_{10}$
- (d) $0.08465 \text{ mol C}_4\text{H}_{10} \left(\frac{58.0 \text{ g C}_4\text{H}_{10}}{1 \text{ mol C}_4\text{H}_{10}} \right) = 4.91 \text{ g C}_4\text{H}_{10}$
- (e) $14.9 \text{ g CO}_2 \left(\frac{1 \text{ mol CO}_2}{44.0 \text{ g CO}_2} \right) \left(\frac{2 \text{ mol C}_4\text{H}_{10}}{8 \text{ mol CO}_2} \right) \left(\frac{58.0 \text{ g C}_4\text{H}_{10}}{1 \text{ mol C}_4\text{H}_{10}} \right) = 4.91 \text{ g C}_4\text{H}_{10}$

- 10.35** (a) $\text{CoCl}_3\text{(aq)} + 3 \text{AgC}_2\text{H}_3\text{O}_2\text{(aq)} \rightarrow 3 \text{AgCl(s)} + \text{Co(C}_2\text{H}_3\text{O}_2)_3\text{(aq)}$
 $4.00 \text{ mol AgCl} \left(\frac{1 \text{ mol CoCl}_3}{3 \text{ mol AgCl}} \right) \left(\frac{165 \text{ g CoCl}_3}{1 \text{ mol CoCl}_3} \right) = 220 \text{ g CoCl}_3$
- (b) $\text{CaCl}_2\text{(aq)} + 2 \text{AgC}_2\text{H}_3\text{O}_2\text{(aq)} \rightarrow 2 \text{AgCl(s)} + \text{Ca(C}_2\text{H}_3\text{O}_2)_2\text{(aq)}$
 $4.00 \text{ mol AgCl} \left(\frac{1 \text{ mol CaCl}_2}{2 \text{ mol AgCl}} \right) \left(\frac{111 \text{ g CaCl}_2}{1 \text{ mol CaCl}_2} \right) = 222 \text{ g CaCl}_2$
- (c) $\text{KCl(aq)} + \text{AgC}_2\text{H}_3\text{O}_2\text{(aq)} \rightarrow \text{AgCl(s)} + \text{KC}_2\text{H}_3\text{O}_2\text{(aq)}$
 $4.00 \text{ mol AgCl} \left(\frac{1 \text{ mol KCl}}{1 \text{ mol AgCl}} \right) \left(\frac{74.6 \text{ g KCl}}{1 \text{ mol KCl}} \right) = 298 \text{ g KCl}$
- 10.39** $10.0 \times 10^6 \text{ g Al} \left(\frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right) \left(\frac{1 \text{ mol Al}_2\text{O}_3}{2 \text{ mol Al}} \right) \left(\frac{102 \text{ g Al}_2\text{O}_3}{1 \text{ mol Al}_2\text{O}_3} \right) = 1.89 \times 10^7 \text{ g Al}_2\text{O}_3$
- 10.41** (a) $\text{Zn(s)} + 2 \text{AgNO}_3\text{(aq)} \rightarrow 2 \text{Ag(s)} + \text{Zn(NO}_3)_2\text{(aq)}$
- (b) $12.10 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.37 \text{ g Zn}} \right) = 0.1851 \text{ mol Zn}$
- (c) $0.1851 \text{ mol Zn} \left(\frac{2 \text{ mol Ag}}{1 \text{ mol Zn}} \right) = 0.3702 \text{ mol Ag}$
- (d) $0.3702 \text{ mol Ag} \left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} \right) = 39.94 \text{ g Ag}$
- (e) $12.10 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.37 \text{ g Zn}} \right) \left(\frac{2 \text{ mol Ag}}{1 \text{ mol Zn}} \right) \left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} \right) = 39.94 \text{ g Ag}$
- 10.42** $2 \text{KOH(aq)} + \text{H}_2\text{C}_2\text{O}_4\text{(aq)} \rightarrow \text{K}_2\text{C}_2\text{O}_4\text{(aq)} + 2 \text{H}_2\text{O(l)}$
 $71.3 \text{ g H}_2\text{C}_2\text{O}_4 \left(\frac{1 \text{ mol H}_2\text{C}_2\text{O}_4}{90.0 \text{ g H}_2\text{C}_2\text{O}_4} \right) \left(\frac{2 \text{ mol KOH}}{1 \text{ mol H}_2\text{C}_2\text{O}_4} \right) = 1.58 \text{ mol KOH}$

- 10.43** (a) and (b) $12.2 \text{ g NaHCO}_3 \left(\frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g NaHCO}_3} \right) \times \left(\frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol NaHCO}_3} \right) \left(\frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} \right) = 7.70 \text{ g Na}_2\text{CO}_3$
- (c) Parts (a) and (b) are the same problem because Na_2CO_3 is the only solid product.
- 10.44** $82.3 \text{ g HClO}_3 \left(\frac{1 \text{ mol HClO}_3}{84.5 \text{ g HClO}_3} \right) \left(\frac{1 \text{ mol CaCO}_3}{2 \text{ mol HClO}_3} \right) \times \left(\frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \right) = 48.7 \text{ g CaCO}_3$
- 10.46** $2.00 \times 10^6 \text{ g NH}_3 \left(\frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} \right) \left(\frac{1 \text{ mol (NH}_4)_3\text{PO}_4}{3 \text{ mol NH}_3} \right) \times \left(\frac{149 \text{ g (NH}_4)_3\text{PO}_4}{1 \text{ mol (NH}_4)_3\text{PO}_4} \right) = 5.84 \times 10^6 \text{ g (NH}_4)_3\text{PO}_4$
- 10.50** $\text{Ba(NO}_3)_2\text{(aq)} + 2 \text{NaHCO}_3\text{(aq)} \rightarrow \text{BaCO}_3\text{(s)} + 2 \text{NaNO}_3\text{(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$
 $7.27 \text{ g BaCO}_3 \left(\frac{1 \text{ mol BaCO}_3}{197 \text{ g BaCO}_3} \right) \left(\frac{2 \text{ mol NaHCO}_3}{1 \text{ mol BaCO}_3} \right) \times \left(\frac{84.0 \text{ g NaHCO}_3}{1 \text{ mol NaHCO}_3} \right) = 6.20 \text{ g NaHCO}_3$
- 10.52** $\text{AuCl(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{AuCl}_3\text{(s)}$
 $115 \text{ g AuCl} \left(\frac{1 \text{ mol AuCl}}{232 \text{ g AuCl}} \right) \left(\frac{1 \text{ mol Cl}_2}{1 \text{ mol AuCl}} \right) \left(\frac{70.9 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) = 35.1 \text{ g Cl}_2$
- 10.54** $1110 \text{ g H}_2 \left(\frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \right) \left(\frac{1 \text{ mol C}_{18}\text{H}_{36}\text{O}_2}{2 \text{ mol H}_2} \right) \times \left(\frac{284 \text{ g C}_{18}\text{H}_{36}\text{O}_2}{1 \text{ mol C}_{18}\text{H}_{36}\text{O}_2} \right) = 7.82 \times 10^4 \text{ g C}_{18}\text{H}_{36}\text{O}_2$
- 10.57** $7.33 \text{ g NH}_4\text{NO}_3 \left(\frac{1 \text{ mol NH}_4\text{NO}_3}{80.0 \text{ g NH}_4\text{NO}_3} \right) \left(\frac{4 \text{ mol Zn}}{1 \text{ mol NH}_4\text{NO}_3} \right) \times \left(\frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \right) = 24.0 \text{ g Zn}$
- 10.59** $\text{P}_4\text{S}_6\text{(s)} + 11 \text{O}_2\text{(g)} \rightarrow \text{P}_4\text{O}_{10}\text{(s)} + 6 \text{SO}_2\text{(g)}$
 $45.7 \text{ g P}_4\text{S}_6 \left(\frac{1 \text{ mol P}_4\text{S}_6}{316 \text{ g P}_4\text{S}_6} \right) \left(\frac{1 \text{ mol P}_4\text{O}_{10}}{1 \text{ mol P}_4\text{S}_6} \right) \left(\frac{284 \text{ g P}_4\text{O}_{10}}{1 \text{ mol P}_4\text{O}_{10}} \right) = 41.1 \text{ g P}_4\text{O}_{10}$
- 10.60** $175 \text{ g Mg(HCO}_3)_2 \left(\frac{1 \text{ mol Mg(HCO}_3)_2}{146 \text{ g Mg(HCO}_3)_2} \right) \times \left(\frac{1 \text{ mol MgCO}_3}{1 \text{ mol Mg(HCO}_3)_2} \right) \left(\frac{84.3 \text{ g MgCO}_3}{1 \text{ mol MgCO}_3} \right) = 101 \text{ g MgCO}_3$
- 10.62** $\text{P}_4\text{O}_6\text{(s)} + 2 \text{O}_2\text{(g)} \rightarrow \text{P}_4\text{O}_{10}\text{(s)}$
 $41.7 \text{ g P}_4\text{O}_6 \left(\frac{1 \text{ mol P}_4\text{O}_6}{219.9 \text{ g P}_4\text{O}_6} \right) \left(\frac{1 \text{ mol P}_4\text{O}_{10}}{1 \text{ mol P}_4\text{O}_6} \right) \times \left(\frac{283.9 \text{ g P}_4\text{O}_{10}}{1 \text{ mol P}_4\text{O}_{10}} \right) = 53.8 \text{ g P}_4\text{O}_{10}$
- 10.64** $15.00 \times 10^3 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) \left(\frac{2 \text{ mol Fe}}{3 \text{ mol C}} \right) \left(\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \right) = 46,500 \text{ g Fe} = 46.50 \text{ kg Fe}$
- 10.67** $122 \text{ g (NH}_4)_2\text{CO}_3 \left(\frac{1 \text{ mol (NH}_4)_2\text{CO}_3}{96.0 \text{ g (NH}_4)_2\text{CO}_3} \right) \times \left(\frac{2 \text{ mol NH}_3}{1 \text{ mol (NH}_4)_2\text{CO}_3} \right) \left(\frac{17.0 \text{ g NH}_3}{1 \text{ mol NH}_3} \right) = 43.2 \text{ g NH}_3$
- 10.72** Parts (a) through (e) are the same except that they give more or less information to help solve the problem. Part (f) also poses the same problem but has an additional answer

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required. We can do the first part of (f) and solve for the total mass of acids by the law of conservation of mass.

$$20.83 \text{ g PCl}_5 \left(\frac{1 \text{ mol PCl}_5}{208.3 \text{ g PCl}_5} \right) \left(\frac{4 \text{ mol H}_2\text{O}}{1 \text{ mol PCl}_5} \right) \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 7.200 \text{ g H}_2\text{O}$$

The total mass of reactants is equal to the total mass of the products:

$$20.83 \text{ g} + 7.200 \text{ g} = 28.03 \text{ g total acids}$$

10.73 (a) $2.35 \times 10^{23} \text{ Cl atoms} \left(\frac{1 \text{ mol Cl}}{6.02 \times 10^{23} \text{ Cl atoms}} \right) = 0.3904 \text{ mol Cl}$

(b) $0.3904 \text{ mol Cl} \left(\frac{1 \text{ mol PCl}_3}{3 \text{ mol Cl}} \right) = 0.1301 \text{ mol PCl}_3$

(c) $0.1301 \text{ mol PCl}_3 \left(\frac{1 \text{ mol PCl}_5}{1 \text{ mol PCl}_3} \right) = 0.1301 \text{ mol PCl}_5$

(d) $0.1301 \text{ mol PCl}_5 \left(\frac{208.3 \text{ g PCl}_5}{1 \text{ mol PCl}_5} \right) = 27.1 \text{ g PCl}_5$

10.74 $61.7 \text{ mL} \left(\frac{1.49 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1 \text{ mol CHClF}_2}{86.5 \text{ g CHClF}_2} \right) \left(\frac{2 \text{ mol F}}{1 \text{ mol CHClF}_2} \right) = 2.13 \text{ mol F}$

10.76 $4.14 \text{ g N}_2\text{H}_4 \left(\frac{1 \text{ mol N}_2\text{H}_4}{32.0 \text{ g N}_2\text{H}_4} \right) \left(\frac{1 \text{ mol N}_2\text{H}_6(\text{NO}_3)_2}{1 \text{ mol N}_2\text{H}_4} \right) \times \left(\frac{4 \text{ mol N}}{1 \text{ mol N}_2\text{H}_6(\text{NO}_3)_2} \right) \left(\frac{6.02 \times 10^{23} \text{ atoms N}}{1 \text{ mol N}} \right) = 3.12 \times 10^{23} \text{ atoms N}$

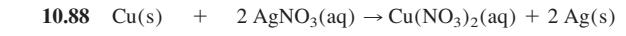
10.77 $2 \text{ P(s)} + 3 \text{ S(s)} \rightarrow \text{P}_2\text{S}_3(\text{s})$
 $1.50 \times 10^{23} \text{ P} \left(\frac{1 \text{ mol P}}{6.02 \times 10^{23} \text{ P}} \right) \left(\frac{1 \text{ mol P}_2\text{S}_3}{2 \text{ mol P}} \right) \times \left(\frac{158 \text{ g P}_2\text{S}_3}{1 \text{ mol P}_2\text{S}_3} \right) = 19.7 \text{ g P}_2\text{S}_3$

10.79 $4 \text{ CrO(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{ Cr}_2\text{O}_3(\text{s})$
 $1.72 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) \left(\frac{2 \text{ mol Cr}_2\text{O}_3}{1 \text{ mol O}_2} \right) \left(\frac{3 \text{ mol O}}{1 \text{ mol Cr}_2\text{O}_3} \right) = 0.3225 \text{ mol O}$
 $0.3225 \text{ mol O} \left(\frac{6.02 \times 10^{23} \text{ atoms O}}{1 \text{ mol O}} \right) = 1.94 \times 10^{23} \text{ atoms O}$

10.82 $\text{SF}_2(\text{g}) + 2 \text{ F}_2(\text{g}) \rightarrow \text{SF}_6(\text{g})$
 $6.11 \text{ g F}_2 \left(\frac{1 \text{ mol F}_2}{38.0 \text{ g F}_2} \right) \left(\frac{1 \text{ mol SF}_6}{2 \text{ mol F}_2} \right) \left(\frac{6 \text{ mol F}}{1 \text{ mol SF}_6} \right) \times \left(\frac{6.02 \times 10^{23} \text{ F}}{1 \text{ mol F}} \right) = 2.90 \times 10^{23} \text{ F atoms}$

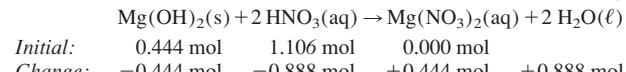
10.84 $1 \text{ HP} + 3 \text{ B} = 1 \text{ Field}$
Initial: 5 HP 12 B 0 Fields
Used: -4 HP -12 B +4 Fields
Final: 1 HP 0 B 4 Fields

10.85 $\text{MgCl}_2(\text{aq}) + 2 \text{ AgNO}_3(\text{aq}) \rightarrow 2 \text{ AgCl(s)} + \text{Mg}(\text{NO}_3)_2(\text{aq})$
(a) $5.00 \text{ mol AgNO}_3 \left(\frac{1 \text{ mol MgCl}_2}{2 \text{ mol AgNO}_3} \right) = 2.50 \text{ mol MgCl}_2$
(b) Because it takes 2.50 mol of MgCl_2 to react with 5.00 mol of AgNO_3 (part [a]), the MgCl_2 is limiting: 2.00 mol MgCl_2 will react.
(c) Because there is more MgCl_2 present than will react with 5.00 mol of AgNO_3 (part [a]), all the AgNO_3 will react with 2.50 mol MgCl_2 (part [a]).

APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems

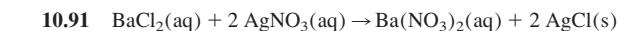
<i>Initial:</i>	0.272 mol	0.576 mol	0.000 mol	0.000 mol
<i>Change:</i>	-0.272 mol	-0.544 mol	+0.272 mol	+0.544 mol
<i>Final:</i>	0.000 mol	0.032 mol	0.272 mol	0.544 mol

10.89 $6.66 \times 10^{23} \text{ molecules HNO}_3 \left(\frac{1 \text{ mol HNO}_3}{6.02 \times 10^{23} \text{ molecules HNO}_3} \right) = 1.106 \text{ mol HNO}_3$



<i>Initial:</i>	0.444 mol	1.106 mol	0.000 mol
<i>Change:</i>	-0.444 mol	-0.888 mol	+0.444 mol
<i>Final:</i>	0.000 mol	0.218 mol	0.444 mol

Thus, 0.888 mol of water is produced and 0.22 mol of HNO_3 remains.



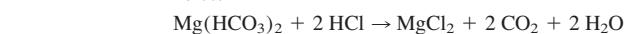
<i>Initial:</i>	1.75 mol	2.70 mol	0.00 mol
<i>Change:</i>	-1.35 mol	-2.70 mol	+1.35 mol
<i>Final:</i>	0.40 mol	0.00 mol	1.35 mol

The AgCl is not in solution.

10.93 $25.0 \text{ g Mg(HCO}_3)_2 \left(\frac{1 \text{ mol Mg(HCO}_3)_2}{146 \text{ g Mg(HCO}_3)_2} \right) = 0.1712 \text{ mol Mg(HCO}_3)_2$

$$41.2 \text{ g HCl} \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) = 1.129 \text{ mol HCl}$$

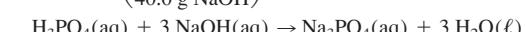
All in moles:



<i>Initial:</i>	0.1712	1.129
<i>Change:</i>	-0.1712	-0.3424
<i>Final:</i>	0.000	0.79

10.98 $91.1 \text{ g H}_3\text{PO}_4 \left(\frac{1 \text{ mol H}_3\text{PO}_4}{98.0 \text{ g H}_3\text{PO}_4} \right) = 0.9296 \text{ mol H}_3\text{PO}_4$

$$145 \text{ g NaOH} \left(\frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} \right) = 3.625 \text{ mol NaOH}$$

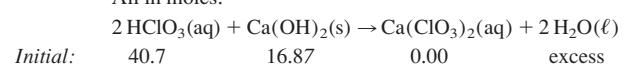


<i>Initial:</i>	0.9296 mol	3.625 mol	0.000 mol
<i>Change:</i>	-0.9296 mol	-2.789 mol	+0.9296 mol
<i>Final:</i>	0.000 mol	0.836 mol	0.9296 mol

$$0.836 \text{ mol NaOH} \left(\frac{40.0 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) = 33 \text{ g NaOH excess}$$

10.99 $1250 \text{ g Ca(OH)}_2 \left(\frac{1 \text{ mol Ca(OH)}_2}{74.1 \text{ g Ca(OH)}_2} \right) = 16.87 \text{ mol Ca(OH)}_2$

All in moles:



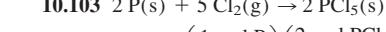
<i>Initial:</i>	40.7	16.87	0.00	excess
<i>Change:</i>	-33.74	-16.87	+16.87	+33.74
<i>Final:</i>	7.0	0.00	16.87	excess

There is 33.7 mol of water produced by the reaction.



(a) $0.160 \text{ mol SO}_2 \left(\frac{1 \text{ mol SO}_2\text{Cl}_2}{1 \text{ mol SO}_2} \right) = 0.160 \text{ mol SO}_2\text{Cl}_2$

(b) $\frac{0.151 \text{ mol obtained}}{0.160 \text{ mol theoretical}} \times 100\% = 94.4\% \text{ yield}$



$$4.50 \text{ g P} \left(\frac{1 \text{ mol P}}{31.0 \text{ g P}} \right) \left(\frac{2 \text{ mol PCl}_5}{2 \text{ mol P}} \right) \left(\frac{208 \text{ g PCl}_5}{1 \text{ mol PCl}_5} \right) = 30.19 \text{ g PCl}_5$$

$$\frac{29.8 \text{ g}}{30.19 \text{ g}} \times 100\% = 98.7\% \text{ yield}$$

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10.104 $10.0 \text{ g C}_4\text{H}_8 \left(\frac{1 \text{ mol C}_4\text{H}_8}{56.1 \text{ g C}_4\text{H}_8} \right) \left(\frac{1 \text{ mol C}_4\text{H}_8\text{Br}_2}{1 \text{ mol C}_4\text{H}_8} \right) \left(\frac{216 \text{ g C}_4\text{H}_8\text{Br}_2}{1 \text{ mol C}_4\text{H}_8\text{Br}_2} \right) = 38.5 \text{ g C}_4\text{H}_8\text{Br}_2$
 $\left(\frac{36.0 \text{ g}}{38.5 \text{ g}} \right) \times 100\% = 93.5\%$

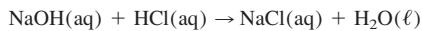
10.105 $25.0 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 0.7813 \text{ mol O}_2$
 $51.2 \text{ g SO}_2 \left(\frac{1 \text{ mol SO}_2}{64.1 \text{ g SO}_2} \right) = 0.7988 \text{ mol SO}_2$
 $2 \text{ SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ SO}_3(\text{g})$

Since they react in a 2:1 ratio, SO_2 is in limiting quantity.

$0.7988 \text{ mol SO}_2 \left(\frac{2 \text{ mol SO}_3}{2 \text{ mol SO}_2} \right) \left(\frac{80.1 \text{ g SO}_3}{1 \text{ mol SO}_3} \right) = 63.98 \text{ g SO}_3$
 $\left(\frac{46.9 \text{ g}}{63.98 \text{ g}} \right) \times 100\% = 73.3\%$

10.106 (a) $0.750 \text{ mol NaOH} \left(\frac{1 \text{ mol Na}^+}{1 \text{ mol NaOH}} \right) = 0.750 \text{ mol Na}^+$

(b) The full equation is

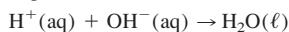


Because the acid and base react in a 1:1 mole ratio, HCl is present in limiting quantity, and 0.600 mol of NaCl will be produced.

(c) The excess will be 0.150 mol of NaOH, equal to the 0.750 mol initially present minus the 0.600 mol that reacts.

(d) There are 0.600 mol of Na^+ from the NaCl and 0.150 mol of Na^+ from the excess NaOH for a total of 0.750 mol of Na^+ .

(e) The 0.750 mol of Na^+ initially present (see part [a]) is still present after the reaction, consistent with Na^+ being a spectator ion in the reaction:



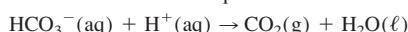
10.110 The Ba^{2+} ion and the NO_3^- ion do not react (they are spectator ions), so there are 1.75 mol of Ba^{2+} ion and 2.70 mol of NO_3^- ion in the final solution. The moles of silver ion and chloride ion are calculated using the net ionic equation:

$\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}(\text{s})$

<i>Initial:</i>	3.50 mol	2.70 mol
<i>Change:</i>	-2.70 mol	-2.70 mol
<i>Final:</i>	0.80 mol	0.00 mol

These results are similar to those of the Problem 10.106.

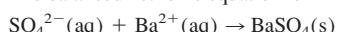
10.112 The balanced net ionic equation is



The H^+ is limiting. The number of moles of CO_2 is given by

$1.80 \text{ mol H}^+ \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol H}^+} \right) = 1.80 \text{ mol CO}_2$

10.114 The balanced net ionic equation is



Since the reacting ratio is 1:1, the limiting quantity is Ba^{2+} . The mass of BaSO_4 is given by

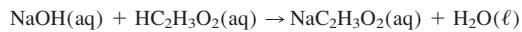
$0.125 \text{ mol Ba}^{2+} \left(\frac{1 \text{ mol BaSO}_4}{1 \text{ mol Ba}^{2+}} \right) \left(\frac{233 \text{ g BaSO}_4}{1 \text{ mol BaSO}_4} \right) = 29.1 \text{ g BaSO}_4$

10.116 (a) Write a balanced equation for the reaction, and multiply the number of moles given in the problem by a mole ratio taken from the equation.

(b) Write a balanced equation for the reaction, and multiply the number of moles given in the problem by a mole ratio taken from that equation to obtain the number of moles of calcium hydroxide. Multiply that number by the molar mass of calcium hydroxide to change it to grams.

(c) Write a balanced equation for the reaction. Calculate the numbers of moles of both reactants, and tabulate the numbers of moles present initially, the changes in numbers of moles, and the final numbers of moles. Multiply the final number of moles of carbon dioxide by its molar mass to change it to grams.

10.117 All quantities in moles:



<i>Initial:</i>	3.11	3.82	0.00
<i>Change:</i>	-3.11	-3.11	+3.11
<i>Final:</i>	0.00	0.71	3.11

The final number of moles of water cannot be calculated because the reagents were in aqueous solution and therefore the initial number of moles of water is unknown.

10.118 (a) $2 \text{ KOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{K}_2\text{SO}_4(\text{aq}) + 2 \text{ H}_2\text{O}(\ell)$

$75.0 \text{ g H}_2\text{SO}_4 \left(\frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4} \right) \left(\frac{1 \text{ mol K}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right) \times \left(\frac{174.3 \text{ g K}_2\text{SO}_4}{1 \text{ mol K}_2\text{SO}_4} \right) = 133 \text{ g K}_2\text{SO}_4$

(b) $\text{NaOH}(\text{aq}) + \text{HClO}_3(\text{aq}) \rightarrow \text{NaClO}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$

$75.0 \text{ g NaOH} \left(\frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} \right) \times \left(\frac{1 \text{ mol NaClO}_3}{1 \text{ mol NaOH}} \right) \left(\frac{106.5 \text{ g NaClO}_3}{1 \text{ mol NaClO}_3} \right) = 200 \text{ g NaClO}_3$

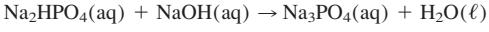
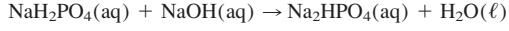
(c) $\text{MgO}(\text{s}) + 2 \text{ HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$

$75.0 \text{ g MgO} \left(\frac{1 \text{ mol MgO}}{40.3 \text{ g MgO}} \right) \left(\frac{1 \text{ mol MgCl}_2}{1 \text{ mol MgO}} \right) \times \left(\frac{95.3 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2} \right) = 177 \text{ g MgCl}_2$

(d) $2 \text{ NaOH}(\text{aq}) + \text{N}_2\text{O}_3(\text{g}) \rightarrow 2 \text{ NaNO}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$

$75.0 \text{ g N}_2\text{O}_3 \left(\frac{1 \text{ mol N}_2\text{O}_3}{76.0 \text{ g N}_2\text{O}_3} \right) \left(\frac{2 \text{ mol NaNO}_2}{1 \text{ mol N}_2\text{O}_3} \right) \times \left(\frac{69.0 \text{ g NaNO}_2}{1 \text{ mol NaNO}_2} \right) = 136 \text{ g NaNO}_2$

10.120 (a) $\text{H}_3\text{PO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaH}_2\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\ell)$



(b) 1.00 mol of NaOH will essentially complete the second reaction, and the 0.50 mol of NaOH remaining will half complete the third, yielding 0.50 mol each of Na_2HPO_4 and Na_3PO_4 .

10.121 None. (Silver does not displace hydrogen from acids.)

10.123 $2 \text{ NaHCO}_3(\text{s}) \xrightarrow{\text{Heat}} \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$

The word *solid* in the statement of this problem is equivalent to Na_2CO_3 because that is the only solid product.

$2110 \text{ g NaHCO}_3 \left(\frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g NaHCO}_3} \right) \left(\frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol NaHCO}_3} \right) \times \left(\frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} \right) = 1330 \text{ g Na}_2\text{CO}_3 = 1.33 \text{ kg Na}_2\text{CO}_3$

636**APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems**

- 10.125** (a) $2 \text{ KClO}_3(\text{s}) \xrightarrow{\text{MnO}_2} 2 \text{ KCl}(\text{s}) + 3 \text{ O}_2(\text{g})$
 (b) Since the catalyst (MnO_2), the KClO_3 , and the KCl are all solids, the loss in mass is equal to the mass of the *gas* produced—oxygen. The oxygen therefore has a mass of $1.221 \text{ g} - 0.998 \text{ g} = 0.223 \text{ g}$
 (c) The mass of KClO_3 that *reacted* can be calculated from the mass of oxygen produced:

$$0.223 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) \left(\frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \right) \left(\frac{122.5 \text{ g KClO}_3}{1 \text{ mol KClO}_3} \right) = 0.5691 \text{ g KClO}_3$$

 (d) The mass of KCl produced can also be calculated from the mass of oxygen produced:

$$0.223 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) \left(\frac{2 \text{ mol KCl}}{3 \text{ mol O}_2} \right) \left(\frac{74.5 \text{ g KCl}}{1 \text{ mol KCl}} \right) = 0.3461 \text{ g KCl}$$

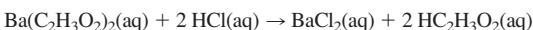
Alternatively, the mass of KCl produced can be calculated from the mass of KClO_3 decomposed minus the mass of oxygen produced:

$$0.5691 \text{ g} - 0.223 \text{ g} = 0.3461 \text{ g}$$

(e) At least 0.569 g of KClO_3 must have been present initially.

- 10.127** $20.2 \text{ g NH}_3 \left(\frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} \right) = 1.188 \text{ mol NH}_3$
 $41.6 \text{ g HNO}_3 \left(\frac{1 \text{ mol HNO}_3}{63.0 \text{ g HNO}_3} \right) = 0.6603 \text{ mol HNO}_3$
 $\text{NH}_3(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$
Initial: 1.188 mol 0.6603 mol 0.000 mol
Change: -0.6603 mol -0.6603 mol $+0.6603 \text{ mol}$
Final: 0.528 mol 0.000 mol 0.6603 mol
 $0.6603 \text{ mol NH}_4\text{NO}_3 \left(\frac{2 \text{ mol N}}{1 \text{ mol NH}_4\text{NO}_3} \right) \left(\frac{14.0 \text{ g N}}{1 \text{ mol N}} \right) = 18.5 \text{ g N}$

10.131 This reaction proceeds because of the formation of the (largely covalent) acetic acid.



<i>Initial:</i>	0.150 mol	0.500 mol	0.000 mol	0.000 mol
<i>Change:</i>	-0.150 mol	-0.300 mol	$+0.150 \text{ mol}$	$+0.300 \text{ mol}$
<i>Final:</i>	0.000 mol	0.200 mol	0.150 mol	0.300 mol

- 10.132** $\$233.00 + \text{CT} + 4 \text{ Ch} \rightarrow \text{Set}$
Initial: 5000.00 31 98 0
Change: -4893.00 -21 -84 $+21$
Final: 107.00 10 14 21

The manager can buy only 21 sets; money (as usual) is the limiting quantity. Here, three “reactants” have to be considered to see which is limiting.

11 Molarity

- 11.1** (a) 3.000 M (The small sample is the same concentration as the original solution because it has not been changed.)
 (b) 2.000 mL
 (c) 6.000 mmol (one-thousandth of the 6.000 mol in the sample)
 (d) $6.000 \text{ mmol}/2.000 \text{ mL} = 3.000 \text{ mmol/mL} = 3.000 \text{ M}$
- 11.2** (a) $\frac{1.70 \text{ mol}}{1.00 \text{ L}} = 1.70 \text{ M}$ (b) $\frac{1.70 \text{ mol}}{2.00 \text{ L}} = 0.850 \text{ M}$
 (c) $\frac{1.70 \text{ mol}}{5.00 \text{ L}} = 0.340 \text{ M}$ (d) $\frac{1.70 \text{ mol}}{0.500 \text{ L}} = 3.40 \text{ M}$
- 11.3** (a) Less than 40.0 mL of water is used.
 (b) Exactly 40.0 mL of water is used, and more than 40.0 mL of solution is produced.

- 11.4** The two solutions have the same initial concentration. When they are combined, the final concentration is also the same. (The two initial solutions and the final solution would all taste equally sweet. Try it.) As an analogy, if a car travels 50 mph during the first half of a trip and 50 mph during the second half of the trip, its overall speed is 50 mph. Alternatively, we may calculate the final concentration:

$$0.0250 \text{ L} \left(\frac{1.22 \text{ mol}}{1 \text{ L}} \right) = 0.0305 \text{ mol}$$

$$0.0350 \text{ L} \left(\frac{1.22 \text{ mol}}{1 \text{ L}} \right) = 0.0427 \text{ mol}$$

$$\frac{0.0732 \text{ mol}}{0.0600 \text{ L}} = 1.22 \text{ M}$$

- 11.5** (a) $\frac{0.365 \text{ mol}}{0.4000 \text{ L}} = 0.9125 \text{ M}$
 (b) Because 365 mmol is 0.365 mol, this problem is the same as (a).
 (c) Because 400.0 mL is 0.4000 L, this problem is the same as (a).
 (d) $\frac{365 \text{ mmol}}{400.0 \text{ mL}} = 0.9125 \text{ M} = \frac{0.365 \text{ mol}}{0.4000 \text{ L}}$

- 11.6** The concentration of the portion is 0.693 M, the same as the concentration of the original sample. (Tea would taste as sweet if sipped from a 100.0 mL portion or from 3.13 mL poured directly from that 100.0 mL portion.)

- 11.7** (a) 2 dozen brides, 2 dozen grooms
 (b) 2.0 M NH_4^+ , 2.0 M NO_3^-

- 11.8** (a) 1.0 M Na^+ and 1.0 M Cl^-
 (b) 1.0 M Mg^{2+} and 2.0 M Cl^-
 (c) 1.0 M Cr^{3+} and 3.0 M Cl^-
 (d) 1.0 M Li^+ and 1.0 M NO_3^-
 (e) 1.0 M Co^{2+} and 2.0 M NO_3^-
 (f) 1.0 M Al^{3+} and 3.0 M NO_3^-

Note that the subscript after the O in the formulas in parts (d)–(f) represents the number of oxygen atoms per nitrate ion, not the number of nitrate ions per formula unit.

- (g) 2.0 M Al^{3+} and 3.0 M SO_4^{2-}
 (h) 2.0 M NH_4^+ and 1.0 M SO_4^{2-}

- 11.9** (a) The final volume is about 5.5 L.
 (b) The final volume is 3.3 L. Note the small difference in the wording of the parts of this problem, which makes a large difference in the answer.

- 11.10** (a) A chemical reaction occurs.
 (b) The number of moles of nitrate ion must be calculated from the numbers of moles in the two solutions.
 (c) The number of moles of chloride ion must be calculated.
 (d) A chemical reaction occurs.
 (e) Each solution merely dilutes the concentrations of the ions in the other.
 (f) The number of moles of hydroxide ion in the final solution must be calculated.

- 11.11** (a) To determine the concentration of the NaHCO_3 solution. 2.542 M
 (b) To determine the number of moles of HA, and from that the molar mass of HA. 57.81 g/mol

- 11.12** (a) The H^+ ions react with the CO_3^{2-} ions, forming water and carbon dioxide, two covalent compounds, and leaving fewer ions in solution.
 (b) There is no interaction between the ions in these compounds.

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- (c) There is no interaction between the ions in these compounds.
 (d) There is no interaction between the ions in these compounds.
 (e) There are ions in common. The concentration of the chloride ion is the sum of that provided by CuCl₂ and that provided by KCl.
 (f) The H⁺ ions react with the OH⁻ ions, forming water and leaving fewer ions in solution.

11.13 (a) $\frac{0.123 \text{ mol}}{0.7000 \text{ L}} = 0.176 \text{ M}$ (b) $\frac{123 \text{ mmol}}{700.0 \text{ mL}} = 0.176 \text{ M}$

11.15 $\frac{79.4 \text{ mmol}}{122.5 \text{ mL}} = 0.648 \text{ M}$

Note that molarity is the number of millimoles per milliliter, as well as the number of moles per liter.

11.18 $0.175 \text{ mol} \left(\frac{1 \text{ L}}{0.881 \text{ mol}} \right) = 0.199 \text{ L}$

11.19 $122 \text{ mg} \left(\frac{1 \text{ mmol}}{58.5 \text{ mg}} \right) \left(\frac{1 \text{ mL}}{1.38 \text{ mmol}} \right) = 1.51 \text{ mL}$

11.22 $0.8122 \text{ L} \left(\frac{2.163 \text{ mol}}{1 \text{ L}} \right) = 1.757 \text{ mol}$

11.23 $41.0 \text{ mL} \left(\frac{2.611 \text{ mmol}}{1 \text{ mL}} \right) = 107 \text{ mmol}$

11.25 The initial solution contains

$225 \text{ mL} \left(\frac{0.500 \text{ mmol}}{1 \text{ mL}} \right) = 112.5 \text{ mmol}$

(a) The final volume is about 1.325 L, so the final concentration is

$$\frac{112.5 \text{ mmol}}{1325 \text{ mL}} = 0.0849 \text{ M}$$

(b) The final volume is 1.100 L, so the final concentration is

$$\frac{0.1125 \text{ mol}}{1.100 \text{ L}} = 0.102 \text{ M}$$

11.28 The initial solution contains

$20.8 \text{ mL} \left(\frac{2.11 \text{ mmol}}{1 \text{ mL}} \right) = 43.89 \text{ mmol}$

The final solution contains the same number of moles of solute, so its concentration is

$$\frac{43.89 \text{ mmol}}{50.0 \text{ mL}} = 0.878 \text{ M}$$

11.30 The numbers of moles of solute are the same in the initial and final solutions. Use the known volume and molarity of the final solution to calculate that number of moles, and then use the number of moles to find the volume of the initial solution:

$$6.00 \text{ L} \left(\frac{0.450 \text{ mol}}{1 \text{ L}} \right) = 2.70 \text{ mol}$$

$$2.70 \text{ mol} \left(\frac{1 \text{ L}}{2.50 \text{ mol}} \right) = 1.08 \text{ L}$$

- 11.34** (a) 0.688 M Al³⁺ and 1.03 M SO₄²⁻
 (b) 4.83 M NH₄⁺ and 1.61 M PO₄³⁻
 (c) 0.0808 M Ba²⁺ and 0.162 M OH⁻
 (d) 3.75 M K⁺ and 3.75 M Br⁻
 (e) 3.09 M Na⁺ and 3.09 M ClO₃⁻

11.35 Both, because weak acids (mostly covalent) are formed:

- (a) KC₂H₃O₂(aq) + HCl(aq) → HC₂H₃O₂(aq) + KCl(aq)
 (b) CaF₂(aq) + 2 HNO₃(aq) → Ca(NO₃)₂(aq) + 2 HF(aq)

- 11.38** (a) The compound consists of Hg²⁺ ions and NO₃⁻ ions. There are 0.128 mol of Hg²⁺ ions per liter and twice that concentration of NO₃⁻ ions: 0.256 M NO₃⁻.
 (b) 0.128 M Hg₂²⁺ and 0.256 M NO₃⁻

11.39 $12.3 \text{ mL} \left(\frac{0.816 \text{ mmol BaCl}_2}{1 \text{ mL}} \right) = 10.04 \text{ mmol BaCl}_2$

$$14.3 \text{ mL} \left(\frac{0.806 \text{ mmol AlCl}_3}{1 \text{ mL}} \right) = 11.53 \text{ mmol AlCl}_3$$

10.04 mmol BaCl₂ consists of 10.04 mmol Ba²⁺ and 20.08 mmol Cl⁻

11.53 mmol AlCl₃ consists of 11.53 mmol Al³⁺ and 34.59 mmol Cl⁻

There is a total of 54.67 mmol of Cl⁻ in the final solution. The final concentrations are

$$\frac{10.04 \text{ mmol Ba}^{2+}}{50.0 \text{ mL}} = 0.201 \text{ M Ba}^{2+}$$

$$\frac{11.53 \text{ mmol Al}^{3+}}{50.0 \text{ mL}} = 0.231 \text{ M Al}^{3+}$$

$$\frac{54.67 \text{ mmol Cl}^{-}}{50.0 \text{ mL}} = 1.09 \text{ M Cl}^{-}$$

11.41 The 0.217 mol of Li₂SO₄ consists of

$$0.217 \text{ mol Li}_2\text{SO}_4 \left(\frac{2 \text{ mol Li}^{+}}{1 \text{ mol Li}_2\text{SO}_4} \right) = 0.434 \text{ mol Li}^{+}$$

and

$$0.217 \text{ mol Li}_2\text{SO}_4 \left(\frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol Li}_2\text{SO}_4} \right) = 0.217 \text{ mol SO}_4^{2-}$$

The 0.217 mol of K₂SO₄ consists of

$$0.217 \text{ mol K}_2\text{SO}_4 \left(\frac{2 \text{ mol K}^{+}}{1 \text{ mol K}_2\text{SO}_4} \right) = 0.434 \text{ mol K}^{+}$$

and

$$0.217 \text{ mol K}_2\text{SO}_4 \left(\frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol K}_2\text{SO}_4} \right) = 0.217 \text{ mol SO}_4^{2-}$$

The total number of moles of SO₄²⁻ is

$$0.217 \text{ mol} + 0.217 \text{ mol} = 0.434 \text{ mol}$$

The concentrations are

$$\frac{0.434 \text{ mol K}^{+}}{0.6500 \text{ L}} = 0.668 \text{ M K}^{+}$$

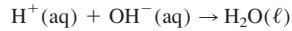
$$\frac{0.434 \text{ mol Li}^{+}}{0.6500 \text{ L}} = 0.668 \text{ M Li}^{+}$$

$$\frac{0.434 \text{ mol SO}_4^{2-}}{0.6500 \text{ L}} = 0.668 \text{ M SO}_4^{2-}$$

11.44 (a) $30.00 \text{ mL NaOH} \left(\frac{4.000 \text{ mmol}}{1 \text{ mL}} \right) = 120.0 \text{ mmol NaOH}$

$$60.00 \text{ mL HCl} \left(\frac{1.250 \text{ mmol}}{1 \text{ mL}} \right) = 75.00 \text{ mmol HCl}$$

The net ionic equation is



The H⁺ ion is in limiting quantity, and there is 45.0 mmol of OH⁻ ion in excess. The final concentrations are

$$\frac{45.0 \text{ mmol OH}^{-}}{90.00 \text{ mL}} = 0.500 \text{ M OH}^{-}$$

$$\frac{75.00 \text{ mmol Cl}^{-}}{90.00 \text{ mL}} = 0.8333 \text{ M Cl}^{-}$$

$$\frac{120.0 \text{ mmol Na}^{+}}{90.00 \text{ mL}} = 1.333 \text{ M Na}^{+}$$

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- (b) Calculations as in part (a) yield 120.0 mmol NaCl and 75.00 mmol HCl. There is no reaction, so the Cl⁻ concentration is

$$\frac{120.0 \text{ mmol} + 75.00 \text{ mmol}}{90.00 \text{ mL}} = 2.167 \text{ M Cl}^-$$

The Na⁺ and H⁺ concentrations are 1.333 M and 0.8333 M, respectively. Note the similarities and differences between parts (a) and (b).

- 11.47** The NaCl solution contains 200 mmol of NaCl, or 200 mmol of Na⁺ and 200 mmol of Cl⁻. The NaBr solution contains 125 mmol of NaBr, or 125 mmol of Na⁺ and 125 mmol of Br⁻. The total number of millimoles of Na⁺ is 125 mmol + 200 mmol = 325 mmol. These values may be tabulated for clarity:

Solute	Millimoles of Compound	Millimoles of Na ⁺	Millimoles of Cl ⁻	Millimoles of Br ⁻
NaCl	200	200	200	
NaBr	125	125		125
Totals for ions:		325	200	125

The concentrations are

$$\frac{325 \text{ mmol Na}^+}{100.0 \text{ mL}} = 3.25 \text{ M Na}^+$$

$$\frac{200 \text{ mmol Cl}^-}{100.0 \text{ mL}} = 2.00 \text{ M Cl}^-$$

$$\frac{125 \text{ mmol Br}^-}{100.0 \text{ mL}} = 1.25 \text{ M Br}^-$$

- 11.49** 25.0 mL CoCl₂ $\left(\frac{0.919 \text{ mmol CoCl}_2}{1 \text{ mL CoCl}_2}\right) = 22.98 \text{ mmol CoCl}_2$

The 22.98 mmol of CoCl₂ consists of 22.98 mmol of Co²⁺ and 45.96 mmol of Cl⁻. The concentrations are

$$\frac{22.98 \text{ mmol Co}^{2+}}{100.0 \text{ mL}} = 0.230 \text{ M Co}^{2+}$$

$$\frac{45.96 \text{ mmol Cl}^-}{100.0 \text{ mL}} = 0.460 \text{ M Cl}^-$$

- 11.51** H₂SO₄(aq) + 2 NaOH(aq) \rightarrow Na₂SO₄(aq) + 2 H₂O(ℓ)

The number of millimoles of NaOH is

$$21.73 \text{ mL} \left(\frac{4.000 \text{ mmol}}{1 \text{ mL}}\right) = 86.92 \text{ mmol NaOH}$$

$$86.92 \text{ mmol NaOH} \left(\frac{1 \text{ mmol H}_2\text{SO}_4}{2 \text{ mmol NaOH}}\right) = 43.46 \text{ mmol H}_2\text{SO}_4$$

The concentration of the H₂SO₄ is

$$\frac{43.46 \text{ mmol}}{25.00 \text{ mL}} = 1.738 \text{ M}$$

- 11.55** 2.818 g KHPH $\left(\frac{1 \text{ mol KHPH}}{204.2 \text{ g KHPH}}\right) \left(\frac{1 \text{ mol KOH}}{1 \text{ mol KHPH}}\right) = 1.3800 \times 10^{-2} \text{ mol KOH}$

$$\frac{1.3800 \times 10^{-2} \text{ mol KOH}}{31.74 \times 10^{-3} \text{ L}} = 0.4348 \text{ M KOH}$$

- 11.57** 2 NaOH(aq) + H₂SO₄(aq) \rightarrow Na₂SO₄(aq) + 2 H₂O(ℓ)

$$12.88 \text{ mL} \left(\frac{1.500 \text{ mmol NaOH}}{1 \text{ mL}}\right) \left(\frac{1 \text{ mmol H}_2\text{SO}_4}{2 \text{ mmol NaOH}}\right) = 9.660 \text{ mmol H}_2\text{SO}_4$$

- 11.59** Ca(OH)₂(s) + 2 HClO₃(aq) \rightarrow Ca(ClO₃)₂(aq) + 2 H₂O(ℓ)

$$29.17 \text{ mL} \left(\frac{4.000 \text{ mmol HClO}_3}{1 \text{ mL}}\right) \left(\frac{1 \text{ mmol Ca(OH)}_2}{2 \text{ mmol HClO}_3}\right) = 58.34 \text{ mmol Ca(OH)}_2$$

- 11.61** HCl(aq) + NaHCO₃(s) \rightarrow NaCl(aq) + CO₂(g) + H₂O(ℓ)

$$31.3 \text{ g NaHCO}_3 \left(\frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g NaHCO}_3}\right) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol NaHCO}_3}\right) \times \left(\frac{1 \text{ L}}{2.84 \text{ mol HCl}}\right) = 0.131 \text{ L HCl}$$

The tablet can neutralize 131 mL of stomach acid.

- 11.63** The HCl solution contains

$$37.22 \text{ mL} \left(\frac{1.000 \text{ mmol}}{1 \text{ mL}}\right) = 37.22 \text{ mmol Cl}^- \text{ and } 37.22 \text{ mmol H}^+$$

The NaOH solution contains

$$19.29 \text{ mL} \left(\frac{4.107 \text{ mmol}}{1 \text{ mL}}\right) = 79.224 \text{ mmol Na}^+ \text{ and } 79.224 \text{ mmol OH}^-$$

The H⁺ ions react with OH⁻ ions:



The limiting quantity is the quantity of H⁺ ions, therefore 37.22 mmol of OH⁻ reacts with 37.22 mmol of H⁺ to produce water. This leaves 79.224 mmol - 37.22 mmol = 42.004 mmol of OH⁻ ions remaining. The chloride and sodium ions are spectator ions; they do not react. Therefore, there are 37.22 mmol of Cl⁻ and 79.224 mmol of Na⁺ in the final solution. The final volume is assumed to be 37.22 mL + 19.29 mL = 56.51 mL, and so the final concentrations are

$$\frac{42.004 \text{ mmol OH}^-}{56.51 \text{ mL}} = 0.7433 \text{ M OH}^-$$

$$\frac{79.224 \text{ mmol Na}^+}{56.51 \text{ mL}} = 1.402 \text{ M Na}^+$$

$$\frac{37.22 \text{ mmol Cl}^-}{56.51 \text{ mL}} = 0.6586 \text{ M Cl}^-$$

- 11.64** Millimolar means the number of *millimoles per liter* of solution. Thus

$$0.725 \text{ L} \left(\frac{715 \text{ mmol}}{1 \text{ L}}\right) \left(\frac{106 \text{ mg}}{1 \text{ mmol}}\right) = 54,900 \text{ mg}$$

- 11.65** $\frac{0.300 \text{ mol Cu}^{2+}}{1 \text{ L}} \left(\frac{2 \text{ mol H}^+}{1 \text{ mol Cu}^{2+}}\right) = \frac{0.600 \text{ mol H}^+}{1 \text{ L}} = 0.600 \text{ M H}^+$

- 11.66** (a) 1.0 M (b) 2.0 M

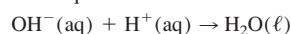
- 11.67** 47.33 mL $\left(\frac{1.807 \text{ mmol NaOH}}{1 \text{ mL}}\right) = 85.525 \text{ mmol NaOH}$

$$39.19 \text{ mL} \left(\frac{0.5093 \text{ mmol H}_2\text{SO}_4}{1 \text{ L}}\right) = 19.959 \text{ mmol H}_2\text{SO}_4$$

85.525 mmol NaOH consists of 85.525 mmol Na⁺ and 85.525 mmol OH⁻

19.959 mmol H₂SO₄ consists of 19.959 mmol SO₄²⁻ and 39.918 mmol H⁺

The OH⁻ ions react with the H⁺ ions according to the net ionic equation



There is a limiting quantity of H⁺, so 85.525 mmol - 39.918 mmol = 45.607 mmol of OH⁻ will remain in the solution. The final concentrations are

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$$\frac{85.525 \text{ mmol Na}^+}{100.0 \text{ mL}} = 0.8553 \text{ M Na}^+$$

$$\frac{19.959 \text{ mmol SO}_4^{2-}}{100.0 \text{ mL}} = 0.1996 \text{ M SO}_4^{2-}$$

$$\frac{45.607 \text{ mmol OH}^-}{100.0 \text{ mL}} = 0.4561 \text{ M OH}^-$$

11.68 The solution contains CH₂O from two sources:

$$125 \text{ mL} \left(\frac{6.13 \text{ mmol}}{1 \text{ mL}} \right) = 766.3 \text{ mmol}$$

$$175 \text{ mL} \left(\frac{4.34 \text{ mmol}}{1 \text{ mL}} \right) = 759.5 \text{ mmol}$$

$$766.3 \text{ mol} + 759.5 \text{ mmol} = 1525.8 \text{ mmol}$$

$$\text{Molarity} = \frac{1525.8 \text{ mmol}}{500.0 \text{ mL}} = 3.052 \text{ M}$$

11.72 The original number of millimoles of Na⁺ is

$$(20.0 \text{ mL}) \left(\frac{3.00 \text{ mmol}}{1 \text{ mL}} \right) = 60.0 \text{ mmol}$$

The sodium ion is a spectator ion in the acid-base reaction, so 60.0 mmol Na⁺ is present in the final solution:

$$\frac{60.0 \text{ mmol}}{100.0 \text{ mL}} = 0.600 \text{ M}$$

11.74 Represent the acids as HX. Then

$$\text{HX(aq)} + \text{NaOH(aq)} \rightarrow \text{NaX(aq)} + \text{H}_2\text{O}(\ell)$$

$$37.88 \text{ mL NaOH} \left(\frac{0.2000 \text{ mmol NaOH}}{1 \text{ mL NaOH}} \right) \left(\frac{1 \text{ mmol HX}}{1 \text{ mmol NaOH}} \right) = 7.576 \text{ mmol HX}$$

$$\frac{7.576 \text{ mmol HX}}{20.0 \text{ mL HX}} = 0.379 \text{ M HX}$$

The total concentration of all acids is 0.379 M.

11.75 (a) Assume any volume, such as 1.00 mL (or use the algebraic variable, V):

$$1.00 \text{ mL} \left(\frac{1.25 \text{ mmol}}{1 \text{ mL}} \right) = 1.25 \text{ mmol HCl}$$

$$1.00 \text{ mL} \left(\frac{1.25 \text{ mmol}}{1 \text{ mL}} \right) = 1.25 \text{ mmol NaCl}$$

The 2.00 mL of solution contains 1.25 mmol H⁺, 1.25 mmol Na⁺, and 2.50 mmol of Cl⁻.

$$\frac{1.25 \text{ mmol H}^+}{2.00 \text{ mL}} = 0.625 \text{ M H}^+$$

$$\frac{1.25 \text{ mmol Na}^+}{2.00 \text{ mL}} = 0.625 \text{ M Na}^+$$

$$\frac{2.50 \text{ mmol Cl}^-}{2.00 \text{ mL}} = 1.25 \text{ M Cl}^-$$

(b) The number of millimoles of acid and salt are the same here as they were in part (a), but HC₂H₃O₂ is a *weak* acid, which will ionize only insignificantly.

Thus we have

$$\frac{1.25 \text{ mmol Na}^+}{2.00 \text{ mL}} = 0.625 \text{ M Na}^+$$

$$\frac{1.25 \text{ mmol C}_2\text{H}_3\text{O}_2^-}{2.00 \text{ mL}} = 0.625 \text{ M C}_2\text{H}_3\text{O}_2^-$$

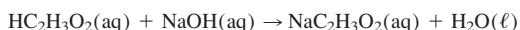
In this solution, the acid contributes essentially no H⁺ or C₂H₃O₂⁻.

11.77 (a) Assuming no reaction,

$$\frac{0.150 \text{ mol HC}_2\text{H}_3\text{O}_2}{1.00 \text{ L}} = 0.150 \text{ M HC}_2\text{H}_3\text{O}_2$$

$$\frac{0.100 \text{ mol C}_2\text{H}_3\text{O}_2^-}{1.00 \text{ L}} = 0.100 \text{ M C}_2\text{H}_3\text{O}_2^-$$

(b) The base reacts with the acid:



Initial:	0.250 mol	0.100 mol	0.000 mol
Change:	-0.100 mol	-0.100 mol	+0.100 mol
Final:	0.150 mol	0.000 mol	0.100 mol

These quantities are exactly what was presented in part (a), so the concentrations are the same also.

$$11.79 \quad 0.0943 \text{ L} \left(\frac{2.14 \text{ mol MgCl}_2}{1 \text{ L}} \right) = 0.2018 \text{ mol MgCl}_2$$

$$0.0828 \text{ L} \left(\frac{0.700 \text{ mol AlCl}_3}{1 \text{ L}} \right) = 0.05796 \text{ mol AlCl}_3$$

0.2018 mol MgCl₂ consists of 0.2018 mol Mg²⁺ and 0.4036 mol Cl⁻

0.05796 mol AlCl₃ consists of 0.05796 mol Al³⁺ and 0.1739 mol Cl⁻

There is a total of 0.5775 mol of Cl⁻ ions in the final solution. The final concentrations are

$$\frac{0.2018 \text{ mol Mg}^{2+}}{0.5000 \text{ L}} = 0.404 \text{ M Mg}^{2+}$$

$$\frac{0.05796 \text{ mol Al}^{3+}}{0.5000 \text{ L}} = 0.116 \text{ M Al}^{3+}$$

$$\frac{0.5775 \text{ mol Cl}^-}{0.5000 \text{ L}} = 1.16 \text{ M Cl}^-$$

11.80 Li₃N(s) + 3 H₂O(ℓ) → NH₃(aq) + 3 Li⁺(aq) + 3 OH⁻(aq)

$$0.110 \text{ mol Li}_3\text{N} \left(\frac{3 \text{ mol OH}^-}{1 \text{ mol Li}_3\text{N}} \right) = 0.330 \text{ mol OH}^-$$

The 0.330 mol of OH⁻ in 0.1000 L of solution represents a 3.30 M OH⁻ solution.

11.83 Na₂CO₃(s) + 2 HCl(aq) → 2 NaCl(aq) + CO₂(g) + H₂O(ℓ)

$$32.74 \text{ mL HCl} \left(\frac{5.000 \text{ mmol HCl}}{1 \text{ mL HCl}} \right) = 163.7 \text{ mmol HCl added}$$

$$4.20 \text{ mL NaOH} \left(\frac{1.000 \text{ mmol NaOH}}{1 \text{ mL NaOH}} \right) = 4.20 \text{ mmol NaOH}$$

Of the 163.7 mmol of HCl added, 4.20 mmol was in excess and was neutralized by the NaOH. The rest, 163.7 mmol - 4.20 mmol = 159.5 mmol, reacted with the Na₂CO₃:

$$159.5 \text{ mmol HCl} \left(\frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol HCl}} \right) \left(\frac{106.0 \text{ mg Na}_2\text{CO}_3}{1 \text{ mmol Na}_2\text{CO}_3} \right) = 8454 \text{ mg Na}_2\text{CO}_3 = 8.454 \text{ g Na}_2\text{CO}_3$$

$$\% \text{ Na}_2\text{CO}_3 = \left(\frac{8.454 \text{ g}}{10.0 \text{ g}} \right) \times 100\% = 84.5\%$$

11.86 The numbers of millimoles of acid and base are calculated from the volumes and molarities:

$$25.00 \text{ mL H}_3\text{PO}_4 \left(\frac{2.500 \text{ mmol H}_3\text{PO}_4}{1 \text{ mL H}_3\text{PO}_4} \right) = 62.50 \text{ mmol H}_3\text{PO}_4$$

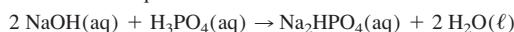
$$39.66 \text{ mL NaOH} \left(\frac{3.152 \text{ mmol NaOH}}{1 \text{ mL NaOH}} \right) = 125.0 \text{ mmol NaOH}$$

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The ratio of acid to base is

$$\frac{125.0 \text{ mmol NaOH}}{62.50 \text{ mmol H}_3\text{PO}_4} = \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_3\text{PO}_4}$$

The balanced equation is therefore



11.89 $10.0 \text{ mL HC}_2\text{H}_3\text{O}_2 \left(\frac{1.50 \text{ mmol HC}_2\text{H}_3\text{O}_2}{1 \text{ mL HC}_2\text{H}_3\text{O}_2} \right) = 15.0 \text{ mmol HC}_2\text{H}_3\text{O}_2$

$$10.0 \text{ mL OH}^- \left(\frac{0.850 \text{ mmol OH}^-}{1 \text{ mL OH}^-} \right) = 8.50 \text{ mmol OH}^-$$

The $\text{HC}_2\text{H}_3\text{O}_2$ is in excess, so 8.50 mmol of $\text{HC}_2\text{H}_3\text{O}_2$ will react, producing 8.50 mmol of $\text{C}_2\text{H}_3\text{O}_2^-$ and leaving 6.5 mmol of $\text{HC}_2\text{H}_3\text{O}_2$ in excess. The final concentrations of $\text{C}_2\text{H}_3\text{O}_2^-$ and $\text{HC}_2\text{H}_3\text{O}_2$ are

$$\frac{8.50 \text{ mmol C}_2\text{H}_3\text{O}_2^-}{20.0 \text{ mL}} = 0.425 \text{ M C}_2\text{H}_3\text{O}_2^-$$

$$\frac{6.5 \text{ mmol HC}_2\text{H}_3\text{O}_2}{20.0 \text{ mL}} = 0.33 \text{ M HC}_2\text{H}_3\text{O}_2$$

(Note that the concentration of $\text{HC}_2\text{H}_3\text{O}_2$ was reduced by reaction with OH^- and reduced more by the doubling of the original volume of the solution.)

11.91 (a) The NaCl consists of 49.68 mmol Na^+ and 49.68 mmol Cl^- .
The NaOH consists of 28.43 mmol Na^+ and 28.43 mmol OH^- .

The total number of millimoles of Na^+ is 78.11 mmol.

The concentrations are

$$\frac{78.11 \text{ mmol Na}^+}{111.23 \text{ mL}} = 0.7022 \text{ M Na}^+$$

$$\frac{28.43 \text{ mmol OH}^-}{111.23 \text{ mL}} = 0.2556 \text{ M OH}^-$$

$$\frac{49.68 \text{ mmol Cl}^-}{111.23 \text{ mL}} = 0.4466 \text{ M Cl}^-$$

(b) $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell)$

When the

$$33.12 \text{ mL} \left(\frac{1.500 \text{ mmol}}{1 \text{ mL}} \right) = 49.68 \text{ mmol of HCl}$$

reacts with the excess NaOH , 49.68 mmol of NaCl is formed, and 28.43 mmol of NaOH remains unreacted because it is in excess. The same concentrations are obtained as in part (a).

(c) Because both part (a) and part (b) have the same volumes and the same quantities of the same compounds, the results are the same.

11.93 $0.03838 \text{ L} \left(\frac{5.000 \text{ mol}}{1 \text{ L}} \right) = 0.1919 \text{ mol NaOH}$

Because the HA and the NaOH react in a 1 : 1 ratio, the sample contained 0.1919 mol of acid:

$$\text{MM} = \frac{12.11 \text{ g}}{0.1919 \text{ mol}} = 63.11 \text{ g/mol}$$

12 Gases

- 12.1** (a) $x = 0.2$ (b) $V = 0.2$ (c) $x = 14.4$
 (d) $x = 8$ (e) $x = 15.75$ (f) $x = 5.04$
 (g) $x = 6.41$ (h) $x = 0.172$

Note that parts (a) and (b) are the same, despite the difference in variable identity.

Always check your calculations to see that they are (approximately) correct.

- 12.2** (a) A given sample of gas and constant temperature
 (b) A given sample of gas and constant pressure (as well as Kelvin temperatures)
 (c) A given sample of gas (as well as Kelvin temperatures)
- 12.3** The gas laws apply only to gases; under the given conditions, all but I_2 and Al are gases.
- 12.5** The volume will go down because the temperature is going down. Celsius temperature is *not* directly proportional to volume.
- 12.6** The volume of a gas may be increased by allowing it to expand into an evacuated vessel, as shown in part (a) of the problem, by withdrawing a piston in a cylinder, as shown in part (b), or by other means.
- (a) If a 4.00-L sample is allowed to expand into a 6.00-L evacuated vessel, its final volume is 10.00 L. The gas starts out in the left vessel; there is nothing in the right vessel. The gas is expanded 6.00 L, or expanded *by* 6.00 L, finally occupying both vessels with a volume of 10.00 L.
 (b) If a 4.00-L sample is expanded in a cylinder to a total volume of 6.00 L, its final volume is 6.00 L. It is expanded *to* 6.00 L.
- 12.7** The combined gas law equation is
- $$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
- (a) If the temperature is constant, $T_1 = T_2$. Multiplying both sides of the combined gas law equation by this equation yields $P_1 V_1 = P_2 V_2$, which is the Boyle's law equation.
 (b) If the pressure is constant, $P_1 = P_2$. Dividing both sides of the combined gas law equation by this equation yields the Charles' law equation:
- $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
- 12.8** Because the temperature and volume do not change, the pressure also does not change.
- 12.9** The average distance between molecules in a liquid is very much smaller than the average distance between molecules in a gas, as illustrated in Example 12.31.
- 12.10** The molecules get farther apart on the average.
- 12.11** Three significant digits: $5^\circ\text{C} + 273^\circ = 278 \text{ K}$
- 12.12** (a) The final volume is 7.00 L.
 (b) The final volume is 4.00 L.
 (c) The final volume is 7.00 L.
- 12.13** The Kelvin (absolute) scale
- 12.14** (a) $0.985 \text{ atm} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) = 749 \text{ torr}$
 (b) $1.75 \text{ atm} \left(\frac{760 \text{ mm Hg}}{1 \text{ atm}} \right) = 1330 \text{ mm Hg}$
 (c) $698 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.918 \text{ atm}$
 (d) $909 \text{ torr} \left(\frac{1 \text{ mm Hg}}{1 \text{ torr}} \right) = 909 \text{ mm Hg}$
 (e) $355 \text{ mm Hg} \left(\frac{1 \text{ torr}}{1 \text{ mm Hg}} \right) = 355 \text{ torr}$
 (f) $472 \text{ mm Hg} \left(\frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) = 0.621 \text{ atm}$

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12.15 (a) $76.0 \text{ cm} \times 1.00 \text{ cm}^2 = 76.0 \text{ cm}^3$

(b) $76.0 \text{ cm}^3 \left(\frac{13.6 \text{ g}}{1 \text{ cm}^3} \right) = 1.03 \times 10^3 \text{ g} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 1.03 \text{ kg}$

(c) The mass is three times as great, 3.09 kg.

(d) The weight of the wider column is three times as great because its mass is three times as great. The force pushing it up is also three times as great, however, because its area is three times as great, and the force is equal to pressure times area:

$$f = PA$$

Thus, the height of mercury in a simple barometer is independent of the cross-sectional area of the tube.

12.16 (a) $93.44 \text{ kPa} \left(\frac{1.000 \text{ atm}}{101.3 \text{ kPa}} \right) \left(\frac{760.0 \text{ torr}}{1 \text{ atm}} \right) = 701.0 \text{ torr}$

(b) $1.00 \times 10^2 \text{ Pa} \left(\frac{1 \text{ kPa}}{1000 \text{ Pa}} \right) \left(\frac{1.000 \text{ atm}}{101.3 \text{ kPa}} \right) \left(\frac{760.0 \text{ torr}}{1 \text{ atm}} \right) = 0.750 \text{ torr}$

(c) $2.35 \times 10^3 \text{ torr}$

12.18 The gas will push the piston out until the pressures are equal.

12.19 $P_2 = \frac{P_1 V_1}{V_2} = \frac{(828 \text{ torr})(7.55 \text{ L})}{14.3 \text{ L}} = 437 \text{ torr}$

12.21 (a) $548 \text{ mL} \left(\frac{0.001 \text{ L}}{1 \text{ mL}} \right) = 0.548 \text{ L}$

(b) $P_2 = \frac{P_1 V_1}{V_2} = \frac{(1.75 \text{ atm})(6.44 \text{ L})}{0.548 \text{ L}} = 20.6 \text{ atm}$

12.23 (a) $V_2 = 3.00 \text{ L} + 5.00 \text{ L} = 8.00 \text{ L}$

$P_2 = \frac{P_1 V_1}{V_2} = \frac{(1.00 \text{ atm})(3.00 \text{ L})}{8.00 \text{ L}} = 0.375 \text{ atm}$

(b) $V_2 = 5.00 \text{ L}$

$P_2 = \frac{(1.00 \text{ atm})(3.00 \text{ L})}{5.00 \text{ L}} = 0.600 \text{ atm}$

12.24 $P_1 V_1 = P_2 V_2$

(a) $P_2 = \frac{P_1 V_1}{V_2} = \frac{(1.13 \text{ atm})(0.992 \text{ L})}{3.79 \text{ L}} = 0.296 \text{ atm}$

(b) $P_1 = \frac{P_2 V_2}{V_1} = \frac{(1.13 \text{ atm})(0.992 \text{ L})}{3.79 \text{ L}} = 0.296 \text{ atm}$

Note that parts (a) and (b) have the same answer. It does not matter whether we are solving for the initial or the final pressure, as long as the 1.13 atm is the pressure at 0.992 L.

12.26 (a) 1.3 L

(b) Estimating the volume at a pressure of 11.00 atm is difficult because it is not easy to estimate how much the line will curve at a point past the experimental data.

12.27 Because the temperature does not change (it is constant), this is a Boyle's law problem. Change the second volume to milliliters to match the units of the first volume:

$$1.31 \text{ L} \left(\frac{1 \text{ mL}}{0.001 \text{ L}} \right) = 1310 \text{ mL}$$

Tabulate the data:

P	V
1 P_1	712 torr 689 mL
2 P_2	1310 mL

Rearrange the equation and solve:

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{(712 \text{ torr})(689 \text{ mL})}{1310 \text{ mL}} = 374 \text{ torr}$$

12.31 $V_2 = \frac{P_1 V_1}{P_2} = \frac{P_1 (4.68 \text{ L})}{3P_1} = 1.56 \text{ L}$

V **T**

1	5.41 L	353 K
2	V_2	302 K

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(5.41 \text{ L})(302 \text{ K})}{353 \text{ K}} = 4.63 \text{ L}$$

V **T**

1	V_1	301 K
2	52.5 mL	285 K

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = \frac{V_2 T_1}{T_2} = \frac{(52.5 \text{ mL})(301 \text{ K})}{285 \text{ K}} = 55.4 \text{ mL}$$

12.34 (a) No; the volume is *not* proportional to the Celsius temperature.

(b) The ratio is equal to the ratio of absolute (Kelvin) temperatures:

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} = \frac{294 \text{ K}}{280 \text{ K}} = 1.05$$

V **T**

1	122 mL	328 K
2	V_2	402 K

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(122 \text{ mL})(402 \text{ K})}{328 \text{ K}} = 150 \text{ mL}$$

12.41 Sample B will be increased more because the Kelvin temperature ratio is larger for B:

For A: $\frac{293 \text{ K}}{283 \text{ K}} = 1.04$

For B: $\frac{473 \text{ K}}{373 \text{ K}} = 1.27$

12.42 (a) $\frac{V_1}{312 \text{ K}} = \frac{1.55 \text{ L}}{393 \text{ K}}$

$$V_1 = 1.23 \text{ L}$$

(b) 221 K (c) 198 K (d) 0.209 m³

P **V** **T**

1	1.00 atm	6.40 L
2	1.17 atm	V_2

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{(1.00 \text{ atm})(6.40 \text{ L})(310 \text{ K})}{(273 \text{ K})(1.17 \text{ atm})} = 6.21 \text{ L}$$

12.45 $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

(a) $T_1 = \frac{P_1 V_1 T_2}{P_2 V_2} = \frac{(3.50 \text{ atm})(2.03 \text{ L})(259 \text{ K})}{(1.72 \text{ atm})(3.11 \text{ L})} = 344 \text{ K}$

(b) $P_1 = \frac{P_2 V_2 T_1}{V_1 T_2} = \frac{(903 \text{ torr})(0.794 \text{ L})(317 \text{ K})}{(1.33 \text{ L})(291 \text{ K})} = 587 \text{ torr}$

(c) $P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = \frac{(0.999 \text{ atm})(16.5 \text{ L})(297 \text{ K})}{(12.9 \text{ L})(282 \text{ K})} = 1.35 \text{ atm}$

(d) $T_1 = \frac{P_1 V_1 T_2}{P_2 V_2} = \frac{(2.00 \text{ atm})(6.00 \text{ L})(695 \text{ K})}{(4.50 \text{ atm})(0.975 \text{ L})} = 1900 \text{ K}$

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$$(e) V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(1.57 \text{ atm})(829 \text{ mL})(289 \text{ K})}{(1.292 \text{ atm})(303 \text{ K})} = 961 \text{ mL}$$

$$(f) V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(717 \text{ torr})(602 \text{ mL})(320 \text{ K})}{(2280 \text{ torr})(320 \text{ K})} = 189 \text{ mL}$$

$$(g) T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = \frac{(665 \text{ torr})(4.48 \text{ L})(382 \text{ K})}{(1011 \text{ torr})(6.12 \text{ L})} = 184 \text{ K}$$

$$(h) P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = \frac{(797 \text{ torr})(2.13 \text{ L})(351 \text{ K})}{(9.11 \text{ L})(304 \text{ K})} = 215 \text{ torr}$$

- 12.47** The pressure in torr is converted to atmospheres, and Kelvin temperatures are used for each part:

$$(a) 696 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.9158 \text{ atm}$$

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{(1.00 \text{ atm})(7.10 \text{ L})(306 \text{ K})}{(273 \text{ K})(0.9158 \text{ atm})} = 8.69 \text{ L}$$

$$(b) 792 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.042 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(0.977 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(306 \text{ K})}{1.042 \text{ atm}} = 23.6 \text{ L}$$

- 12.48** The number of moles of gas before the change may be calculated as follows:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(7.10 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 \text{ K})} = 0.3168 \text{ mol}$$

The same number of moles is present after the change because it is the same sample of gas. The new pressure in atmospheres is

$$696 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.9158 \text{ atm}$$

The new volume is

$$V = \frac{nRT}{P} = \frac{(0.3168 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(306 \text{ K})}{0.9158 \text{ atm}} = 8.69 \text{ L}$$

- 12.49** (a) $T = \frac{PV}{nR} = \frac{(1.25 \text{ atm})(14.0 \text{ L})}{(1.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})} = 142 \text{ K}$

(b) The gas is more likely to be H₂ because H₂O would be a solid at that temperature.

- 12.51** $P = \frac{nRT}{V} = \frac{(0.515 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(307 \text{ K})}{8.05 \text{ L}} = 1.61 \text{ atm}$

- 12.54** $n = \frac{PV}{RT} = \frac{(0.5026 \text{ atm})(0.152 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(419 \text{ K})} = 0.00222 \text{ mol}$

- 12.58** $P = \frac{nRT}{V} = \frac{(0.300 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(303 \text{ K})}{14.7 \text{ L}} = 0.508 \text{ atm}$

- 12.60** The total number of moles is 6.00 mol. The ideal gas law works for both the gas mixture and the individual components, so

$$P_{\text{total}} = n_{\text{total}} RT/V \quad \text{and} \quad P_{\text{He}} = n_{\text{He}} RT/V$$

Dividing the second of these equations by the first yields

$$\frac{P_{\text{He}}}{P_{\text{total}}} = \frac{n_{\text{He}} RT/V}{n_{\text{total}} RT/V}$$

R, T, and V all cancel out, leaving

$$\frac{P_{\text{He}}}{P_{\text{total}}} = \frac{n_{\text{He}}}{n_{\text{total}}}$$

The partial pressures are directly proportional to the numbers of moles present.

$$P_{\text{He}} = \frac{n_{\text{He}} P_{\text{total}}}{n_{\text{total}}} = \frac{(2.00 \text{ mol})(6.69 \text{ atm})}{6.00 \text{ mol}} = 2.23 \text{ atm}$$

The pressures of the other gases can be calculated in the same way:

$$P_{\text{Ne}} = P_{\text{Ar}} = 2.23 \text{ atm}$$

As a check, calculate the total pressure:

$$2.23 \text{ atm} + 2.23 \text{ atm} + 2.23 \text{ atm} = 6.69 \text{ atm}$$

- 12.63** The numbers of moles of all the components are the same, so the partial pressures are also the same. The volumes and temperatures of all gases in any gaseous mixture are the same, and in this mixture, the pressures are also the same. Because $P = nRT/V$, and all the factors on the right side of the equation are the same for all the gases, the value of P must also be the same for all the gases.

- 12.65** The partial pressure of water vapor in this system is 782 torr – 752 torr = 30 torr.

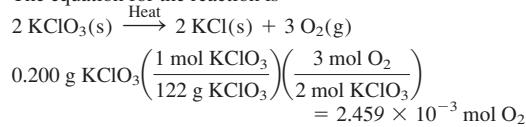
The temperature is determined from Table 12.3 to be 29°C.

- 12.66** The vapor pressure of water is determined from Table 12.3.

$$P_{\text{O}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}}$$

$$= 781 \text{ torr} - 42.2 \text{ torr} = 739 \text{ torr}$$

- 12.67** The equation for the reaction is



The oxygen pressure is the total pressure minus the water vapor pressure (from Table 12.3):

$$866.4 \text{ torr} - 23.76 \text{ torr} = 842.6 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.109 \text{ atm}$$

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

$$= \frac{(2.459 \times 10^{-3} \text{ mol O}_2)(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})}{1.109 \text{ atm}}$$

$$= 0.0542 \text{ L}$$

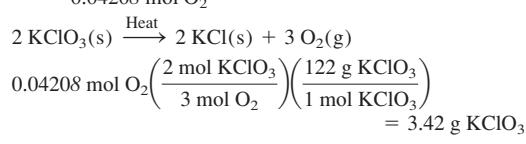
- 12.70** The partial pressure of the oxygen is

$$P_{\text{O}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}} = 769 \text{ torr} - 12.8 \text{ torr} = 756.2 \text{ torr}$$

$$= 0.995 \text{ atm}$$

$$n_{\text{O}_2} = \frac{P_{\text{O}_2} V}{RT} = \frac{(0.995 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(288 \text{ K})}$$

$$= 0.04208 \text{ mol O}_2$$



- 12.73** (a) $0.901 \text{ g N}_2 \left(\frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} \right) = 0.03218 \text{ mol N}_2$

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

$$= \frac{(0.03218 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})}{12.4 \text{ L}}$$

$$= 0.0635 \text{ atm}$$

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(b) $0.901 \text{ g Cl}_2 \left(\frac{1 \text{ mol Cl}_2}{70.9 \text{ g Cl}_2} \right) = 0.01271 \text{ mol Cl}_2$

$$P = \frac{nRT}{V} = \frac{(0.01271 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})}{12.4 \text{ L}} = 0.0251 \text{ atm}$$

(c) Equal numbers of grams of N_2 and Cl_2 are different numbers of moles.

12.75 $n = \frac{PV}{RT} = \frac{(1.10 \text{ atm})(5.52 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(285 \text{ K})} = 0.2595 \text{ mol}$

$$\frac{11.4 \text{ g}}{0.2595 \text{ mol}} = 43.9 \text{ g/mol}$$

12.79 $682 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.8974 \text{ atm}$

$$n = \frac{PV}{RT} = \frac{(0.8974 \text{ atm})(1.55 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} = 0.05685 \text{ mol}$$

$$\frac{1.60 \text{ g}}{0.05685 \text{ mol}} = 28.1 \text{ g/mol}$$

The empirical formula is calculated as in Section 7.4:

$$85.63 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.130 \text{ mol C}$$

$$14.37 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 14.26 \text{ mol H}$$

$$\frac{14.26 \text{ mol H}}{7.130 \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

The empirical formula is CH_2 . The empirical formula mass is therefore 14.0 amu per empirical formula unit. The number of empirical formula units per molecule is given by

$$\frac{28.1 \text{ amu/molecule}}{14.0 \text{ amu/empirical formula unit}} = \frac{2 \text{ empirical formula units}}{1 \text{ molecule}}$$

The molecular formula is $(\text{CH}_2)_2$, or C_2H_4 .

12.81 The gas laws apply to moles of *molecules*, whether the molecules are monatomic, diatomic, or polyatomic. In any case, the correct number of atoms per molecule is necessary to calculate masses of gaseous elements from the numbers of their moles.

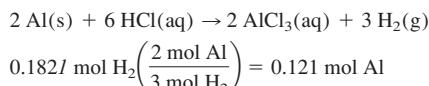
12.82 $n = \frac{PV}{RT} = \frac{(0.989 \text{ atm})(0.912 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(385 \text{ K})} = 0.02854 \text{ mol H}_2\text{O(g)}$

$$2 \text{ H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{ H}_2\text{O(g)}$$

$$0.02854 \text{ mol H}_2\text{O} \left(\frac{2 \text{ mol H}_2}{2 \text{ mol H}_2\text{O}} \right) \left(\frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} \right) = 0.0575 \text{ g H}_2$$

12.84 $n = \frac{PV}{RT} = \frac{(1.11 \text{ atm})(4.04 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(300 \text{ K})} = 0.1821 \text{ mol}$

Be careful; this is the number of moles of H_2 gas, not the number of moles of aluminum! We must determine the number of moles of aluminum from the balanced chemical equation.



12.87 $n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(2.26 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(296 \text{ K})} = 0.0930 \text{ mol}$

Be careful; this is the number of moles of O_2 gas, not the number of moles of HgO ! We must determine the number of moles of HgO from the balanced chemical equation.



$$0.0930 \text{ mol O}_2 \left(\frac{2 \text{ mol HgO}}{1 \text{ mol O}_2} \right) = 0.186 \text{ mol HgO}$$

12.90 $2 \text{ NaHCO}_3\text{(s)} \xrightarrow{\text{Heat}} \text{Na}_2\text{CO}_3\text{(s)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(g)}$

$$14.2 \text{ g NaHCO}_3 \left(\frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g NaHCO}_3} \right) \left(\frac{1 \text{ mol CO}_2}{2 \text{ mol NaHCO}_3} \right) = 0.08452 \text{ mol CO}_2$$

$$V = \frac{nRT}{P} = \frac{(0.08452 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})}{1.00 \text{ atm}} = 2.07 \text{ L}$$

12.93 (a) $5 \text{ O}_2\text{(g)} + 4 \text{ NH}_3\text{(g)} \rightarrow 4 \text{ NO(g)} + 6 \text{ H}_2\text{O(l)}$

(b) $\frac{(5.00 \text{ mol O}_2)(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}} = 112 \text{ L}$

$$\frac{(4.00 \text{ mol NH}_3)(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}} = 89.7 \text{ L}$$

$$\frac{(4.00 \text{ mol NO})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})}{1.00 \text{ atm}} = 89.7 \text{ L}$$

(c) The ratios of part (b) and of the balanced chemical equation are both 5 : 4 : 4.

12.96 $2 \text{ L SO}_2 : 1 \text{ L O}_2 : 2 \text{ L SO}_3$

12.98 For each gas, $PV = nRT$. Because the two volumes are the same, the two temperatures are the same, and the two pressures are the same (and R is always the same), the numbers of moles must be the same and therefore the numbers of molecules must be the same.

12.99 $18.8 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.0188 \text{ L}$

$$\left(\frac{0.0188 \text{ L}}{30.6 \text{ L}} \right) \times 100\% = 0.0614\%$$

The molecules themselves occupy less than 0.10% of the volume of the gas, in accord with the kinetic molecular theory.

12.101 The more moles of the gas present, the more molecules bombard the walls and, therefore, the greater the force and pressure, all other factors being equal.

12.103 $n = \frac{PV}{RT} = \frac{(0.950 \text{ atm})(4.38 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} = 0.170 \text{ mol}$

$$\text{MM} = \frac{5.43 \text{ g}}{0.170 \text{ mol}} = 31.9 \text{ g/mol}$$

The gas is O_2 .

12.105 (a) At constant pressure, the volume of a gas is proportional to its absolute temperature (Charles' law). After the volume increases with temperature, it can be brought back to the original volume by increasing the pressure (Boyle's law) by the same factor. Thus, at constant volume, the pressure is directly proportional to the absolute temperature. For example, if we heat a gas to double its original absolute temperature at constant pressure, the volume will double. Then doubling the pressure will halve the volume to its original value. The gas is now at double the absolute temperature and double the original pressure at the original volume. Thus, the pressure is directly proportional to the absolute temperature at constant volume.

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- (b) Divide the combined gas law equation, $P_1V_1/T_1 = P_2V_2/T_2$, by an equation that states that the volume is constant, $V_1 = V_2$. The result is

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

12.107

	P	V	T
1	P_1	355 mL	T_1
2	$1.25P_1$	V_2	$0.900T_1$
$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{P_1(355 \text{ mL})(0.900T_1)}{(1.25P_1)T_1} = 256 \text{ mL}$			

- 12.109** (a) The volume of each gas is 1.00 L, and the pressures of the two gases are given by the ideal gas law equation:

$$P_{\text{Ne}} = \frac{nRT}{V} = 0.269 \text{ atm} \quad P_{\text{Ar}} = \frac{nRT}{V} = 0.489 \text{ atm}$$

There is no mixture, so there is no total pressure. The total volume is 2.00 L.

- (b) The volume is 1.00 L, and the pressures of the two gases are the same as they were in part (a). The total pressure is the sum of those two partial pressures:

$$P_{\text{total}} = 0.269 \text{ atm} + 0.489 \text{ atm} = 0.758 \text{ atm}$$

(Note: If gases are mixed, their volumes are the same and their pressures are added. If they are not mixed, their volumes are added.)

$$\text{12.116 } n = \frac{PV}{RT} = \frac{(2.59 \text{ atm})(6.87 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(320 \text{ K})} = 0.6773 \text{ mol}$$

$$\text{MM} = \frac{2.71 \text{ g}}{0.6773 \text{ mol}} = 4.00 \text{ g/mol} \quad \text{The gas is helium.}$$

Ordinarily, one cannot identify a substance from its molar mass, but the only stable gaseous substances with molar masses this low are H₂ (MM = 2.016 g/mol) and He (MM = 4.0026 g/mol).

- 12.119** Problem 12.45 (f) and 12.46 (h) can be solved with Boyle's law because the temperature is constant in each. Problem 12.46 (b) can be solved with Charles' law because the pressure is constant.

$$\text{12.121 (a) } n = \frac{PV}{RT} = \frac{(0.975 \text{ atm})(10.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.3985 \text{ mol}$$

- (b) The number of moles of O₂ that escapes is

$$5.75 \text{ g} \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 0.1797 \text{ mol O}_2$$

- (c) The number of moles remaining in the vessel is

$$0.3985 \text{ mol} - 0.1797 \text{ mol} = 0.2188 \text{ mol}$$

Because the volume of the steel vessel does not change, the final pressure is given by

$$P = \frac{nRT}{V} = \frac{(0.2188 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})}{10.0 \text{ L}} = 0.535 \text{ atm}$$

13 Atomic and Molecular Properties

- 13.1** (a) IA, alkali metals
(b) IA, alkali metals

13.2

	Number of Protons	Number of Electrons	Relative Size
(a) F	9	9	Smaller
	F ⁻	10	Larger
(b) Ne	10	10	Smaller
	O ²⁻	10	Larger

(c) Na	11	11	Larger
Na ⁺	11	10	Smaller
(d) Ar	18	18	Smaller
Cl ⁻	17	18	Larger

- 13.3** (a) Li is larger.
(b) N³⁻ is larger because it has 8 electrons in the second shell, whereas Li⁺ has none.

- 13.4** The polyatomic ions are larger.

- 13.5** (a) Li (b) Li (c) Li (d) No difference

- 13.6** (a) No
(b) Ionization energies are all positive; that is, it takes energy to remove the electron.

- 13.7** A polar bond is a covalent bond that exists between two atoms having an electronegativity difference greater than 0.2. A polar molecule results if one or more polar bonds in a molecule is not balanced by other polar bonds in the molecule.

- 13.8** (a) Any perfectly symmetrical molecule with polar bonds, such as CO₂ or BCl₃

- (b) No

	Electron Groups	Molecule
(a) CCl ₄	Tetrahedral	Tetrahedral
(b) NCl ₃	Tetrahedral	Trigonal pyramidal
(c) Cl ₂ O	Tetrahedral	Angular

- 13.10** The bond in H₂ is a covalent chemical bond. The hydrogen bond is an intermolecular force between molecules containing hydrogen atoms and nitrogen, oxygen, or fluorine atoms.

- 13.11** (a) Na (b) Rb⁺ (c) Br⁻
(d) S²⁻ (e) Br⁻ (f) S²⁻

- 13.14** F⁻ (It has the greatest nuclear charge.)

- 13.15** Ac (Size diminishes toward the right in the periodic table.)

- 13.16** (a) Fr (b) He

- 13.17** (a) I (b) P (c) K
(d) K (e) Cs (f) Ge

- 13.19** (a) He (b) Fr

- 13.20** (a) Noble gases (b) Alkali metals

- 13.23** (a) O (b) Li (c) Kr
(d) O (e) O (f) F

- 13.24** Groups IIA and 0. (Their electron affinities are negative.)

- 13.25** (a) Polar covalent (b) Ionic (c) Nonpolar covalent

- 13.27** (a) Ionic (b) Polar covalent

- 13.30** (a) Linear (b) Angular

- 13.32** (a), (b), (c), and (d) Tetrahedral

- 13.34** (a) Angular (b) Angular

- 13.35** (a) Angular (b) No

- 13.36** Nonpolar bonds have atoms of equal electronegativity that share electrons equally. Nonpolar molecules either have all bonds nonpolar or have any polar bonds oriented so that they cancel out each other's effects.

- 13.37** Yes, if the orientations of the polar bonds in the molecule cancel each other's effects.

- 13.44** (a) (The fluorine atoms are symmetrically oriented.)

- 13.45** (a) No, the molecules are nonpolar.
(b) Yes, the molecules are polar.

- 13.46** (a) Hydrogen bonding
(b) van der Waals forces only
(c) van der Waals forces only
(d) Dipole moments but no hydrogen bonding

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- (e) van der Waals forces only
(f) van der Waals forces only

13.49 SI_2 and NCl_3
(S and I have the same electronegativities, as do N and Cl.)

- 13.50** (a) Angular
(b) The angle in NO_2 is less because the single electron does not repel the other electron groups as well as the electron pair in NO_2^- .
- 13.51** (a) Na 5058 kJ/mol Al 5140 kJ/mol
(b) It takes less energy to produce $\text{Na}^{2+}(\text{g})$ from $\text{Na}(\text{g})$ than it takes to form $\text{Al}^{3+}(\text{g})$ from $\text{Al}(\text{g})$.
(c) Al^{3+} is the familiar ion in the solid state and in solution; Na^{2+} is not a stable species.

- 13.54** (a) It is trigonal planar. (We know because the polar bonds cancel.)
(b) It is probably trigonal pyramidal.

- 13.56** (a) Trigonal planar at each nitrogen atom
(b) Nonlinear at each oxygen atom

13.59 For twice the distance, $d_2 = 2d_1$:

$$f_2 = k/(2d_1)^2 = k/4d_1^2 = f_1/4$$

The force of attraction is reduced to one fourth.

For the larger distance,

$$\frac{3 \times 10^{-9} \text{ m}}{2.0 \times 10^{-10} \text{ m}} = 15$$

The force is reduced to $(\frac{1}{15})^2$ or $\frac{1}{225}$ times that in the lattice.

- 13.61** (a) $\frac{22,400 \text{ cm}^3}{6.02 \times 10^{23} \text{ molecules}} = 3.721 \times 10^{-20} \text{ cm}^3$
(b) $\sqrt[3]{V} = 3.34 \times 10^{-7} \text{ cm} = 3.34 \times 10^{-9} \text{ m}$
(c) $\frac{3.34 \times 10^{-9} \text{ m}}{2.00 \times 10^{-10} \text{ m}} = 16.7$

The molecules are on average about 16.7 times as far apart, so their attraction would be *reduced* $(16.7)^2 = 279$ times to 1/279th of that in the solid.

13.62 H^-

- 13.66** The line extends to about -60°C , 160°C below its real normal boiling point.

- 13.67** In water, there are two hydrogen atoms and two lone pairs in each molecule, allowing for a three-dimensional hydrogen bonded structure.

- 13.68** No pairs are as successful in hydrogen bonding as G–C and A–T.

14 Solids and Liquids, Energies of Physical and Chemical Changes

14.1 Forces Example

Chemical bonds	
Ionic bonds	NaCl
Covalent bonds	Diamond
Metallic bonds	Copper
Intermolecular forces	
van der Waals forces	I_2
Dipolar attractions	ICl
Hydrogen bonding	Ice

- 14.2** Gases have very small attractive forces between the particles (Section 12.10). An ionic substance has strong ionic bonds between its ions. If an ionic substance were in the gaseous state at room temperature, it would condense into a solid very quickly.

- 14.3** (a) The solid phase
(b) The liquid phase

- 14.4** (a) One is the reverse of the other. (See Figure 14.4.)
(b) Vaporization is endothermic.
(c) They have the same magnitude but opposite signs:
 $\text{Heat}_{\text{vap}} = -\text{Heat}_{\text{cond}}$

- 14.6** When metal is placed in water, both the metal and the water will finally come to the same temperature. The final temperature of the metal is thus 31.7°C .

- 14.7** It takes -7.30 kJ . The same quantity of energy is involved, but in the cooling process, the energy is *removed*, and its sign is minus.

- 14.8** (a) 31.3°C (b) 18.7°C

Initial ($^\circ\text{C}$)	Final ($^\circ\text{C}$)	Change ($^\circ\text{C}$)
(a) 21.2	33.1	11.9
(b) 21.2	54.3	33.1
(c) 21.2	54.3	33.1
(d) 21.2	54.3	33.1
(e) 33.1	87.4	54.3
(f) 33.1	21.2	-11.9

- 14.10** (a) Heat = $mc\Delta t = (16.9 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(12.6^\circ\text{C}) = 890.9 \text{ J}$
(b) Heat = $m\Delta H_{\text{vap}} = (16.9 \text{ g})(2260 \text{ J/g}) = 38,190 \text{ J}$
(c) Heat = $mc\Delta t = (16.9 \text{ g})(2.042 \text{ J/g}\cdot^\circ\text{C})(22.2^\circ\text{C}) = 766.1 \text{ J}$
(d) Heat = $890.9 \text{ J} + 38,190 \text{ J} + 766.1 \text{ J} = 39,800 \text{ J} = 39.8 \text{ kJ}$

- 14.11** (a) Enthalpy of sublimation
(b) Enthalpy of vaporization
(c) Enthalpy of formation of CO_2 or of combustion of carbon
(d) Enthalpy of combustion of C_3H_4
(e) Enthalpy of formation of C_3H_4

- 14.12** We would do a specific heat calculation for the warming of the ice to 0°C , a heat of fusion calculation for the melting of the ice, a specific heat calculation for the warming of the water, a heat of vaporization calculation for the vaporization of the water and another specific heat calculation for the warming of the resulting water vapor. Finally, we would add the five values together.

- 14.13** (a) High ΔH_{vap} (b) Low molar mass

- 14.14** LiF has strong bonds holding its ions together; CF_4 has only van der Waals forces holding its molecules to one another.

- 14.15** The compound with the doubly charged ions will melt at a higher temperature. The stronger attractions of the dipoles and dianionic charges require higher temperatures to disrupt. For example, NaF melts at 993°C and MgO melts at 2800°C .

- 14.18** SCl_4 (a molecular solid)

- 14.19** They have about the same van der Waals forces. Neither substance can exhibit hydrogen bonding because neither contains hydrogen. ICl has a dipole and Br_2 does not, so ICl should have the greater intermolecular forces. Because it has greater intermolecular forces, ICl boils at a higher temperature (ICl, 97.4°C ; Br_2 , 58.78°C).

- 14.21** The substance is a crystalline solid. The regularity of the positions of the particles is a characteristic of crystalline solids.

- 14.22** P_2O_3 is a molecular solid; Al_2O_3 is an ionic solid.

- 14.23** HI has the greater molar mass and the greater number of electrons. Therefore it has greater intermolecular forces, it boils at a higher temperature (HI, -35.5°C , HCl, -85°C).

- 14.27** (a) The water boils.

- (b) The water warms up.

- 14.30** There will be no change. Vapor pressure depends on temperature, not surface area.

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14.31 Nothing. No net quantity of water vaporizes, and no net quantity of steam condenses.

14.32 No; the pressure will be equal to the vapor pressure if the liquid and vapor phases are both present at equilibrium, but if all the liquid is vaporized, the pressure may be below the vapor pressure of water at that temperature.

14.33 (a) Heat = $mc\Delta t$
 $= (35.0 \text{ g})(4.184 \text{ J/g}\cdot\text{C})(41.6^\circ\text{C} - 10.5^\circ\text{C})$
 $= 4550 \text{ J} = 4.55 \text{ kJ}$

(b) Heat = $mc\Delta t$
 $= (35.0 \text{ g})(4.184 \text{ J/g}\cdot\text{C})(10.5^\circ\text{C} - 41.6^\circ\text{C})$
 $= -4550 \text{ J} = -4.55 \text{ kJ}$

In part (b), 4.55 kJ of heat must be *removed* from the water.

14.35 The specific heat of iron, listed in Table 14.4, is $0.442 \text{ J/g}\cdot\text{C}$. The change in temperature is given by

$$\Delta t = \frac{\text{heat}}{mc} = \frac{127 \text{ J}}{(51.5 \text{ g})(0.442 \text{ J/g}\cdot\text{C})} = 5.579^\circ\text{C}$$

The initial temperature was 23.0°C , and the change in temperature is 5.579°C , so the final temperature is $23.0^\circ\text{C} + 5.579^\circ\text{C} = 28.6^\circ\text{C}$.

14.36 The total heat added to the metal and water is zero. Thus,

$$0 = (46.0 \text{ g})(c_{\text{metal}})(36.1^\circ\text{C} - 78.0^\circ\text{C}) + (32.0 \text{ g})(4.184 \text{ J/g}\cdot\text{C})(36.1^\circ\text{C} - 23.1^\circ\text{C})$$
 $c_{\text{metal}} = 0.903 \text{ J/g}\cdot\text{C}$

The metal is most likely aluminum.

14.37 The specific heat of iron, listed in Table 14.4, is $0.442 \text{ J/g}\cdot\text{C}$. The heat required is given by

$$\text{Heat} = mc\Delta t = (23.9 \text{ g})(0.442 \text{ J/g}\cdot\text{C})(41.7^\circ\text{C}) = 441 \text{ J}$$

14.42 $(m_{\text{water}})(c_{\text{water}})(t_f - t_{\text{water}}) + m_{\text{Cr}}c_{\text{Cr}}(t_f - t_{\text{Cr}}) = 0$
 $(215 \text{ g})(4.184 \text{ J/g}\cdot\text{C})(t_f - 19.0^\circ\text{C}) + (25.0 \text{ g})(0.45 \text{ J/g}\cdot\text{C})(t_f - 54.5^\circ\text{C}) = 0$
 $899.6t_f - 17,090 + 11.3t_f - 613 = 0$

$$910.9t_f = 17,700$$

$$t_f = 19.4^\circ\text{C}$$

14.48 Heat = $mc\Delta t$

$$3950 \text{ J} = (250.0 \text{ g})(4.184 \text{ J/g}\cdot\text{C})(\Delta t)$$

$$\Delta t = 3.78^\circ\text{C}$$

14.49 The heat is calculated in three steps: (a) warming the ice to 0°C , (b) melting the ice, and (c) heating the liquid water. The answer is (d), the sum of these three:

- (a) Heat = $mc\Delta t = (27.7 \text{ g})(2.09 \text{ J/g}\cdot\text{C})(15.9^\circ\text{C}) = 920.5 \text{ J}$
 (b) Heat = $m\Delta H_{\text{fusion}} = (27.7 \text{ g})(335 \text{ J/g}) = 9280 \text{ J}$
 (c) Heat = $mc\Delta t = (27.7 \text{ g})(4.184 \text{ J/g}\cdot\text{C})(25.0^\circ\text{C}) = 2897 \text{ J}$
 (d) Heat = $920.5 \text{ J} + 9280 \text{ J} + 2897 \text{ J} = 13,100 \text{ J} = 13.10 \text{ kJ}$

14.51 Heat = 0 = $(m_{\text{cold}})(c_{\text{cold}})(t_f - t_{\text{cold}}) + (m_{\text{hot}})(c_{\text{hot}})(t_f - t_{\text{hot}})$

(a) Since the masses are equal and the specific heat is the same, this equation reduces to

$$t_f - t_{\text{cold}} = -t_f + t_{\text{hot}}$$

$$2t_f = 50.0^\circ\text{C} + 20.0^\circ\text{C}$$

$$t_f = 35.0^\circ\text{C}$$

The final temperature is merely the average of the original temperatures.

(b) The mass of the hot water is twice that of the cold water:
 $t_f - t_{\text{cold}} = 2(-t_f + t_{\text{hot}})$

$$3t_f = 100.0^\circ\text{C} + 20.0^\circ\text{C}$$

$$t_f = 40.0^\circ\text{C}$$

The final temperature is merely the *weighted* average of the original temperatures.

- 14.52** (a) $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g})$
 (b) $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
 (c) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 (d) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 (e) (c) and (d)

- 14.54** (a) $8 \text{ C}(\text{s}) + 9 \text{ H}_2(\text{g}) \rightarrow \text{C}_8\text{H}_{18}(\ell)$
 (b) $\text{C}_8\text{H}_{18}(\ell) + \frac{25}{2}\text{O}_2(\text{g}) \rightarrow 8 \text{ CO}_2(\text{g}) + 9 \text{ H}_2\text{O}(\ell)$

14.56 (a) $\text{CH}_2\text{O}(\ell) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$
 $\Delta H = -561 \text{ kJ}$

(b) $\Delta H = \Delta H_f(\text{CO}_2) + \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{CH}_2\text{O})$
 $-561 \text{ kJ} = (-393 \text{ kJ}) + (-286 \text{ kJ}) - \Delta H_f(\text{CH}_2\text{O})$
 $\Delta H_f = -118 \text{ kJ}$

(c) $68.3 \text{ g CH}_2\text{O} \left(\frac{1 \text{ mol CH}_2\text{O}}{30.0 \text{ g CH}_2\text{O}} \right) \left(\frac{-118 \text{ kJ}}{1 \text{ mol CH}_2\text{O}} \right) = -269 \text{ kJ}$

14.57 The last two equations represent the reverse of the formation reactions of H_2O and CO_2 , respectively. For the first reaction:

$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$
 $-561 \text{ kJ} = (-393 \text{ kJ}) + (-286 \text{ kJ}) - \Delta H_f(\text{CH}_2\text{O})$
 $\Delta H_f(\text{CH}_2\text{O}) = -118 \text{ kJ}$

Alternatively, the three equations could be added, along with their ΔH values, to give

$$\text{CH}_2\text{O} \rightarrow \text{C} + \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \Delta H = +118 \text{ kJ}$$

This is the reverse of the formation reaction for CH_2O , so $\Delta H_f = -118 \text{ kJ}$

- 14.59** $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

For 1 mol of CO:

$$\Delta H = (-393.5 \text{ kJ}) - (-110.5 \text{ kJ}) = -283.0 \text{ kJ}$$

For 125 g of CO:

$$125 \text{ g CO} \left(\frac{1 \text{ mol CO}}{28.0 \text{ g CO}} \right) \left(\frac{-283.0 \text{ kJ}}{1 \text{ mol CO}} \right) = -1260 \text{ kJ}$$

- 14.60** (a) 16.0 kJ (the sum of the two given equations)
 (b) +27.0 kJ (the reverse of the first equation)
 (c) +54.0 kJ (double the answer in part [b])

- 14.61** $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + 12 \text{ O}_2(\text{g}) \rightarrow 12 \text{ CO}_2(\text{g}) + 11 \text{ H}_2\text{O}(\ell)$
 $\Delta H = -5648 \text{ kJ}$

$$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{ O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\ell) \quad \Delta H = -2816 \text{ kJ}$$

$$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{ O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\ell) \quad \Delta H = -2824 \text{ kJ}$$

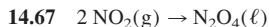
Subtracting the second and third of these equations from the first yields:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + \text{H}_2\text{O}(\ell) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \quad \Delta H = -8 \text{ kJ}$$

- 14.63** The second equation. The *complete* combustion (to give CO_2) by definition has associated with it ΔH_{comb} .

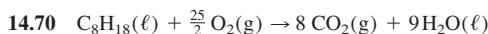
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$$\Delta H = 9.67 \text{ kJ} + (-67.70 \text{ kJ}) = -58.03 \text{ kJ}$$

Because the N_2O_4 is much more stable (the ΔH is very negative), the reaction is apt to be spontaneous.



(a) The reactants are present in the same ratio as the coefficients in the balanced equation. Both will react completely. For 1 mol of C_8H_{18} :

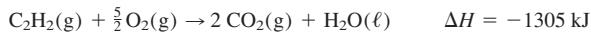
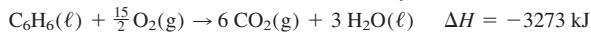
$$\begin{aligned}\Delta H &= \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) \\ &= 8\Delta H_f(\text{CO}_2) + 9\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_8\text{H}_{18}) \\ &= 8(-393.5 \text{ kJ}) + 9(-285.9 \text{ kJ}) - (-208 \text{ kJ}) \\ &= -5513 \text{ kJ}\end{aligned}$$

For 0.660 mol of C_8H_{18} :

$$0.660 \text{ mol} (-5513 \text{ kJ/mol}) = -3640 \text{ kJ}$$

(b) The same quantity of heat would have been produced because the octane would have been the limiting quantity.

14.71 Note that $\Delta H_{\text{combustion}}$ values, not ΔH_f values, are given.



For the given reaction,

$$\Delta H = -(-3273 \text{ kJ}) + 3(-1305 \text{ kJ}) = -642 \text{ kJ}$$

For 25.0 g of C_2H_2 :

$$25.0 \text{ g C}_2\text{H}_2 \left(\frac{1 \text{ mol C}_2\text{H}_2}{26.0 \text{ g C}_2\text{H}_2} \right) \left(\frac{-642 \text{ kJ}}{1 \text{ mol C}_2\text{H}_2} \right) = -617 \text{ kJ}$$

14.76 It came from potential energy—the energy of ordering the molecules or ions to their regular arrangement in the lattice.

14.77 NH_3 and AsH_3 each has greater intermolecular forces than does PH_3 . (NH_3 has hydrogen bonding, and AsH_3 has greater van der Waals forces.)

14.79 (a) No

(b) Because energy is produced, ΔH is negative for the reaction.

(c) Because energy is absorbed, ΔH is positive for the warming process.

(d) The overall enthalpy change is zero. Because the energy from the reaction is added to the solution, no energy is gained by or lost from the system.

14.80 For hydrogen:

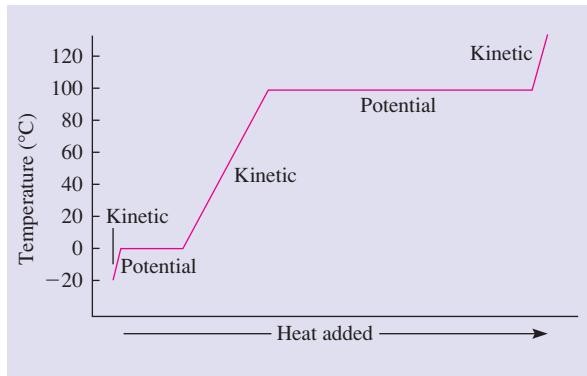
$$(14.4 \text{ J/g} \cdot ^\circ\text{C})(2.016 \text{ g/mol}) = 29.0 \text{ J/mol} \cdot ^\circ\text{C}$$

The molar heat capacities of the other elements are calculated in the same manner, giving the following results (in $\text{J/mol} \cdot ^\circ\text{C}$):

H_2	29.0	Al	24	Fe	24.7
O_2	29.5	Ag	26	Mg	24
N_2	29.1	Au	25.4	Pb	27
		Co	27	Sn	26
		Cr	23	Zn	25.4
		Cu	24.5		

Despite a wide range of specific heat capacities, the diatomic gases have molar heat capacities of about $29 \text{ J/mol} \cdot ^\circ\text{C}$, and the molar heat capacities of all the metallic elements are close to $26 \text{ J/mol} \cdot ^\circ\text{C}$. The latter generalization is known as the law of Dulong and Petit.

14.81



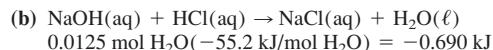
14.84 Because the concentration of water that can be held by the air decreases with decreasing temperature but the actual concentration of water in the air does not change, the relative humidity increases.

14.85 (a) $50.0 \text{ mL} \left(\frac{1.01 \text{ g}}{1 \text{ mL}} \right) = 50.5 \text{ g}$

$$\text{Heat} = mc \Delta t = 690 \text{ J} = (50.5 \text{ g})(4.10 \text{ J/g} \cdot ^\circ\text{C})\Delta t$$

$$\Delta t = 3.33^\circ\text{C}$$

$$t_f = 25.0^\circ\text{C} + 3.33^\circ\text{C} = 28.3^\circ\text{C}$$



(c) The final volume is 50.0 mL; the final concentration of NaCl is $(0.0125 \text{ mol})/(0.0500 \text{ L}) = 0.250 \text{ M}$. The heat of reaction in part (b) is -0.690 kJ , which is provided to the solution. Thus, heat added to the solution is $+0.690 \text{ kJ}$. Because all the factors are the same as in part (a), the final temperature is the same, 28.3°C .

14.86 CaO has doubly charged ions, as opposed to singly charged ions in KF . Because CaO has greater forces holding the particles together, it should have the higher melting point. The actual values are 2580°C for CaO and 858°C for KF .

14.88 (a) $15.60 \text{ g} - 15.00 \text{ g} = 0.60 \text{ g}$ of water is present at the end of the process that was not present initially. It has condensed from the steam.

(b) The water has warmed from 15.3°C to 39.4°C ; the heat required for this process is

$$\text{Heat} = mc \Delta t = (15.00 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(24.1^\circ\text{C}) \\ = 1513 \text{ J}$$

(c) The water condensed from steam has cooled from 100°C to 39.4°C . The heat liberated is

$$\text{Heat} = mc \Delta t = (0.60 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(-60.6^\circ\text{C}) \\ = -152 \text{ J}$$

(d) The total heat supplied is -1513 J . If we subtract the heat supplied by the cooling water, -152 J , we get the heat supplied by the condensation process:

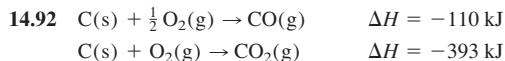
$$-1513 \text{ J} - (-152 \text{ J}) = -1361 \text{ J} = -1.361 \text{ kJ}$$

The heat is negative because the condensation process supplies heat to the cold water.

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- (e) The heat of vaporization per gram is the heat of part (d) divided by the number of grams, but changed in sign because the heat of vaporization is heat *added to the system*:

$$\frac{1.361 \text{ kJ}}{0.60 \text{ g}} = 2.3 \text{ kJ/g}$$



Let x = number of moles of CO formed

$$x(-110 \text{ kJ}) + (1.75 - x)(-393 \text{ kJ}) = -546 \text{ kJ}$$
 $-110x - 687.8 + 393x = -546$
 $283x = 141.8$
 $x = 0.5008 \text{ mol CO}$
 $1.75 - x = 1.25 \text{ mol CO}_2$

0.5008 mol CO takes 0.250 mol O₂

1.25 mol CO₂ takes 1.25 mol O₂

1.50 mol O₂ required

- 14.94** This problem may be thought of as involving limiting quantities, in that the heat available can be compared with the heat required for a certain purpose. The heat required to raise the temperature to 0°C is given by

$$\text{Heat} = mc\Delta t = (35.0 \text{ g})(2.089 \text{ J/g} \cdot ^\circ\text{C})(15^\circ\text{C}) \\ = 1100 \text{ J} = 1.10 \text{ kJ}$$

More heat than that is available. After the ice has been raised to the melting point, there will still be available

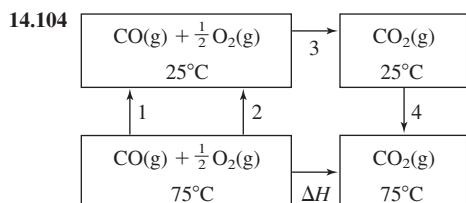
$$2.10 \text{ kJ} - 1.10 \text{ kJ} = 1.00 \text{ kJ}$$

The ice will start to melt. The heat required to melt all the ice is

$$(35.0 \text{ g})(335 \text{ J/g}) = 11,700 \text{ J} = 11.7 \text{ kJ}$$

Because not that much heat is still available, not all the ice will melt. At the end, there will be a mixture of water and ice, so the temperature will be 0°C.

- 14.99** The sudden expansion of liquid CO₂ does work pushing back the atmosphere and overcoming intermolecular forces in the liquid. The energy to do that work comes from the molecules themselves, so the average energy of the molecules is lowered. The CO₂ condenses to a solid because of this loss of energy.



$$\Delta H_1 = mc\Delta t = (28.0 \text{ g})(1.04 \text{ J/g} \cdot ^\circ\text{C})(-50^\circ\text{C}) = -1460 \text{ J}$$

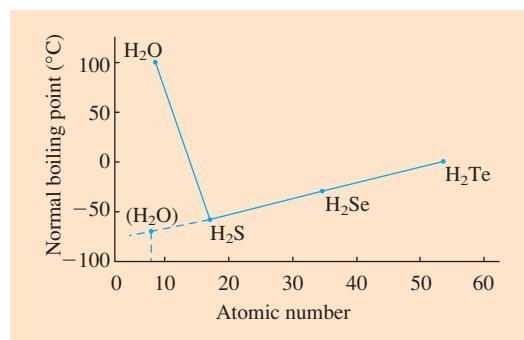
$$\Delta H_2 = mc\Delta t = \frac{1}{2}(32.0 \text{ g})(0.922 \text{ J/g} \cdot ^\circ\text{C})(-50^\circ\text{C}) = -738 \text{ J}$$

$$\Delta H_3 = \Delta H_{\text{combustion}} = -283 \text{ kJ}$$

$$\Delta H_4 = mc\Delta t = (44.0 \text{ g})(0.852 \text{ J/g} \cdot ^\circ\text{C})(+50^\circ\text{C}) = 1870 \text{ J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \\ = (-1.46 \text{ kJ}) + (-0.738 \text{ kJ}) + (-283 \text{ kJ}) + (1.87 \text{ kJ}) \\ = -283 \text{ kJ}$$

- 14.106** A plot of these data shows that water should boil at about -75°C. Because it actually boils 175°C higher than that, the effects of hydrogen bonding are obviously very important.

**15 Solutions**

- 15.1** (a) The first solution is unsaturated because it could hold 2.00 g additional of the solute at the temperature specified.

- (b) The second solution is saturated.

- (c) The third solution is obviously saturated because it is in contact with excess solid.

- 15.2** (a) KCl is more soluble at 10°C.
(b) KNO₃ is more soluble at 40°C.

- 15.3** The names differ by only one letter. The symbol for molality is lowercase *m*; for molarity, it is capital *M*. Kilograms rather than liters are involved in molality. A quantity of solvent rather than a quantity of solution appears in the denominator of the expression for molality.

- 15.4** They are similar in that they both are ratios of each component to the total and in that the total is specified in each case (100% for percent composition and 1 mol for mole fraction). They differ in the units used to calculate them—moles for mole fraction and masses for percent composition.

- 15.5** (a) A change of temperature will change the volume of the solution, and thus change its molarity.

- (b) No

$$\text{15.6 } 12.0 \text{ g NaCl} \left(\frac{1 \text{ mol NaCl}}{55.85 \text{ g NaCl}} \right) = 0.2149 \text{ mol NaCl}$$

$$\frac{0.2149 \text{ mol NaCl}}{0.125 \text{ kg H}_2\text{O}} = 1.72 \text{ m}$$

- 15.7** The percentage of water is

$$100.0\% \text{ total} - 25.0\% \text{ formaldehyde} = 75.0\% \text{ water}$$

- 15.8** By definition, the sum of the mole fractions must be 1.000; therefore,

$$X_{\text{alcohol}} = 1.000 - 0.930 = 0.070$$

- 15.9** By definition, the sum of the mole fractions must be 1.000; therefore,

$$X_{\text{CH}_3\text{O}} = 1.000 - 0.911 - 0.0450 = 0.044$$

$$\text{15.10 } 43.0 \text{ g KCl} \left(\frac{1 \text{ mol KCl}}{74.6 \text{ g KCl}} \right) = 0.5764 \text{ mol KCl}$$

$$\frac{0.5764 \text{ mol KCl}}{275 \text{ g H}_2\text{O}} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 15.28 \text{ mol H}_2\text{O}$$

$$X_{\text{KCl}} = \frac{0.5764}{0.5764 + 15.28} = 0.0364$$

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- 15.11** (a) Mole fraction (b) Molality (c) Molality
 (d) Molarity

15.12 The identity of the molecular solute does not affect the vapor pressure lowering (as long as the solute does not ionize); it is the number of molecules per unit mass of solvent that affects the extent of the vapor pressure lowering. Therefore, for all three parts of the problem,

$$P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\circ} = (0.850)(92.51 \text{ torr}) \\ = 78.63 \text{ torr}$$

$$\Delta P = 92.51 \text{ torr} - 78.63 \text{ torr} = 13.9 \text{ torr}$$

- 15.13** (a) The greater the molality, the greater the boiling-point elevation, so the 2.00 m solution has the greater elevation.
 (b) The greater the boiling-point elevation, the higher the boiling point, so the 2.00 m solution has the higher boiling point.

- 15.14** (a) The greater the molality, the greater the freezing-point depression, so the 2.00 m solution has the greater depression.
 (b) The greater the freezing-point depression, the lower the freezing point, so the 1.00 m solution has the higher freezing point.

15.15 % KCl = $\frac{43.0 \text{ g}}{43.0 \text{ g} + 275 \text{ g}} \times 100\% = 13.5\% \text{ KCl}$

$$\% \text{ H}_2\text{O} = 100.0\% - 13.5\% = 86.5\% \text{ H}_2\text{O}$$

15.17 Both C₈H₁₈ and C₆H₆ are nonpolar hydrocarbons. They are so similar that they readily dissolve in each other. C₆H₆ is nonpolar, and Na₂SO₄ is ionic. They are so different that Na₂SO₄ is not expected to dissolve in C₆H₆, and it does not.

15.18 Both CH₃OH and H₂O consist of polar molecules, and they can engage in hydrogen bonding. They are similar so they readily dissolve in each other. C₆H₆ is not polar and does not form hydrogen bonds; it is so different from water that it is not expected to dissolve appreciably in water, and it does not.

15.20 The —OH groups are very similar to water in their polarity and in their ability to form hydrogen bonds: "Like dissolves like."

- 15.21** (a) The negative end (b) The positive end
 (c) The positive end, because the oxygen atom has a small negative charge. Hydrogen bonding is expected between the hydrogen atoms of water and the oxygen atoms of formaldehyde.

15.22 Add excess salt to about 550 mL of water, and allow the mixture to stand until no more dissolves. Carefully pour off 500 mL of the solution (or filter off the remaining solid).

15.23 The 10 water molecules of hydration are lost.

- 15.24** (a) The added crystal would dissolve.
 (b) The excess solute would crystallize out.
 (c) The added crystal would not dissolve, nor would any more solid form.

15.26 Of these compounds, KNO₃ changes solubility most with increasing temperature.

15.28 About 175 g of KNO₃ will dissolve in 100 g of water at 80°C.

15.29 Unsaturated

15.33 NaCl dissolves about 38 g in 100 g of water, so its percent by mass is

$$\frac{38 \text{ g}}{138 \text{ g}} \times 100\% = 28\% \text{ NaCl}$$

15.34 75.0 g solution $\left(\frac{1.75 \text{ g solute}}{100.0 \text{ g solution}} \right) \left(\frac{100.0 \text{ g stock}}{5.00 \text{ g solute}} \right) = 26.3 \text{ g stock}$

15.36 200.0 g solution $\left(\frac{1.750 \text{ g KNO}_3}{100.0 \text{ g solution}} \right) = 3.500 \text{ g KNO}_3$
 Dissolve 3.500 g KNO₃ in 196.5 g H₂O.

15.38 The number of moles of HC₂H₃O₂ and the number of kilograms of H₂O are calculated first:

$$6.17 \text{ g HC}_2\text{H}_3\text{O}_2 \left(\frac{1 \text{ mol HC}_2\text{H}_3\text{O}_2}{60.0 \text{ g HC}_2\text{H}_3\text{O}_2} \right) = 0.1028 \text{ mol HC}_2\text{H}_3\text{O}_2$$

$$72.3 \text{ g} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.0723 \text{ kg H}_2\text{O}$$

The molality is

$$m = \frac{0.1028 \text{ mol}}{0.0723 \text{ kg}} = 1.42 \text{ m HC}_2\text{H}_3\text{O}_2$$

15.40 139 g H₂O $\left(\frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}} \right) \left(\frac{2.73 \text{ mol solute}}{1 \text{ kg H}_2\text{O}} \right) = 0.379 \text{ mol solute}$

15.41 0.707 mol solute $\left(\frac{1 \text{ kg solvent}}{1.33 \text{ mol solute}} \right) = 0.532 \text{ kg solvent}$

15.42 The number of moles of Na₂SO₄ is

$$1.33 \text{ kg H}_2\text{O} \left(\frac{0.507 \text{ mol Na}_2\text{SO}_4}{1 \text{ kg H}_2\text{O}} \right) \left(\frac{2 \text{ mol Na}^+}{1 \text{ mol Na}_2\text{SO}_4} \right) = 1.35 \text{ mol Na}^+$$

15.46 0.0149 kg H₂O $\left(\frac{0.600 \text{ mol Cl}^-}{1 \text{ kg H}_2\text{O}} \right) \left(\frac{1 \text{ mol MgCl}_2}{2 \text{ mol Cl}^-} \right) = 0.00447 \text{ mol MgCl}_2$

15.48 $M = \frac{0.515 \text{ mol}}{0.207 \text{ L}} = 2.49 \text{ M}$

$$m = \frac{0.515 \text{ mol}}{0.182 \text{ kg}} = 2.83 \text{ m}$$

15.51 The molarity is the number of moles of solute per liter of solution:

$$\frac{0.5142 \text{ mol}}{0.2683 \text{ L}} = 1.917 \text{ M}$$

The molality is the number of moles of solute per kilogram of solvent:

$$m = \frac{0.5142 \text{ mol}}{0.1975 \text{ kg}} = 2.604 \text{ m CsCl}$$

15.53 Assume 100.0 g of solution. Then there are

$$7.50 \text{ g glycol} \left(\frac{1 \text{ mol glycol}}{62.0 \text{ g glycol}} \right) = 0.1210 \text{ mol glycol}$$

and 92.5 g = 0.0925 kg water.

$$\frac{0.121 \text{ mol glycol}}{0.0925 \text{ kg water}} = 1.31 \text{ m glycol}$$

15.55 The volume of the solution can be calculated from its mass and density. The mass of the solution is that of the solute and the solvent:

$$0.255 \text{ mol} \left(\frac{165 \text{ g}}{1 \text{ mol}} \right) = 42.08 \text{ g solute}$$

The mass of the solution is 298 g + 42.08 g = 340.1 g.
 The volume of the solution is

$$340.1 \text{ g} \left(\frac{1 \text{ mL}}{0.903 \text{ g}} \right) = 376.6 \text{ mL} = 0.3766 \text{ L}$$

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The molarity is $\frac{0.255 \text{ mol}}{0.3766 \text{ L}} = 0.677 \text{ M}$

The molality is $\frac{0.255 \text{ mol}}{0.298 \text{ kg}} = 0.856 \text{ m}$

15.56 (a) $X_{\text{H}_2\text{O}} = \frac{6.00 \text{ mol H}_2\text{O}}{10.00 \text{ mol total}} = 0.600$

(b) The numbers of moles are calculated first:

$$1.50 \text{ g C}_2\text{H}_4(\text{OH})_2 \left(\frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.0 \text{ g C}_2\text{H}_4(\text{OH})_2} \right) = 0.02419 \text{ mol C}_2\text{H}_4(\text{OH})_2$$

$$2.50 \text{ g CH}_2\text{O} \left(\frac{1 \text{ mol CH}_2\text{O}}{30.0 \text{ g CH}_2\text{O}} \right) = 0.08333 \text{ mol CH}_2\text{O}$$

$$6.00 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 0.3333 \text{ mol H}_2\text{O}$$

The total number of moles in the solution is 0.4408 mol.
The mole fraction of water is

$$X_{\text{H}_2\text{O}} = \frac{0.3333 \text{ mol H}_2\text{O}}{0.4408 \text{ mol total}} = 0.756$$

15.58 Assume 1.000 kg water:

$$1000 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 55.56 \text{ mol H}_2\text{O}$$

$$X_{\text{NH}_3} = \frac{7.50 \text{ mol}}{7.50 \text{ mol} + 55.56 \text{ mol}} = 0.119$$

15.59 Assume 15.7 g of CH₃OH, and thus 84.3 g of H₂O.

$$15.7 \text{ g CH}_3\text{OH} \left(\frac{1 \text{ mol CH}_3\text{OH}}{32.0 \text{ g CH}_3\text{OH}} \right) = 0.4906 \text{ mol CH}_3\text{OH}$$

$$84.3 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 4.683 \text{ mol H}_2\text{O}$$

$$X_{\text{H}_2\text{O}} = \frac{4.683}{0.4906 + 4.683} = 0.905$$

$$X_{\text{CH}_3\text{OH}} = 1.000 - 0.905 = 0.095$$

15.61 The mass of glycerine is

$$1.50 \text{ mol} \left(\frac{92.0 \text{ g}}{1 \text{ mol}} \right) = 138 \text{ g}$$

The mass of water is 715 g – 138 g = 577 g

$$\text{There is } 577 \text{ g} \left(\frac{1 \text{ mol}}{18.0 \text{ g}} \right) = 32.06 \text{ mol H}_2\text{O}$$

$$X_{\text{gly}} = \frac{1.50 \text{ mol}}{1.50 \text{ mol} + 32.06 \text{ mol}} = 0.0447$$

15.62 In a solution containing 1.000 mol total, there are 0.180 mol alcohol and 0.820 mol water. The mass of water is

$$0.820 \text{ mol} \left(\frac{18.0 \text{ g}}{1 \text{ mol}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.01476 \text{ kg}$$

The molality is (0.180 mol)/(0.01476 kg) = 12.2 m

15.65 $P_{\text{C}_6\text{H}_6} = X_{\text{C}_6\text{H}_6} P_{\text{C}_6\text{H}_6}^{\circ} = \left(\frac{1.66 \text{ mol C}_6\text{H}_6}{1.973 \text{ mol total}} \right) 96.0 \text{ torr} = 80.8 \text{ torr}$

15.67 $P_{\text{total}} = P_{\text{benzene}} + P_{\text{toluene}} = 80.8 \text{ torr} + 4.28 \text{ torr} = 85.1 \text{ torr}$

- 15.68** (a) The temperature is below the freezing point of water, so the sample is solid.
(b) The temperature is above the freezing point, so the sample is liquid.
(c) Lowering the freezing point (without changing the temperature of the sample) can cause melting, which is the rationale for salting icy roads and sidewalks.

15.69 Assume 100.0 g of each:

$$100.0 \text{ g C}_6\text{H}_6 \left(\frac{1 \text{ mol C}_6\text{H}_6}{78.0 \text{ g C}_6\text{H}_6} \right) = 1.282 \text{ mol C}_6\text{H}_6$$

$$100.0 \text{ g C}_2\text{H}_5\text{OH} \left(\frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.0 \text{ g C}_2\text{H}_5\text{OH}} \right) = 2.174 \text{ mol C}_2\text{H}_5\text{OH}$$

The mole fractions are

$$X_{\text{C}_6\text{H}_6} = \frac{1.282 \text{ mol C}_6\text{H}_6}{3.456 \text{ mol total}} = 0.3709 \text{ and therefore}$$

$$X_{\text{C}_2\text{H}_5\text{OH}} = 0.6291$$

$$P_{\text{C}_6\text{H}_6} = P_{\text{C}_6\text{H}_6}^{\circ} X_{\text{C}_6\text{H}_6} = (96.0 \text{ torr})(0.3709) = 35.61 \text{ torr}$$

$$P_{\text{C}_2\text{H}_5\text{OH}} = P_{\text{C}_2\text{H}_5\text{OH}}^{\circ} X_{\text{C}_2\text{H}_5\text{OH}} = (44.0 \text{ torr})(0.6291) = 27.68 \text{ torr}$$

The total pressure is 35.61 torr + 27.68 torr = 63.3 torr

15.70 The freezing-point depression is $5.5^{\circ}\text{C} - 4.02^{\circ}\text{C} = 1.48^{\circ}\text{C}$

$$m = \frac{\Delta t}{k_f} = \frac{1.48^{\circ}\text{C}}{5.12^{\circ}\text{C}/\text{m}} = 0.29 \text{ m}$$

15.72 (a) $\Delta t = k_f m = (1.86^{\circ}\text{C}/\text{m})(3.15 \text{ m}) = 5.859^{\circ}\text{C}$
 $t_f = 0.00^{\circ}\text{C} - 5.859^{\circ}\text{C} = -5.86^{\circ}\text{C}$

(b) $\Delta t = k_b m = (0.512^{\circ}\text{C}/\text{m})(3.15 \text{ m}) = 1.613^{\circ}\text{C}$
 $t_b = 100.00^{\circ}\text{C} + 1.613^{\circ}\text{C} = 101.61^{\circ}\text{C}$

15.75 The solution would freeze below -11.5°C because the presence of a solute—the water—depresses the freezing point, even of antifreeze. It should be noted that some mixtures of antifreeze and water freeze far below -11.5°C (equal to 11.3°F).

15.76 No matter what the molecular solute is, the freezing-point depression is determined using the constant for the solvent (Table 15.2). Thus, for (a)–(c),

$$\Delta t = k_f m = (1.86^{\circ}\text{C}/\text{m})(0.800 \text{ m}) = 1.49^{\circ}\text{C}$$

15.79 $P = P^{\circ}X$

$$X = P/P^{\circ} = (0.157 \text{ atm})/(0.211 \text{ atm}) = 0.744$$

15.80 $m = \frac{\Delta t}{k_f} = \frac{0.908^{\circ}\text{C}}{1.86^{\circ}\text{C}/\text{m}} = 0.488 \text{ m}$

15.82 $\pi V = nRT$

$$\begin{aligned} \pi &= \frac{nRT}{V} = \left(\frac{n}{V} \right) RT \\ &= \left(\frac{0.0100 \text{ mol}}{1 \text{ L}} \right) (0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K}) \\ &= 0.2447 \text{ atm} = 186 \text{ torr} \end{aligned}$$

15.84 (a) Assume 1.000 kg of solution. Then there is

$$75.00 \text{ g NaCl} \left(\frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) = 1.2834 \text{ mol NaCl}$$

$$\frac{1.2834 \text{ mol NaCl}}{0.9250 \text{ kg H}_2\text{O}} = 1.387 \text{ m}$$

(b) $0.9250 \text{ kg H}_2\text{O} \left(\frac{1000 \text{ g H}_2\text{O}}{1.000 \text{ kg H}_2\text{O}} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 51.332 \text{ mol H}_2\text{O}$

$$X_{\text{NaCl}} = \frac{1.2834 \text{ mol}}{1.2834 \text{ mol} + 51.332 \text{ mol}} = 0.02439$$

15.89 The freezing-point depression is 2.50°C , and therefore, the molality of the solution is

$$m = \frac{\Delta t}{k_f} = \frac{2.50^{\circ}\text{C}}{1.86^{\circ}\text{C}/\text{m}} = 1.344 \text{ m}$$

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The number of grams of solute per kilogram of solvent is

$$1.000 \text{ kg solvent} \left(\frac{14.5 \text{ g solute}}{0.0500 \text{ kg solvent}} \right) = 290 \text{ g solute}$$

The molar mass is the number of grams in a kilogram of solvent divided by the number of moles in a kilogram of solvent:

$$\text{Molar mass} = \frac{290 \text{ g}}{1.344 \text{ mol}} = 216 \text{ g/mol}$$

- 15.91** KNO_3 changes solubility the most with increasing temperature, so it would be purified most effectively by this technique.

15.93 $P_{\text{benzene}} = \left(\frac{1.13 \text{ mol}}{3.00 \text{ mol}} \right) 105 \text{ torr} = 39.55 \text{ torr}$

$$P_{\text{toluene}} = \left(\frac{1.87 \text{ mol}}{3.00 \text{ mol}} \right) 34.0 \text{ torr} = 21.19 \text{ torr}$$

The total pressure is $39.55 \text{ torr} + 21.19 \text{ torr} = 60.7 \text{ torr}$

15.96 (a) $\Delta P_{\text{solvent}} = P_{\text{solvent}} - P_{\text{solvent}}$
 $= P_{\text{solvent}}^{\circ} - X_{\text{solvent}} P_{\text{solvent}}^{\circ}$
 $= P_{\text{solvent}}^{\circ} (1 - X_{\text{solvent}})$
 $= P_{\text{solvent}}^{\circ} X_{\text{solute}}$

(b) $\Delta P_{\text{solvent}} = P_{\text{solvent}}^{\circ} X_{\text{solute}}$
 $P_{\text{solvent}} = P_{\text{solvent}}^{\circ} X_{\text{solvent}}$

The mole fractions of different components are used in the two equations.

15.97 $\pi V = nRT$
 $n = \pi V / RT$
 $n = \frac{[(27.1 \text{ torr}) / (760 \text{ torr}/1 \text{ atm})] (0.0600 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) (298 \text{ K})}$
 $= 8.745 \times 10^{-5} \text{ mol}$
 $\text{mass}_{\text{solute}} = (8.745 \times 10^{-5} \text{ mol}) (78.0 \text{ g/mol})$
 $= 6.821 \times 10^{-3} \text{ g}$
 $\text{mass}_{\text{solution}} = (60.0 \text{ mL}) (1.01 \text{ g/mL}) = 60.6 \text{ g}$
 $\text{mass}_{\text{solvent}} = 60.6 \text{ g} - 6.821 \times 10^{-3} \text{ g} = 60.6 \text{ g}$
 $= 0.0606 \text{ kg}$
 $\text{molality} = (8.745 \times 10^{-5} \text{ mol}) / (0.0606 \text{ kg})$
 $= 1.443 \times 10^{-3} \text{ m}$
 $\Delta t = k_b m = (1.86^\circ/\text{m})(1.443 \times 10^{-3} \text{ m})$
 $= 0.00268^\circ\text{C}$

The example illustrates that the osmotic pressure is much more sensitive and can be used with substances of high molar mass. There is practically no change of freezing point, but the osmotic pressure is easily determined at 27.1 torr.

- 15.99 (c)** CaCl_2 (This compound contains 3 mol of ions per mole of compound, therefore its concentration of solute particles is greatest.)

- 15.101** Assume 100.00 g of solution, containing

$$10.0 \text{ g AlCl}_3 \left(\frac{1 \text{ mol AlCl}_3}{133.4 \text{ g AlCl}_3} \right) = 0.07496 \text{ mol AlCl}_3$$

$$0.07496 \text{ mol AlCl}_3 \left(\frac{3 \text{ mol Cl}^-}{1 \text{ mol AlCl}_3} \right) = 0.2249 \text{ mol Cl}^-$$

$$90.0 \text{ g H}_2\text{O} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.0900 \text{ kg}$$

$$\frac{0.2249 \text{ mol}}{0.0900 \text{ kg}} = 2.50 \text{ mol Cl}^-$$

- 15.103** From the boiling-point elevation, the molality of the solution can be calculated:

$$m = \frac{\Delta t}{k_b} = \frac{2.60^\circ\text{C}}{0.512^\circ\text{C/m}} = 5.078 \text{ m}$$

From that molality, the freezing-point depression can be calculated:

$$\Delta t = k_f m = (1.86^\circ\text{C/m})(5.078 \text{ m}) = 9.45^\circ\text{C}$$

The freezing point is -9.45°C .

- 15.104** The number of moles per liter of solution is known, and the number of moles per kilogram of solvent is to be found. Assume that there is 1.000 L of solution. That volume of solution contains 0.503 mol of $\text{Sn}(\text{NO}_3)_2$ and has the following mass:

$$1.000 \text{ L solution} \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{1.083 \text{ g}}{1 \text{ mL}} \right) = 1083 \text{ g solution}$$

The mass of the $\text{Sn}(\text{NO}_3)_2$ is

$$0.503 \text{ mol Sn}(\text{NO}_3)_2 \left(\frac{242.7 \text{ g}}{1 \text{ mol}} \right) = 122.1 \text{ g Sn}(\text{NO}_3)_2$$

The mass of the solvent is

$$1083 \text{ g solution} - 122.1 \text{ g Sn}(\text{NO}_3)_2 = 960.9 \text{ g solvent}$$

Therefore, the molality is

$$m = \frac{0.503 \text{ mol Sn}(\text{NO}_3)_2}{0.9609 \text{ kg solvent}} = 0.523 \text{ m}$$

- 15.105** This compound is a hydrocarbon, which is nonionic. The empirical formula is determined as in Section 7.4:

$$93.71 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.803 \text{ mol C}$$

$$6.29 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 6.24 \text{ mol H}$$

The ratio is 1.25 mol of carbon to 1 mol of hydrogen or 5 mol of carbon to 4 mol of hydrogen. The empirical formula is C_5H_4 . The freezing-point depression is $5.5^\circ - (-2.90^\circ\text{C}) = 8.4^\circ\text{C}$, and therefore the molality of the solution is

$$m = \frac{\Delta t}{k_f} = \frac{8.4^\circ\text{C}}{5.12^\circ\text{C/m}} = 1.64 \text{ m}$$

The number of grams in 1.00 kg of solvent is

$$1.00 \text{ kg solvent} \left(\frac{18.6 \text{ g solute}}{0.0866 \text{ kg solvent}} \right) = 215 \text{ g solute}$$

The molar mass is the number of grams in a kilogram of solvent divided by the number of moles in a kilogram of solvent:

$$\text{Molar mass} = \frac{215 \text{ g solute}}{1.64 \text{ mol solute}} = 131 \text{ g/mol}$$

The empirical formula mass for C_5H_4 is 64 amu. The number of moles of empirical formula units per mole of molecules is

$$\frac{131 \text{ g/mol}}{64 \text{ g/mol empirical formula units}} = \frac{2 \text{ empirical formula units}}{1 \text{ molecule}}$$

The molecular formula is C_{10}H_8 .

- 15.107** $m = \frac{\Delta t}{k_f} = \frac{1.151^\circ\text{C}}{1.86^\circ\text{C/m}} = 0.6188 \text{ m} = \frac{0.6188 \text{ mol}}{1 \text{ kg water}}$
- $$\frac{6.11 \text{ g solute}}{0.2500 \text{ kg water}} = \frac{24.44 \text{ g solute}}{1 \text{ kg water}}$$

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Because 0.6188 mol of solute is 24.44 g, the molar mass is

$$\frac{24.44 \text{ g}}{0.6188 \text{ mol}} = 39.5 \text{ g/mol}$$

15.110 $P = P^{\circ}X = 231 \text{ torr} = (268 \text{ torr})X$

$$X = \frac{231 \text{ torr}}{268 \text{ torr}} = 0.8619$$

Let y = number of moles of solute per mole of benzene.
Then

$$X = 0.8619 = \frac{1.000 \text{ mol benzene}}{1.000 \text{ mol} + y}$$

$$0.8619(1.000 + y) = 1.000 \text{ mol}$$

$$0.8619y = 0.138/\text{mol}$$

$$y = 0.160 \text{ mol}$$

$$\text{Check: } \frac{1.000 \text{ mol}}{1.160 \text{ mol}} = 0.862$$

15.113 Assume any mass of CH_3OH , such as 70.0 g. (Then there is 30.0 g CH_2O .) Calculate the number of moles of each substance:

$$70.0 \text{ g CH}_3\text{OH} \left(\frac{1 \text{ mol CH}_3\text{OH}}{32.0 \text{ g CH}_3\text{OH}} \right) = 2.188 \text{ mol CH}_3\text{OH}$$

$$30.0 \text{ g CH}_2\text{O} \left(\frac{1 \text{ mol CH}_2\text{O}}{30.0 \text{ g CH}_2\text{O}} \right) = 1.00 \text{ mol CH}_2\text{O}$$

The total number of moles is 3.188 mol, and the mole fraction of CH_3OH is

$$\frac{2.188 \text{ mol}}{3.188 \text{ mol}} = 0.686$$

15.120 The number of moles of gas in a liter is given by the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(298 \text{ K})} = 0.0409 \text{ mol}$$

The number of moles of ammonia in a liter of 15 M solution is 15 mol. The ratio of numbers of moles is

$$\frac{15 \text{ mol}}{0.0409 \text{ mol}} = \frac{370}{1}$$

15.121 For 1.00 kg of water:

$$55.2 \text{ mol CH}_3\text{OH} \left(\frac{32.0 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 1.766 \text{ kg CH}_3\text{OH}$$

$$1000 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 55.56 \text{ mol H}_2\text{O}$$

$$\text{Molality} = \frac{55.56 \text{ mol H}_2\text{O}}{1.766 \text{ kg CH}_3\text{OH}} = 31.5 \text{ M H}_2\text{O}$$

15.123 The mole fraction of water must be 0.809 because the total of both mole fractions must equal 1.000. In a solution containing 1.000 mol total, there are 0.191 mol of methyl alcohol and 0.809 mol of water. The mass of the water is

$$0.809 \text{ mol H}_2\text{O} \left(\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 14.56 \text{ g H}_2\text{O}$$

Thus,

$$\text{Molality} = \frac{0.191 \text{ mol alcohol}}{0.01456 \text{ kg water}} = 13.1 \text{ M}$$

15.124 (a) Assume 100.0 g of each solution. Then we have

$$\frac{12.00 \text{ g solute} + 2.00 \text{ g solute}}{200.0 \text{ g solution}} = 7.00\% \text{ solution}$$

(b) Assume 100.0 g of water in each solution.

$$100.0 \text{ g H}_2\text{O} \left(\frac{12.00 \text{ g solute}}{88.00 \text{ g H}_2\text{O}} \right) = 13.64 \text{ g solute}$$

$$100.0 \text{ g H}_2\text{O} \left(\frac{2.00 \text{ g solute}}{98.00 \text{ g H}_2\text{O}} \right) = 2.041 \text{ g solute}$$

There is a total of 15.68 g solute in 215.68 g solution, so the percent by mass is

$$\frac{15.68 \text{ g solute}}{215.68 \text{ g solution}} \times 100.0\% = 7.270\% \text{ solute}$$

16 Oxidation Numbers

16.1 (a) MA_3 (b) YZ_3

16.2 Electrons are present, and at least one type of ion must be present to balance the charge.

16.3 The sum of the oxidation numbers of all the atoms is equal to the charge on the species (rule 1).

(a) -12 (b) +2 (c) -4

16.4 (a) +3 (b) -1 (c) +2

16.5 (a) The oxidation number of copper is +2; that of the sulfur atom is -2.

(b) The oxidation number of copper is +1; that of the sulfur atom is -2.

(c) Copper(II) sulfide and copper(I) sulfide, respectively.

16.6 The elemental silver (on the left) has an oxidation number of 0 (rule 2), and the silver in Ag_2O has an oxidation number of +1. Note that silver always has +1 as its oxidation number in its compounds.

16.7 (a) The oxidation number of the nitrogen atom is -3; that of each hydrogen atom is +1, and that of the chlorine atom is -1.

(b) The oxidation number of sulfur is +4; that of each fluorine atom is -1.

16.9 Right

16.10 (a) Two electrons for each of three A's, or six electrons in all
(b) Six electrons
(c) 3 : 1

16.11 The element that changed oxidation number has already been balanced, so oxygen needs to have an oxidation number of -2.

16.12 Six electrons must be added to the left side.

16.14 (a) Double substitution is one reaction type described in Chapter 8 in which oxidation numbers do not change. Combinations and decompositions of *compounds* to form new compounds (for example, calcium oxide plus carbon dioxide yielding calcium carbonate, or vice versa) also have no changes of oxidation numbers.

(b) No. (We balanced simple oxidation-reduction equations in Chapter 8.)

16.15



The oxidation number of phosphorus is $5 - 0 = +5$; that of the sulfur atom is $6 - 8 = -2$; and that of each of the chlorine atoms is $7 - 8 = -1$. Thus, the sulfur in PSCl_3 is like the oxygen in POCl_3 , and the phosphorus has the same oxidation number in both compounds.

16.17 (a) +4 (b) +6 (c) +4
(d) +2 (e) +4

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16.19 (a) +3 (b) +1 (c) +3
 (d) +5 (e) -1 (f) +5

16.21 (a) +6 (b) +6

16.23 (a) -1 (b) +1 (c) -1 (d) -1

16.24 (a) +4 (b) +2 (c) 0
 (d) -2 (e) -4

16.25 (a) +2 (b) +3 (c) -1 (d) +4
 (e) +5 (f) +4 (g) -3 (h) -2
 (i) +1 (j) $-\frac{1}{3}$ (k) 0

16.26 (a) +2 (b) +3 (c) $+2\frac{2}{3}$

16.28 (a) +4 (b) +4 (c) +4 (d) +4

- 16.34** (a) Lead(IV) oxide
 (b) Barium peroxide
 (c) Potassium superoxide

16.36 (a) $\text{Hg}_2(\text{CN})_2$ (b) Au_2O_3 (c) Au_2S

16.38 -ic

16.39 +1 (in most of its compounds); -1 (in its compounds with active metals)

16.40 In the anions with the prefix *per*, the halogens have the oxidation number +7, their highest oxidation number.

16.45 The highest oxidation numbers are associated with covalent bonding. The four oxygen atoms in OsO_4 are covalently bonded to the osmium atom, and no ions are formed. For any monatomic ion, +4 is the maximum charge.

16.46 (a) +6 and -2 (b) 0 and -1
 (c) +5 and -3 (d) +4 and 0

16.48 (a) -4 (b) 0 (c) 0

16.49 +3 H_3AsO_3

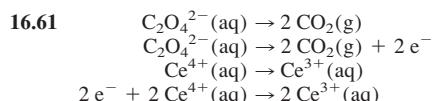
16.51 Because fluorine in its compounds exhibits only a negative oxidation number, the iodine must have positive oxidation numbers in all four compounds. It can exhibit a +7 oxidation number (its maximum), as well as +5, +3, and +1 (steps of 2). The formulas are therefore IF_7 , IF_5 , IF_3 , and IF .

16.53 Copper and gold have oxidation numbers that exceed the group number. Most group VII elements have maximum oxidation numbers that are not as large as the group number.

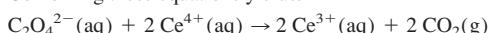
Oxidizing Agent	Reducing Agent	Element Oxidized	Element Reduced
(a) KMnO_4	HCl	Cl	Mn^{VII}
(b) MnO_4^-	Cl^-	Cl	Mn^{VII}

16.58 Usually, the net ionic equation (b) is easier to work with. (See the answer to the next problem.) (a) 10 chloride atoms of the 16 are actually reduced, and 6 remain as chloride ions with the Mn^{2+} and K^+ ions. (b) All 10

Oxidizing Agent	Reducing Agent	Element Oxidized	Element Reduced
(a) NO_3^-	Cu	Cu ⁺	N ^V
(b) Cu_2O	Cu_2O	Cu ⁺	Cu ⁺
(c) CuCl_2	Zn	Zn	Cu^{2+}



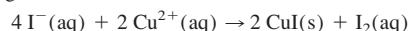
Combining these equations yields:



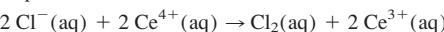
Doubling the reduction half-reaction:



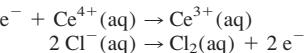
Combining:



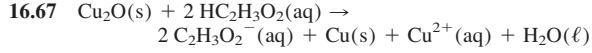
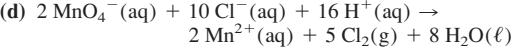
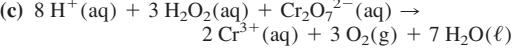
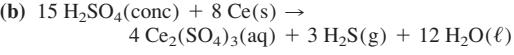
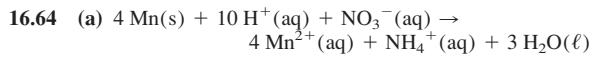
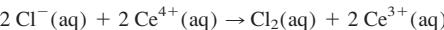
16.63 The atoms and charges in this equation can be balanced by inspection:



Alternatively, the equation can be balanced by the systematic method:



Doubling the first equation and then combining these equations yields the overall equation:

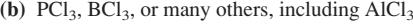


16.69 The ion whose central element has the higher oxidation number is named with the ending *-ate*.

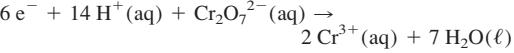
16.71 There is no change in oxidation number. Chromium is in the +6 oxidation state on both sides.



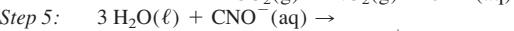
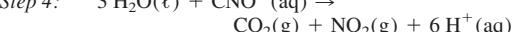
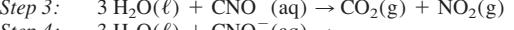
The oxidation number of carbon is +2; that of nitrogen is -3. The carbon in CO has an oxidation number of +2 because it retains control of only two electrons. The oxygen has an oxidation number of -2. There is a difference because there is no charge on the CO molecule.



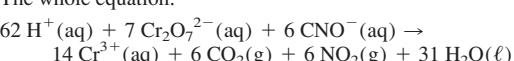
16.79 (a)-(c) The reduction half-reaction

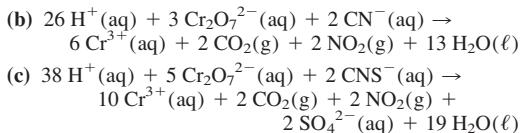


(a) For the oxidation half-reaction:



The whole equation:



654**APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems****16.82** Titanium(IV) chloride and titanium tetrachloride**17 Electrochemistry****17.1** In the lead storage cell, all the reactants and products are solids and cannot migrate in the sulfuric acid, so both electrodes can be placed in the same solution.**17.2** Yes**17.3** Since electrons appear in the equation, there must be at least one ionic species to balance the charge.**17.4** (a) The coefficients in the equation for any systems do not matter; standard state is 1 M for any solute and 1 atm for any gas.**17.5** (a) 0.90 V (Changing the coefficients does not alter the potential.)
 (b) -0.90 V (Reversing the equation requires changing the sign of the potential.)**17.6** No. No matter what its potential, a half-reaction cannot proceed without another half-reaction.**17.7** (a) Coulomb (b) Ampere**17.9** (a) $5.00 \text{ C} \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) = 5.18 \times 10^{-5} \text{ mol e}^-$
 (b) $\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^-$
 1 mol of e^-
 (c) $2.00 \times 10^{11} \text{ e}^- \left(\frac{1 \text{ mol e}^-}{6.02 \times 10^{23} \text{ e}^-} \right) = 3.32 \times 10^{-13} \text{ mol e}^-$
 (d) 2 mol e⁻ (e) 1 mol e⁻**17.10** $\text{Al}_2\text{O}_3(\text{in solution}) + 3 \text{C(s)} \xrightarrow{\text{Heat}} 2 \text{Al}(\ell) + 3 \text{CO(g)}$

$$2.50 \text{ mol Al}_2\text{O}_3 \left(\frac{2 \text{ mol Al}}{1 \text{ mol Al}_2\text{O}_3} \right) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \right) = 15.0 \text{ mol e}^-$$

17.12 The mass of copper deposited is $25.782 \text{ g} - 20.171 \text{ g} = 5.611 \text{ g}$.

$$\frac{5.611 \text{ g}}{10.69 \text{ g}} \times 100\% = 52.49\% \text{ Cu}$$

17.13 Merely change the zinc and zinc ion in the Daniell cell (Figure 17.1) to lead and lead(II) ion. Lead will be oxidized.**17.15** (a) MnO_4^- (b) Equal (c) Fe^{3+} **17.17** (a) $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$
 (b) $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$ **17.18** It turns to heat.**17.19** (a) $\text{Cu} \rightarrow \text{Cu}^{2+} + 2 \text{e}^-$ $\varepsilon^0 = -0.34 \text{ V}$
 $\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$ $\varepsilon^0 = -0.44 \text{ V}$
 $\text{Fe}^{2+} + \text{Cu} \rightarrow \text{Fe} + \text{Cu}^{2+}$ $\varepsilon^0 = -0.78 \text{ V}$

(b) -1.24 V (c) +0.43 V (d) -0.47 V

17.21 (a) No (b) Yes (c) Z will reduce X²⁺.**17.22** Cu⁺ disproportionates (reacts with itself) to yield Cu and Cu²⁺. (Reverse the Cu²⁺/Cu⁺ equation, add it to the Cu⁺/Cu, and get a positive potential.)**17.24** (a) $\varepsilon = \varepsilon^0 - \left(\frac{0.0592}{n} \right) \log \left(\frac{1}{[\text{Fe}^{2+}]} \right)$
 $= -0.44 - \left(\frac{0.0592}{2} \right) \log \left(\frac{1}{(0.100)} \right) = -0.47 \text{ V}$

(b) 0.77 V (c) -0.14 V
 (d) $\varepsilon = \varepsilon^0 - \left(\frac{0.0592}{n} \right) \log \left(\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \right)$
 $= 1.51 - \left(\frac{0.0592}{5} \right) \log \left(\frac{0.500}{(2.00)(1.00)^8} \right) = 1.52 \text{ V}$

Note that water is not included in the argument of the log, since in dilute aqueous solutions it is regarded as pure.

17.28 (a) $\varepsilon = \varepsilon^0 - \left(\frac{0.0592}{n} \right) \log \left(\frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{H}^+]^8[\text{Fe}^{2+}]^5} \right)$
 $= 0.74 - \left(\frac{0.0592}{5} \right) \log \left(\frac{(0.500)(0.900)^5}{(0.125)(1.00)^8(0.600)^5} \right) = 0.72 \text{ V}$

The reaction goes as written. Note that water is not included in the argument of the log, since in dilute aqueous solutions it is regarded as pure.

(b) $\text{Sn}^{2+} + \text{Pb}^{2+} \rightarrow \text{Pb} + \text{Sn}^{4+}$ $\varepsilon^0 = -0.26 \text{ V}$
 $\varepsilon = \varepsilon^0 - \left(\frac{0.0592}{2} \right) \log \left(\frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}][\text{Pb}^{2+}]} \right)$
 $= -0.26 - 0.0296 \log \left(\frac{(0.500)}{(3.00)(2.00)} \right) = -0.23 \text{ V}$ Opposite direction

(c) 1.58 V As written

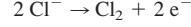
17.30 Hydrogen and oxygen. (Water is more easily reduced than aluminum ion and more easily oxidized than sulfate ion.)**17.31** Iron(II) sulfate**17.35** (a) iii (b) i (c) ii**17.36** (a) Voltaic (The reaction goes spontaneously.)
 (b) Electrolysis (The reaction does not go spontaneously.)
 (c) Voltaic (d) Voltaic (e) Electrolysis**17.37** The charge that passes through the first cell is given by

$$1.500 \text{ g Ag} \left(\frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \right) \left(\frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \right) = 0.01390 \text{ mol e}^-$$

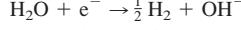
The mass of the other elements is given by

$$0.01390 \text{ mol e}^- \left(\frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \right) \left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 0.4417 \text{ g Cu}$$

$$0.01390 \text{ mol e}^- \left(\frac{1 \text{ mol Ga}}{3 \text{ mol e}^-} \right) \left(\frac{69.72 \text{ g Ga}}{1 \text{ mol Ga}} \right) = 0.3230 \text{ g Ga}$$

17.38 $19,200 \text{ C} \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left(\frac{1 \text{ mol Hg}_2^{2+}}{2 \text{ mol e}^-} \right) \left(\frac{2 \text{ mol Hg}}{1 \text{ mol Hg}_2^{2+}} \right) \left(\frac{200.6 \text{ g Hg}}{1 \text{ mol Hg}} \right) = 39.9 \text{ g Hg}$ **17.40** The oxidation of the chloride ion does not affect the hydrogen ion concentration:

The reduction reaction produces hydroxide ion:



$$500.0 \text{ s} \left(\frac{0.400 \text{ C}}{1 \text{ s}} \right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left(\frac{1 \text{ mol OH}^-}{1 \text{ mol e}^-} \right) = 0.002073 \text{ mol OH}^-$$

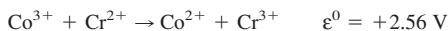
$$\frac{0.002073 \text{ mol}}{0.02500 \text{ L}} = 0.0829 \text{ M}$$

17.42 The system will not experience any net change.**17.43** (a) The freezing (melting) point is lowered (Section 15.5).
 (b) To save energy in heating the salt.
 (c) It cannot be more easily reduced; if it were, the sodium would not be reduced first.

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- 17.44** The standard potentials may be used, since all reagents are 1.00 M.



- 17.46** Fe^{3+} is much easier to reduce than Fe^{2+} than Fe^{2+} is to reduce to Fe. Each is easier to reduce than water is to reduce to hydrogen. (Table 17.2) Thus iron(III) will be reduced to iron(II) first, and if it all gets reduced, then iron(II) will get reduced to iron. So this is a limiting quantities problem.

$$2.00 \text{ h} \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \left(\frac{3.00 \text{ C}}{1 \text{ s}} \right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left(\frac{1 \text{ mol Fe}^{3+}}{1 \text{ mol e}^-} \right) \\ = 0.224 \text{ mol Fe}^{3+}$$

Since there is 1.50 mol of iron(II) ion, the electrons are in limiting supply and the only product is 0.224 mol Fe^{2+} .

- 17.48** It would disproportionate, yielding Cu^{2+} and Cu. (See Table 17.2.)

- 17.50** (a) 1 mol (The oxidation number is reduced from +1 to 0.)
 (b) Generally, positive ions migrate to the negative electrode, where they are reduced. However, this is a negative ion, so stirring is necessary to get it near the negative electrode.

18 Chemical Equilibrium

- 18.1** No. A stress is imposed on the equilibrium system; it is not caused by the equilibrium.

- 18.2** The equation regulates the ratio that reacts, not how much can be placed in a vessel. The reacting ratio does not control the extent of the reaction. Therefore, statements (a), (b), and (c) are incorrect. Statement (d) is also incorrect because the reaction is an equilibrium and does not go to completion. Statement (e) is the only correct one.

- 18.3** The concentration ratio is the same as the mole ratio because the volume of every solute in a particular solution is the same.

$$\frac{[\text{A}]}{[\text{B}]} = \frac{(\text{mol A})/V_A}{(\text{mol B})/V_B} = \frac{\text{mol A}}{\text{mol B}}$$

- 18.4** (a) At the start of the reaction, the rate of decomposition is zero because there is no ammonia present.
 (b) The rate increases as the combination reaction proceeds, producing ammonia. At the point when the rate of decomposition is equal to the rate of combination, equilibrium is established.

$$18.5 \quad K = \frac{[\text{CH}_3\text{OCHO}][\text{H}_2\text{O}]}{[\text{CH}_3\text{OH}][\text{HCHO}_2]}$$

$$18.6 \quad (\text{a}) \quad K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad (\text{b}) \quad K = \frac{[\text{HI}]}{[\text{H}_2][\text{I}_2]}$$

Note that the two chemical equations state the same facts, as do the two equilibrium constant expressions. This pair of equations shows why the coefficient in the balanced chemical equation becomes an exponent in the equilibrium constant expression.

$$(\text{c}) \quad K = \frac{[\text{HI}]^2}{[\text{H}_2]}$$

The solid iodine is not included in the equilibrium constant expression.

- 18.7** The equilibrium constant expression is the same for both parts; the heat is not included in the equilibrium constant expression.

$$K = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

- 18.9** (a) K for the first equation is the reciprocal of that for the second equation.
 (b) K for the first equation is the square of that for the second equation.

$$18.10 \quad (\text{a}) \quad K = \frac{[\text{SO}_2]}{[\text{O}_2]} \quad (\text{b}) \quad K = \frac{[\text{CO}]^2}{[\text{O}_2]}$$

$$(\text{c}) \quad K = [\text{H}_2\text{O}][\text{CO}_2]$$

$$18.11 \quad PV = nRT$$

$$(\text{a}) \quad \frac{n}{V} = \frac{P}{RT} = \frac{0.800 \text{ atm}}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} \\ = 0.327 \text{ mol/L}$$

$$(\text{b}) \quad \frac{n}{V} = \frac{2.00 \text{ atm}}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} = 0.0817 \text{ mol/L}$$

- (c) If T is constant, $n/V = P/RT = P/\text{constant}$.
 Part (b) has 2.5 times the pressure of part (a), and also 2.5 times the concentration.

- 18.12** Chop it into small pieces.

- 18.13** Add a catalyst.

- 18.15** (a) and (b) 500°C

$$18.16 \quad (\text{a}) \quad 6.00 \text{ cm}^2 \quad (\text{b}) \quad 2.00 \text{ cm}^2 \quad (\text{c}) \quad 60.0 \text{ cm}^2$$

- 18.17** (a) Because this is the start of the reaction, there is no CO present. Thus, the rate of combination must be zero at this point.

- (b) Because the system is at equilibrium, the rate of decomposition is the same as the rate of combination. Thus, 2.28×10^{-5} mol/L·s of CO is combining with O₂.

- 18.18** Because O₂ is combining at the rate of 6.14×10^{-5} mol/L·s, and the balanced equation shows a 2 : 1 ratio, the CO must be combining at twice that rate— 1.23×10^{-4} mol/L·s.

- 18.23** (a) Left shift (b) Left shift (c) Left shift
 (d) No shift (e) Right shift (f) Right shift
 (g) No shift

- 18.26** (a) Shift to the left (b) Shift to the left
 (c) Shift to the right (d) Shift to the left
 (e) Shift to the right (f) Shift to the left
 (g) No shift

- 18.28** (a) Decreasing the pressure by increasing the volume shifts the equilibrium to the left, to produce more moles of gas.
 (b) Because the same number of moles of gas is on both sides, there is no shift.
 (c) Decreasing the pressure by increasing the volume shifts the equilibrium to the right, to produce more moles of gas. Note that the carbon is not a gas.

- 18.30** (a) and (b) None, since carbon is a solid.

$$18.31 \quad K = \frac{[\text{XeF}_6]}{[\text{Xe}][\text{F}]^3}$$

$$18.32 \quad (\text{a}) \quad K = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}$$

$$(\text{b}) \quad K = \frac{[\text{COF}_2]}{[\text{CO}][\text{F}_2]}$$

$$18.34 \quad (\text{a}) \quad K = \sqrt{6.4 \times 10^9} = 8.0 \times 10^4$$

$$(\text{b}) \quad K = 1/8.0 \times 10^4 = 1.3 \times 10^{-5}$$

$$(\text{c}) \quad K = 1/6.4 \times 10^9 = 1.6 \times 10^{-10}$$

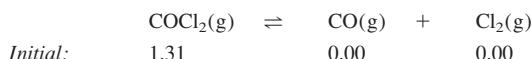
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APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems

- 18.36** The equilibrium constant expression is

$$K = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

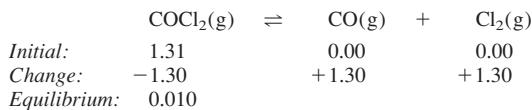
The initial number of moles is converted to concentrations (in moles/liter) and tabulated as follows:



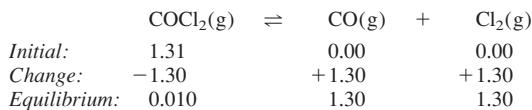
Change:

Equilibrium: 0.010

It is apparent that 1.30 mol/L of COCl_2 has been used up by the reaction, which produces 1.30 mol/L of CO and 1.30 mol/L of Cl_2 . These values are added to the table:



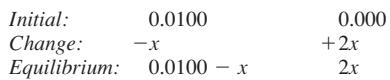
The values involved in the change are added to the initial values to yield the equilibrium values:



The value of the equilibrium constant is given by

$$K = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{(1.30)^2}{0.010} = 170$$

- 18.38** $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$



$$K = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{(2x)^2}{0.0100 - x} = 3.8 \times 10^{-5}$$

Ignoring x when subtracted from 0.0100 yields

$$\frac{(2x)^2}{0.0100} = 3.8 \times 10^{-5}$$

$$(2x)^2 = 3.8 \times 10^{-7} = 4x^2$$

$$x^2 = 9.5 \times 10^{-8}$$

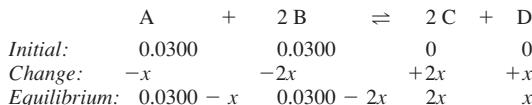
$$x = 3.08 \times 10^{-4}$$

$$2x = [\text{I}] = 6.2 \times 10^{-4} \text{ mol/L}$$

- 18.39** The equilibrium constant expression is

$$K = \frac{[\text{C}]^2[\text{D}]}{[\text{A}][\text{B}]^2} = 4.00 \times 10^{-9}$$

The initial numbers of moles are converted to concentrations (in moles/liter) and then all values are tabulated:



Ignoring x or 2x when subtracted from the larger concentrations yields:

$$K = \frac{[\text{C}]^2[\text{D}]}{[\text{A}][\text{B}]^2} = \frac{4x^3}{(0.0300)(0.0300)^2} = 4.00 \times 10^{-9}$$

$$4x^3 = 1.08 \times 10^{-13}$$

$$x = 3.00 \times 10^{-5}$$

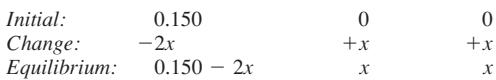
The value of x or 2x is small enough to be ignored when subtracted from the much larger quantity 0.0300.

- 18.41** $\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{BrCl}(\text{g})$



$$K = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = \frac{(0.0400)^2}{(0.0133)(0.0166)} = 7.2$$

- 18.44 (a)** $2\text{T} \rightleftharpoons \text{R} + \text{Z}$



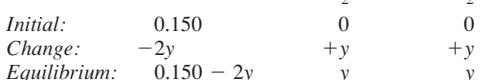
$$\approx 0.150$$

$$K = \frac{[\text{R}][\text{Z}]}{[\text{T}]^2} = \frac{x^2}{(0.150)^2} = 1.0 \times 10^{-10}$$

$$\frac{x}{0.150} = 1.0 \times 10^{-5}$$

$$[\text{R}] = x = 1.5 \times 10^{-6}$$

- (b)** $\text{T} \rightleftharpoons \frac{1}{2}\text{R} + \frac{1}{2}\text{Z}$



$$\approx 0.150$$

$$K = \frac{[\text{R}]^{1/2}[\text{Z}]^{1/2}}{[\text{T}]} = \frac{(y)^{1/2}(y)^{1/2}}{0.150} = 1.0 \times 10^{-5}$$

$$[\text{R}] = y = 1.5 \times 10^{-6}$$

The concentration of R is the same no matter which equation is used.

- 18.45** LeChâtelier's principle applies only to systems already at equilibrium. It cannot predict anything about this initial reaction mixture.

- 18.51 (a)** $K = [\text{CO}_2] = 0.0132 \text{ mol/L}$

(b) The concentration would be 0.0100 mol/L.

All of the CaCO_3 would have decomposed and no equilibrium would exist.

- 18.53 (a)** A catalyst has no effect on the position of the equilibrium and the addition of CO will shift it to the right, so the combination will shift it to the right.

- (b) and (d)** Each stress will shift the equilibrium in a different direction, but we cannot tell by how much, so no prediction can be made about the combined effect.

- (c)** Each of these stresses will shift the equilibrium to the right, so the combination will shift it to the right.

- 18.55** The added nitrogen will cause the equilibrium to shift to the right, producing more heat and causing the temperature to rise.

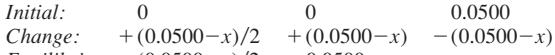
- 18.56** $2\text{NO}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NO}_2\text{Cl}(\text{g})$



$$K = \frac{[\text{NO}_2\text{Cl}]^2}{[\text{NO}_2]^2[\text{Cl}_2]} = \frac{(0.076)^2}{(0.1773)^2(0.0953)} = 1.9$$

- 18.57** Increasing the volume will decrease the pressure and shift the equilibrium to the right, increasing the number of moles of gas. The temperature will thus fall.

- 18.59** $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$



$$K = \frac{x^2}{[(0.0500-x)/2](0.0500-x)^2} = 5.00 \times 10^{-6}$$

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Ignoring x when subtracted from 0.0500 yields

$$K = \frac{x^2}{(0.0250)(0.0500)^2} = 5.00 \times 10^{-6}$$

$$x^2 = 3.13 \times 10^{-10}$$

$$x = 1.77 \times 10^{-5} = [\text{NO}_2]$$

$$[\text{O}_2] = 0.0500 - x = 0.0500 - 1.77 \times 10^{-5} = 0.0500$$

$$[\text{N}_2] = (0.0500 - x)/2 = 0.0250$$

$$\text{Check: } \frac{(1.77 \times 10^{-5})^2}{(0.0250)(0.0500)^2} = 5.0 \times 10^{-6}$$

- 18.62** Because an equilibrium system is *dynamic* (that is, reaction continues in both directions), we expect both the combination reaction and the decomposition reaction to proceed. Therefore, some ND_3 should react with some NH_3 , and some HD will be formed. The reaction of the D_2 and the HD with N_2 will result in the formation of some ND_3 , NHD_2 , and NH_2D molecules. The existence of molecules with both ${}^1\text{H}$ and D in them proves that both reactions are still occurring, even though at equilibrium no *net reaction* occurs.

19 Acid-Base Theory

- 19.1** Compounds **(a)**, **(b)**, **(d)**, and **(e)** exist essentially as ions.

- (a)** K^+ ClO_2^- **(b)** H^+ BrO_3^-
(c) CH_3OH **(d)** NH_4^+ ClO_4^-
(e) Mg^{2+} 2HCO_3^- **(f)** H_3PO_3

- 19.2** **(a)** HNO_2 is weak; no ions are 0.100 M.
(b) Na^+ and NO_3^-
(c) HClO is weak
(d) Na^+ and ClO^-

- 19.4** **(a)** Strong **(b)** Weak **(c)** Weak **(d)** Strong
(e) Weak **(f)** Strong **(g)** Weak **(h)** Strong

- 19.5** **(a)** Strong **(b)** Strong **(c)** Weak **(d)** Weak
(e) Strong

- 19.6** The salt consists of the conjugate acid of a base (the cation) and the conjugate base of an acid (the anion).

- 19.7** The cations are Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+ (and Ag^+). These are the cations of the strong bases containing one OH^- ion per formula unit.

- 19.8** Because $\text{Al}(\text{NO}_3)_3$ is a salt, it is present in solution in the form of Al^{3+} and NO_3^- ions. The concentration 0.433 M means that the solution was made up with 0.433 mol of $\text{Al}(\text{NO}_3)_3$ per liter of solution; it does not mean that un-ionized molecules of $\text{Al}(\text{NO}_3)_3$ are present in the solution. The Al^{3+} is 0.433 M; the NO_3^- is $3(0.433 \text{ M}) = 1.30 \text{ M}$.

- 19.10** Any strong acid could be used to provide the H_3O^+ ions, and any soluble metal nitrite could be used to provide the anion. For example HCl , $\text{Ba}(\text{NO}_2)_2$, and NaNO_2 could be used.

- 19.11** $\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CN}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 Acid Base Base Acid

- 19.12** $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$
 Acid Base Base Acid

- 19.13** **(a)** $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.400) = 0.398$
(b) $\text{pH} = 0.398$ (The HCl ionizes completely, yielding 0.400 M H_3O^+ .)

- 19.15** **(a)** 3.341 **(b)** 6.752 **(c)** 3.218
(d) 8.478 **(e)** 0.000 **(f)** -0.301

- 19.16** **(a)** Basic **(b)** Acidic **(c)** Basic
(d) Neutral **(e)** Neutral **(f)** Basic

- 19.17** The solution has a pH of 7.00. Because the salt is composed of two ions, neither of which reacts with water, the solution is neutral. The pH of a neutral solution is 7.00.

- 19.19** **(a)** 4.67×10^{-8} **(b)** 3.6×10^{-7}
(c) 4.65×10^{-14} **(d)** 6.0×10^{-5}
(e) 0.101 **(f)** 8.7×10^{-7}

- 19.20** H_2S is a weak acid.

- 19.22** H_2S (only K_1 has an effect on pH.)

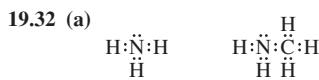
- 19.23** $\text{H}_2\text{C}_2\text{O}_4$ and H_2S

- 19.24** **(a)** $\frac{1.1 \times 10^{-12}}{9.54 \times 10^{-5}} \times 100\% = (1.2 \times 10^{-6})\%$ **(b)** 100%

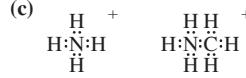
- 19.26** **(a)** NO_2^- **(b)** HSO_3^- **(c)** HSO_4^-

- 19.28** **(a)** H_2O **(b)** H_2O **(c)** HNO_2 **(d)** NH_3

- 19.30** **(a)** Basic (The solution contains a feeble acid and a weak base, $\text{C}_2\text{H}_3\text{O}_2^-$.)
(b) Basic (The solution contains a feeble acid and a weak base, S^{2-} .)
(c) Basic (The solution contains a feeble acid and a weak base, NO_2^- .)
(d) Neutral
(e) Acidic (The solution contains a weak acid, NH_4^+ , and a feeble base.)

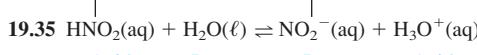


- (b)** The nitrogen atom's lone electron pair can be "donated" to H^+ .

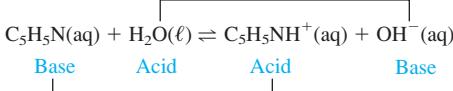


- 19.33** **Acid** **Base**

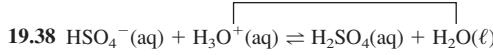
- (a)** H_3O^+ OH^-
(b) H_2SO_4 SO_4^{2-}



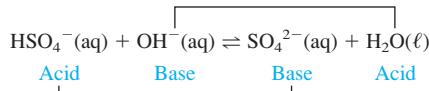
Acid Base Base Acid



Base Acid Acid Base



Base Acid Acid Base



Acid Base Base Acid

- 19.39** **(a)** The solution is 0.180 M NH_3 and 0.060 M NH_4^+ .

- (b)** The solution is 0.180 M NH_3 and 0.060 M NH_4^+ .

- The NH_4^+ ions resulted from the partial neutralization of the NH_3 .

- (c)** No. (The concentration of NH_3 is not lowered significantly by its ionization.)

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- 19.41** The hydronium ion concentration at equilibrium is equal to the concentration of A^- , and the concentration of HA is not affected significantly. Therefore,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(2.50 \times 10^{-5})^2}{0.100} = 6.25 \times 10^{-9}$$

- 19.42** $\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

<i>Initial:</i>	0.350	0	0
<i>Change:</i>	$-x$	$+x$	$+x$
<i>Equilibrium:</i>	$0.350 - x$	x	x

$$K_a = \frac{[\text{CHO}_2^-][\text{H}_3\text{O}^+]}{[\text{HCHO}_2]} = \frac{x^2}{0.350} = 1.7 \times 10^{-4}$$

$$x^2 = 5.95 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 7.7 \times 10^{-3} \text{ M}$$

- 19.44 (a)** $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq})$

<i>Initial:</i>	1.00	0	0
<i>Change:</i>	$-x$	$+x$	$+x$
<i>Equilibrium:</i>	$1.00 - x$	x	x

$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}$$

$$= \frac{x^2}{1.00} = 2.3 \times 10^{-9} \text{ (From Table 19.2)}$$

$$x^2 = 2.3 \times 10^{-9}$$

$$x = 4.8 \times 10^{-5}$$

$$\text{Percent ionization} = \left(\frac{4.8 \times 10^{-5}}{1.00} \right) \times 100\% = 0.0048\%$$

$$(b) K_b = \frac{x^2}{0.100} = 2.3 \times 10^{-9}$$

$$x = 1.52 \times 10^{-5}$$

$$\text{Percent ionization} = \left(\frac{1.52 \times 10^{-5}}{0.100} \right) \times 100\% = 0.015\%$$

$$(c) K_b = \frac{x^2}{0.0500} = 2.3 \times 10^{-9}$$

$$x = 1.07 \times 10^{-5}$$

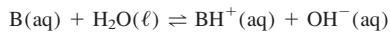
$$\text{Percent ionization} = \left(\frac{1.07 \times 10^{-5}}{0.0500} \right) \times 100\% = 0.021\%$$

In summary,

Initial $[\text{CH}_3\text{NH}_2]$	$[\text{OH}^-]$	Percent Ionization
1.00 M	4.8×10^{-5}	0.0048
0.100 M	1.5×10^{-5}	0.015
0.0500 M	1.1×10^{-5}	0.021

With increasing dilution of the base, the hydroxide ion concentration decreases. However, because the concentration of the un-ionized base decreases more, the percent ionization increases.

- 19.45** The equation for the reaction of a general base, B, with water is



The equilibrium constant expression is

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

From this expression, we can see that the larger the value of K_b , the higher is the concentration of hydroxide ion. Of the bases in Table 19.2, therefore, methylamine has the highest hydroxide ion concentration because it has the highest value of K_b .

- 19.46** From each $[\text{OH}^-]$, the corresponding $[\text{H}_3\text{O}^+]$ is calculated. From that, the pH is obtained.

$$(a) K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{1.17 \times 10^{-6}} = 8.547 \times 10^{-9} \text{ M}$$

$$\text{pH} = 8.068$$

$$(b) \text{pH} = 1.699 \quad (c) \text{pH} = 7.617$$

- 19.47 (a)** 0.0100 M **(b)** 1.00×10^{-12} M
(c) 1.00 M **(d)** 1.00×10^{-14} M

- 19.48 (a)** 2.62×10^{-10} M **(b)** 3.23×10^{-2} M
(c) 2.5×10^{-8} M

- 19.50 (a)** 10.79 **(b)** 6.997 **(c)** 2.658

- 19.51 (a)** 7.71×10^{-6} M **(b)** 9.62×10^{-14} M
(c) 2.29×10^{-5} M

- 19.52 (a)** 11.790 **(b)** 3.762
(c) 12.000 [Two moles of OH^- ions are present per mole of $\text{Ba}(\text{OH})_2$.]

- 19.56 (a)** 2.000 **(b)** 12.000 **(c)** 7.000

- 19.57** From the pH, we can calculate the equilibrium hydronium ion concentration:

$$[\text{H}_3\text{O}^+] = 10^{-11.57} = 2.69 \times 10^{-12} \text{ M}$$

The OH^- concentration is thus

$$\frac{1.00 \times 10^{-14}}{2.69 \times 10^{-12}} = 3.72 \times 10^{-3}$$

which is also equal to the BH^+ concentration. The concentration of B is equal to 0.199 M. Therefore,

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{(3.72 \times 10^{-3})^2}{0.199} = 7.0 \times 10^{-5}$$

- 19.61** From the pH, we can calculate the equilibrium hydronium ion concentration:

$$[\text{H}_3\text{O}^+] = 10^{-3.88} = 1.32 \times 10^{-4} \text{ M}$$

That concentration is equal to the concentration of A^- , and the concentration of HA does not change significantly. Therefore,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(1.32 \times 10^{-4})^2}{0.100} = 1.7 \times 10^{-7}$$

- 19.63** Assume any convenient volume, for example 10.00 mL:

$$10.00 \text{ mL HNO}_3 \left(\frac{0.500 \text{ mmol HNO}_3}{1 \text{ mL}} \right) \left(\frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HNO}_3} \right) = 5.00 \text{ mmol H}_3\text{O}^+$$

$$10.00 \text{ mL Ba}(\text{OH})_2 \left(\frac{0.150 \text{ mmol Ba}(\text{OH})_2}{1 \text{ mL}} \right) \left(\frac{2 \text{ mmol OH}^-}{1 \text{ mmol Ba}(\text{OH})_2} \right) = 3.00 \text{ mmol OH}^-$$

The H_3O^+ is 2.00 mmol in excess, so its concentration is

$$\frac{2.00 \text{ mmol H}_3\text{O}^+}{20.00 \text{ mL}} = 0.100 \text{ M}$$

The pH of this solution is 1.000.

- 19.64** $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

<i>Initial:</i>	0.0100	0.000	0.000
<i>Change:</i>	$-x$	$+x$	$+x$
<i>Final:</i>	$0.0100 - x$	x	x

$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

$$= \frac{x^2}{0.0100 - x} = 4.5 \times 10^{-4}$$

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If we neglect x when subtracted from 0.0100 M, we get about a 20% error. We must use the quadratic equation. (See Appendix A.1.)

$$\begin{aligned}x^2 &= 4.5 \times 10^{-6} - (4.5 \times 10^{-4})x \\x^2 + (4.5 \times 10^{-4})x - 4.5 \times 10^{-6} &= 0 \\x &= \frac{-(4.5 \times 10^{-4}) + \sqrt{(4.5 \times 10^{-4})^2 - 4(-4.5 \times 10^{-6})}}{2} \\&= 1.9 \times 10^{-3} = [\text{H}_3\text{O}^+]\end{aligned}$$

19.65 Parts (a), (d), and (g) each consists of a weak acid or base and its conjugate. Every other part involves a reaction that produces exactly the same conjugate pairs in the same quantities as in the preceding part:

- (b) $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$
- (c) $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{NaCl}(\text{aq})$
- (e) $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq})$
- (f) $\text{NH}_4\text{Cl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\ell)$
- (h) $\text{H}_3\text{PO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaH}_2\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\ell)$

19.68 From the pH, we can calculate the equilibrium hydronium ion concentration, and from that the hydroxide ion concentration:

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 10^{-10.456} = 3.4995 \times 10^{-11} \text{ M} \\[\text{OH}^-] &= K_w/[\text{H}_3\text{O}^+] = 2.858 \times 10^{-4} \text{ M} \\&\text{The concentration of } \text{BH}^+ \text{ is equal to } 0.135 \text{ M, and the concentration of B is } 0.115 \text{ M. Thus,} \\K_b &= \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{(0.135)(2.858 \times 10^{-4})}{0.115} \\&= 3.36 \times 10^{-4}\end{aligned}$$

19.70 From the pH, we can calculate the equilibrium hydronium ion concentration:

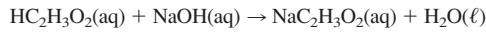
$$[\text{H}_3\text{O}^-] = 10^{-4.94} = 1.15 \times 10^{-5} \text{ M}$$

The concentration of A^- is equal to 0.417 M, and the concentration of un-ionized HA is 0.311 M. Thus,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(1.15 \times 10^{-5})(0.417)}{0.311} \\= 1.5 \times 10^{-5}$$

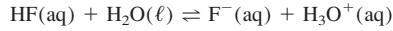
19.72 (a) 0.105 M acetic acid, 0.125 M acetate ion, and 1.48×10^{-5} M H_3O^+

(b) Same as (a), after the reaction



(c) $[\text{H}_3\text{O}^+]$ is negligible to the acid and acetate concentrations.

19.74 (a) Hydrofluoric acid ionizes according to the equation



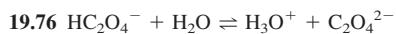
The acid dissociation constant is 6.7×10^{-4} . (The fluoride ion from the sodium fluoride shifts this equilibrium to the left; it does not react directly with the hydrofluoric acid.) Start by assuming that no hydronium ion is present:

$$\begin{array}{ccc} \text{HF}(\text{aq}) + \text{H}_2\text{O}(\ell) & \rightleftharpoons & \text{F}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \\ \text{Initial:} & 0.190 & 0 \\ \text{Change:} & -x & +x \\ \text{Equilibrium:} & 0.190 - x & 0.140 + x \end{array}$$

Ignoring x when subtracted from 0.190 or added to 0.140 yields

$$K_a = \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]} = \frac{(0.140)(x)}{0.190} = 6.7 \times 10^{-4} \\x = 9.09 \times 10^{-4} \\[\text{H}_3\text{O}^+] = 9.1 \times 10^{-4} \text{ M}$$

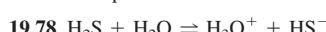
(b) The NaOH reacts with some of the HF, leaving 0.190 mol of HF and producing 0.140 mol of F^- . Therefore, the hydronium ion concentration in part (b) is the same as that in part (a).



$$K_2 = \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{O}_4^{2-}]} = \frac{(0.100)[\text{H}_3\text{O}^+]}{0.100} = 6.40 \times 10^{-5}$$

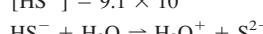
$$[\text{H}_3\text{O}^+] = 6.40 \times 10^{-5}$$

$$\text{pH} = 4.194$$



$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{(1.0 \times 10^{-7})[\text{HS}^-]}{(0.100)} = 9.1 \times 10^{-8}$$

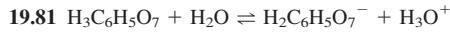
$$[\text{HS}^-] = 9.1 \times 10^{-2}$$



$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(1.0 \times 10^{-7})[\text{S}^{2-}]}{9.1 \times 10^{-2}} = 1.1 \times 10^{-12}$$

$$[\text{S}^{2-}] = 1.0 \times 10^{-6}$$

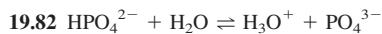
(Compare this value with the value in the unbuffered solution, Example 19.21.)



$$K_1 = \frac{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]} = \frac{x^2}{0.100} = 7.10 \times 10^{-4}$$

$$x = 8.426 \times 10^{-3}$$

$$\text{pH} = 2.074$$

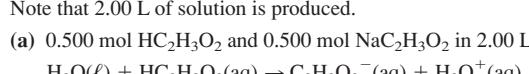
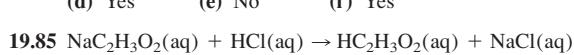


$$K_3 = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = \frac{[\text{H}_3\text{O}^+](0.100)}{0.100} = 2.2 \times 10^{-13}$$

$$[\text{H}_3\text{O}^+] = 2.2 \times 10^{-13}$$

$$\text{pH} = 12.66$$

- 19.84** (a) Yes (b) Yes (c) No
(d) Yes (e) No (f) Yes



Initial: 0.250 M 0.250 M 0 M

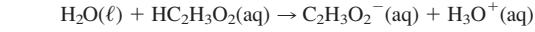
Change: $-x$ $+x$ $+x$

Equilibrium: 0.250 - x 0.250 + x x

$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(0.250)x}{0.250} = 1.76 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = 1.76 \times 10^{-5} \text{ M}$$

(b) 1.00 mol $\text{HC}_2\text{H}_3\text{O}_2$ in 2.00 L



Initial: 0.500 M 0 M 0 M

Change: $-x$ $+x$ $+x$

Equilibrium: 0.500 - x x x

$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.500} = 1.76 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = 2.97 \times 10^{-3} \text{ M}$$

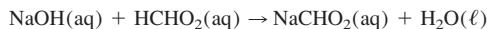
19.87 (a) Reaction of 0.0500 mol OH^- yields 0.0500 mol HC_2O_4^- and leaves 0.0500 mol $\text{H}_2\text{C}_2\text{O}_4$ in solution. This buffer solution, with equal concentrations of its conjugates, has a hydronium ion concentration equal to K_1 . pH = 1.23.

(b) The reaction produces equal concentrations of HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$, with $[\text{H}_3\text{O}^+] = K_2$ and pH = 4.19.

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- 19.89** The neutralization reaction is

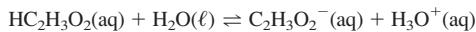


Exactly halfway through the titration, half of the acid will have been neutralized, and half will remain. The concentrations of HCHO_2 and CHO_2^- will be equal no matter what the volume, and the hydronium ion concentration will equal K_a (whose value is given in Table 19.2):

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = [\text{H}_3\text{O}^+] = 1.7 \times 10^{-4}$$

The hydronium ion concentration is 1.7×10^{-4} M, so the pH is 3.77.

- 19.90** The HCl ionizes completely. The acetic acid is the only acid for which an equilibrium calculation need be done. The initial concentration of H_3O^+ is 0.100 M from the ionization of the HCl.



Initial:	0.300	0	0.100
Change:	-x	+x	+x
Equilibrium:	0.300 - x	x	0.100 + x

Ignoring x when subtracted from or added to larger values and using the value of K_a from Table 19.2 yields

$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(0.100)}{0.300} = 1.76 \times 10^{-5}$$

$$x = [\text{C}_2\text{H}_3\text{O}_2^-] = 5.28 \times 10^{-5} \text{ M}$$

We can readily see that the excess H_3O^+ from the HCl has repressed the ionization of the $\text{HC}_2\text{H}_3\text{O}_2$ (compare with Example 19.7). Any weaker acid is affected in this way in the presence of a stronger acid.

- 19.92** The solution has a very weak acid (phenol) and a moderately weak base (phenolate ion). The weak base is stronger than the weak acid, so the solution is basic.

- 19.93** Reactions, if any, or the original reactants yield

- (a) and (b) Strong acid and its salt
- (c), (e), and (g) Salt only
- (d) Acid only (plus inert salt)
- (f) Base only (plus inert salt)

- 19.95** $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is the product of reaction of NH_3 and $\text{HC}_2\text{H}_3\text{O}_2$. Since these have almost identical values of their dissociation constants, they are equally weak. Their conjugates are therefore equally weak and the pH of the solution is about 7.0.

- 19.96** $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$

Initial:	0.0100	0.0000	0.0000
Change:	-x	+x	+x
Final:	0.0100 - x	x	x

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{0.0100 - x} = 7.52 \times 10^{-3}$$

If we try to approximate $[\text{H}_3\text{PO}_4] = 0.0100$, we get a value for x that is 86.7% of 0.0100, so the approximation is not valid. We must use the quadratic formula:

$$x^2 = 7.52 \times 10^{-5} - (7.52 \times 10^{-3})x$$

$$x^2 + (7.52 \times 10^{-3})x - 7.52 \times 10^{-5} = 0$$

$$-(7.52 \times 10^{-3}) + \sqrt{(7.52 \times 10^{-3})^2 - 4(-7.52 \times 10^{-5})}$$

$$x = \frac{-(7.52 \times 10^{-3}) + \sqrt{(7.52 \times 10^{-3})^2 - 4(-7.52 \times 10^{-5})}}{2}$$

$$= 5.69 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$$

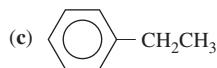
20 Organic Chemistry

- 20.1** There are six carbons in each. The stem *hexa* means “six.”
- 20.2** 30 $[2n + 2 = 2(14) + 2 = 30]$

- 20.3** The radical cannot be hydrogen in organic halides, alcohols, ethers, or amines (which would be hydrogen halides, water, or ammonia if R were hydrogen). In esters, the radical denoted R' in Table 20.4 cannot be hydrogen, but the one denoted R can. In ketones, neither radical can be hydrogen (if it were, the compound would be an aldehyde).

- 20.4** (a) 1-Butene (b) 1-Butyne (c) 3-Ethylpentane
(d) Chlorobenzene

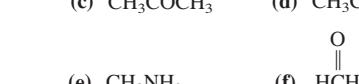
- 20.5** (a) $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ (b) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ | \\ \text{Cl} \end{array}$



- 20.6** (a) An ammonia molecule with one hydrogen replaced by a radical, CH_3CH_2-
(b) A water molecule with both hydrogen atoms replaced by radicals, CH_3CH_2-
(c) An ammonia molecule with two hydrogen atoms replaced by radicals, CH_3CH_2-
(d) Hydrogen chloride, HCl , with the hydrogen replaced by a radical, $\text{CH}_3\text{CH}_2\text{CH}_2-$

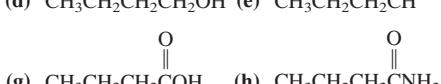
- 20.7** (a) Propanone or acetone
(b) Aminomethane or methylamine
(c) Ethanal or acetaldehyde
(d) Ethanoic acid or acetic acid
(e) Ethene or ethylene
(f) Methanol or methyl alcohol

- 20.8** (a) Water (b) Water (c) Water



20.10

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $\text{CH}_3\text{CH}=\text{CHCH}_3$ (c) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$



- 20.11** (a) A ketone cannot have its carbonyl group at the end of the carbon chain, and there is only one carbon atom not on the end in a three-carbon chain.

- (b) An aldehyde must have its carbonyl group at the end of the carbon chain, and in this compound, it does not make any difference which end.

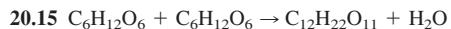
- 20.12** (a) HCOCH_3 (b) HOCH_2CH_3
(c) $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (d) HOCOCH_3

- 20.13** These are the same compounds as in Problem 20.9.

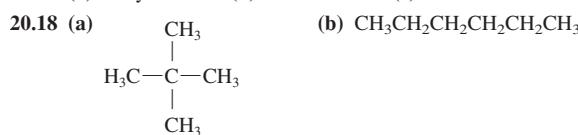
- 20.14** The amide group $-\text{C}(=\text{O})-\text{NH}-$ (known as the peptide linkage in proteins)

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- 20.16** (a) Alkyne (b) Alkane (c) Alkene

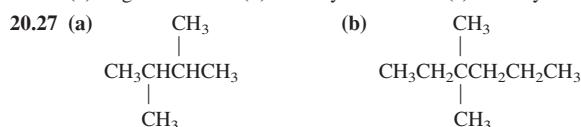


- 20.20** (a) 2-Pentene (b) 4-Methyl-2-pentyne
(c) Heptane (d) 2,2,4-Trimethylpentane

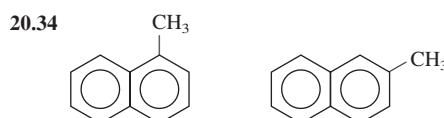
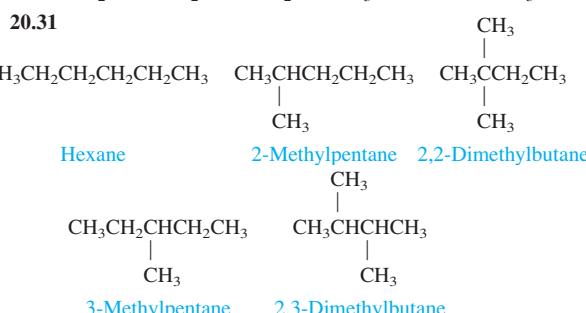
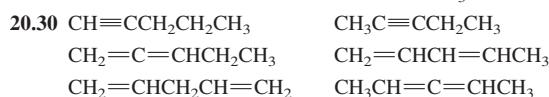
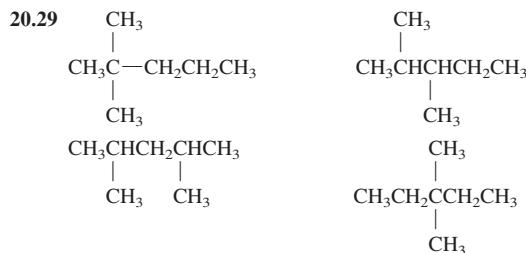
Number of Carbon Atoms	Alkane	Alkene	Alkyne	Alkyl Radical
1	CH_4	None	None	$—\text{CH}_3$
2	C_2H_6	C_2H_4	C_2H_2	$—\text{C}_2\text{H}_5$
3	C_3H_8	C_3H_6	C_3H_4	$—\text{C}_3\text{H}_7$
4	C_4H_{10}	C_4H_8	C_4H_6	$—\text{C}_4\text{H}_9$
5	C_5H_{12}	C_5H_{10}	C_5H_8	$—\text{C}_5\text{H}_{11}$

- 20.23** (a) Eight (There are six in the hexane chain and two additional in the ethyl side chain.)
(b) Eleven (There are two in each side chain.)
(c) Ten (There is one in each of the three side chains.)

- 20.24** (a) Eighteen (b) Twenty-four (c) Twenty-two



(c) If a methyl group is placed on the fourth carbon in the chain, it would be the second carbon from the other end, and the formula would represent 2,3-dimethylpentane.



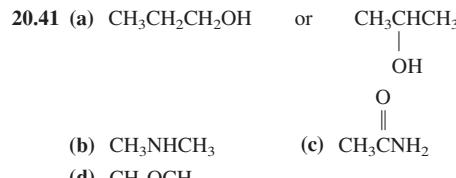
(All other corners are equivalent to one of these two.)

- 20.36** (a) CH_3OCH_3 (b) HCHO
(d) HCONH_2 (e) CH_3COCH_3
(g) CH_3I (h) CH_3OH

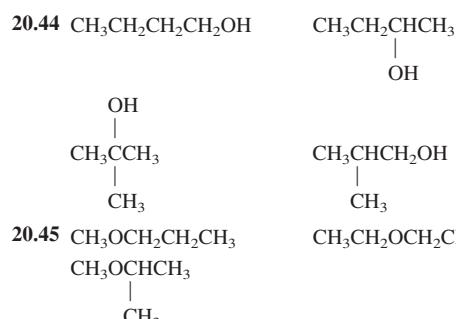
- 20.37** (a) Dimethyl ether
(b) Methanal
(c) Methylamine
(d) Methanamide
(e) Propanone (acetone)
(f) Methanoic acid (formic acid)
(g) Iodomethane (methyl iodide)
(h) Methanol

- 20.38** (a) Ethanol (b) Propane
(c) Ethanal (d) Methanoic acid

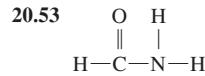
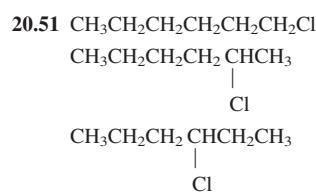
- 20.39** (a) Organic acid (b) Ether (c) Ketone
(d) Amine (e) Alcohol (f) Aldehyde



- 20.43** (a) Methyl ethyl ether and 1-propanol or 2-propanol
(b) Ethylamine and dimethylamine
(c) Methyl methanamide and ethanamide
(d) Ethanol and dimethyl ether



- 20.49** (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Cl
(c) The fourth carbon atom from one end of the chain is the third from the other end, and the compound is 3-chlorohexane.

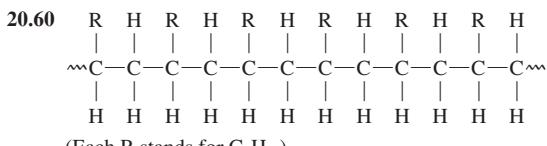


- 20.55** An amide and an amine cannot be isomers. An amide molecule contains oxygen, but an amine does not. However, alco-

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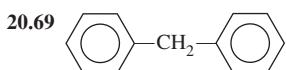
hols and ethers can be isomers of each other, as can aldehydes and ketones, and also organic acids and esters.



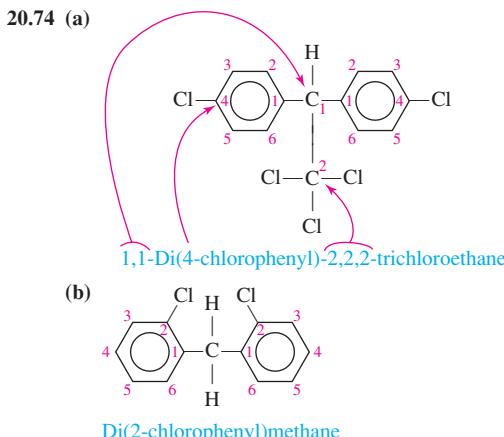
(Each R stands for C₆H₅.)

- 20.62** Gases have little intermolecular forces between their molecules. The molecules of polymers are very large, and intermolecular forces, even in nonpolar polymers, are considerable. We do not expect polymers to be gases under the conditions given.

20.65 An amino acid has both an amine group and an acid group in the same molecule; an amide is the product of the reaction of separate molecules having those two groups:



- 20.73 (a) -2, 0, -2, 0 (b)** The carbon atoms in isomers have the same oxidation number.



- 20.77** 1,1-Dichloroethene

20.79 Aldehydes and acids do not need positional numbers for their functional groups. In these compounds, the functional groups are always at the end of the carbon chain. (Esters and amides do not need positional numbers for the carbon chain of the acid part but might need them for the other part.)

20.84 A fully hydrogenated fat is a saturated fat, whether it started out unsaturated or not. Do not pay extra for it.

20.89 1,2-; 1,3-; 1,4-; 1,5-; 1,6-;
1,7-; 1,8-; 2,3-; 2,6-; 2,7-

20.90 $^+\text{NH}_3\text{CH}_2\text{COO}^-$

$\begin{array}{c} 2 & 1 \\ \text{CH}_3\text{OCH} & \text{CH}_3 \\ | \\ 3 & \text{CH}_3 \end{array}$

20.93 $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$
Diene means two double bonds.

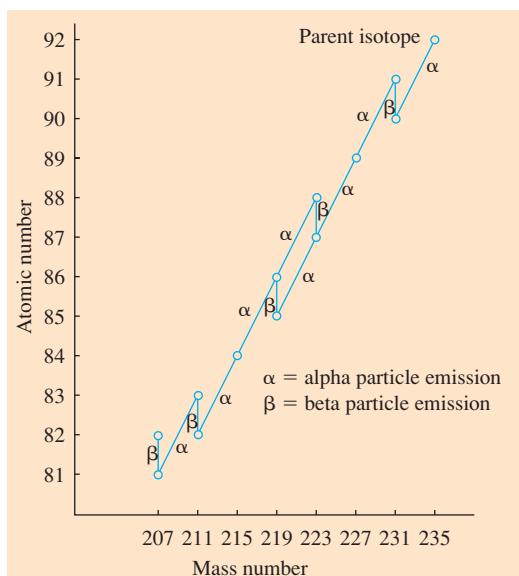
21 Nuclear Reactions

- 21.1** There is no difference. All four are representations for an alpha particle (a helium nucleus).

- 21.2** The symbol U stands for the naturally occurring mixture of isotopes of uranium; ^{238}U stands for only one isotope and represents the nucleus, rather than the entire atom.

- 21.3** (a) β is an electron; $+\beta$ is a positron.
 (b) The $+\beta$ is a positron—a positively charged electron
 (c) There is no difference.

- 21.4** The atomic numbers, which are the subscripts, appear in the periodic table. The superscripts—the mass numbers—are not generally given there. (Mass numbers for the few elements that do not occur naturally are given in parentheses in most periodic tables.) The atomic mass given in a periodic table can give a clue to the mass number of the most abundant isotope for many but not all elements. For example, the atomic mass of bromine is almost exactly 80, but the two isotopes that form the naturally occurring mixture have mass numbers 79 and 81. (They occur in almost a 1:1 ratio.)



- 21.7** The *chemical* properties are the same; only the *nuclear* properties differ.

21.8 The *nuclear* reactions are dangerous.

21.9 When half of the sample has disintegrated, the rate of disintegration is half of what it was before, and only half of what is left will disintegrate in the next 2.00 years.

21.10 The mass will be approximately 0.100 g, with 0.050 g of ^{207}Ti remaining, a tiny mass of beta particles produced, and almost all the rest ^{207}Pb . Only a tiny fraction of the original mass has been transformed into energy, with mass that has escaped from the system.

21.11 Only the $4n + 1$ series has an isotope with half-life as much as 7% of that of the original parent. The other series have no isotope nearly that close.

21.12 (a) Fusion (b) Spontaneous (c) Fission
(d) None

21.13 (a) 1.25×10^9 (b) 1.25×10^9 (c) 6.25×10^8

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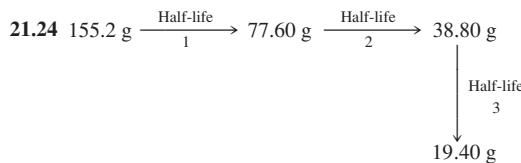
- 21.14** The letter t is the time, $t_{1/2}$ is the half-life, N_0 is the number of atoms of a particular isotope at the start of the time period, N is the number of atoms of that isotope *remaining* at time t , and \ln denotes the natural logarithm. Note that N is *not* the number of atoms that have *disintegrated*.

- 21.15** (a) $^{214}\text{Pb} \rightarrow ^{214}\text{Bi} + {}^0\beta$
 (b) ${}^6_3\text{Li} + {}^1_1\text{H} \rightarrow 2 {}^4_2\text{He}$
 (c) ${}^{13}_7\text{N} \rightarrow {}^0_7\beta + {}^{13}_6\text{C}$
- 21.17** (a) ${}^{10}_4\text{Be} + {}^4_2\text{He} \rightarrow {}^{13}_6\text{C} + {}^1_0\text{n}$
 (b) ${}^7_4\text{Be} \rightarrow {}^7_3\text{Li} + {}^0_4\beta$
 (c) ${}^3_1\text{H} \rightarrow {}^0_1\beta + {}^3_2\text{He}$
 (d) ${}^{64}_{29}\text{Cu} \rightarrow {}^0_6\beta + {}^{64}_{28}\text{Ni}$

- 21.19** ${}^{60}_{27}\text{Co} \rightarrow {}^0_6\beta + {}^{60}_{26}\text{Fe}$

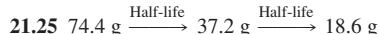
- 21.21** ${}^{222}_{86}\text{Rn}$, because it is a gas

- 21.23** Months have different numbers of days in them.



Three half-lives is 12.9 min, so each

Half-life is $12.9 \text{ min}/3 = 4.30 \text{ min}$.



It takes two half-lives, or 35.0 y, for this disintegration.

- 21.27** Because 18.2 s is four half-lives,

$$29.70 \text{ mg} \xrightarrow[4]{1} 14.85 \text{ mg} \xrightarrow[2]{2} 7.425 \text{ mg} \xrightarrow[3]{3} 3.7125 \text{ mg}$$

$\downarrow 4$
 1.856 mg

1.856 mg will remain.

- 21.29** The total number of atoms at time zero (when the rock solidified) was

$$(1.93 \times 10^{19}) + (5.79 \times 10^{19}) = 7.72 \times 10^{19}$$

$$\frac{1.93 \times 10^{19}}{7.72 \times 10^{19}} = \frac{1}{4}$$

Because one quarter of the ${}^{40}_{19}\text{K}$ remains, two half-lives have passed, and the rock is 2.6×10^9 years old.

21.31 $\frac{102 \text{ y}}{20.4 \text{ y}} = 5$

There have been 5 half-life periods. Working backward:

$$27.25 \text{ mg} \xleftarrow[1]{ } 54.50 \text{ mg} \xleftarrow[2]{ } 109.0 \text{ mg} \xleftarrow[3]{ } 218.0 \text{ mg} \xleftarrow[4]{ } 436.0 \text{ mg}$$

$\uparrow 5$
 872.0 mg

21.32 $\ln\left(\frac{m_0}{m}\right) = \left(\frac{0.693}{t_{1/2}}\right)t$

$$\ln\left(\frac{7.55 \text{ mg}}{0.103 \text{ mg}}\right) = \frac{0.693t}{7.57 \times 10^4 \text{ years}}$$

$$t = 4.69 \times 10^5 \text{ years}$$

- 21.34** The number of atoms of an isotope (N) is equal to Avogadro's number times the mass of the isotope (m) divided by its molar mass (MM), and the same relationship applies for the initial number of atoms (N_0). Thus,

$$\frac{N_0}{N} = \frac{(\text{Avogadro's number})(m_0/\text{MM})}{(\text{Avogadro's number})(m/\text{MM})} = \frac{m_0}{m}$$

The activity of the sample is also directly proportional to the number of radioactive atoms.

$$\frac{N_0}{N} = \frac{kA_0}{kA} = \frac{A_0}{A}$$

Because both m_0/m and A_0/A are equal to N_0/N , they are equal to each other.

21.36 (a) $\ln\left(\frac{m_0}{m}\right) = \left(\frac{0.693}{t_{1/2}}\right)t$

$$\ln\left(\frac{17.3 \text{ mg}}{12.9 \text{ mg}}\right) = \left(\frac{0.693}{t_{1/2}}\right)214 \text{ y}$$

$$0.29348 = (148.3 \text{ y})/t_{1/2}$$

$$t_{1/2} = 505 \text{ y}$$

- (b) If 0.955 mg disintegrates, 5.965 mg remains:

$$\ln\left(\frac{6.92 \text{ mg}}{5.965 \text{ mg}}\right) = \frac{(0.693)(17.4 \text{ min})}{t_{1/2}}$$

$$0.1485 = 12.06 \text{ min}/t_{1/2}$$

$$t_{1/2} = 81.2 \text{ min}$$

- 21.37** (a) ${}^{235}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^{139}_{57}\text{La} + {}^{95}_{35}\text{Br} + 2 {}^1_0\text{n}$
 (b) ${}^{238}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^0_0\gamma + {}^{239}_{92}\text{U}$
 (c) ${}^{239}_{94}\text{Pu} \rightarrow {}^4_2\alpha + {}^{235}_{92}\text{U}$

- 21.39** (a) ${}^4_2\alpha + {}^{14}_7\text{N} \rightarrow {}^{17}_8\text{O} + {}^1_1\text{H}$
 (b) ${}^{235}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^{140}_{56}\text{Ba} + {}^{93}_{36}\text{Kr} + 3 {}^1_0\text{n}$
 (c) ${}^9_4\text{Be} + {}^4_2\text{He} \rightarrow {}^1_0\text{n} + {}^{12}_6\text{C}$
 (d) ${}^{237}_{92}\text{U} + {}^2_1\text{d} \rightarrow {}^1_0\text{n} + {}^{238}_{93}\text{Np}$

- 21.41** (a) ${}^{12}_6\text{C} + {}^1_1\text{H} \rightarrow {}^{13}_7\text{N}$
 (b) ${}^{13}_7\text{N} \rightarrow {}^{13}_6\text{C} + {}^0_6\beta$ (The positron produced can react with an electron, which converts all the matter of both to energy. See Example 21.18.)
 (c) ${}^{13}_6\text{C} \rightarrow {}^1_1\text{H} \rightarrow {}^{14}_7\text{N}$ (d) ${}^{14}_7\text{N} + {}^1_1\text{H} \rightarrow {}^{15}_8\text{O}$
 (e) ${}^{15}_8\text{O} \rightarrow {}^{15}_7\text{N} + {}^0_6\beta$ (f) ${}^{15}_7\text{N} + {}^1_1\text{H} \rightarrow {}^{12}_6\text{C} + {}^4_2\text{He}$

- 21.42** The net reaction, when the annihilation of positrons and electrons is included, is



- 21.45** (a) ${}^1\text{H} + {}^3_2\text{Li} \rightarrow 2 {}^2_1\text{He}$ (b) ${}^9_4\text{Be} + {}^1_1\text{p} \rightarrow {}^4_2\alpha + {}^3_3\text{Li}$
 (c) $2 {}^3_2\text{He} \rightarrow 2 {}^1_1\text{H} + {}^4_2\text{He}$ (d) ${}^3_2\text{He} + {}^1_1\text{H} \rightarrow {}^2_1\text{He} + {}^1_1\text{H}$

- 21.46** (a) Natural (b) Artificially induced
 (c) Artificially induced

- 21.48** Since 87.5% disintegrates, 12.5% is left. Thus 3 half-lives or 140 h has elapsed.

- 21.50** Boiling water is a technique used to kill harmful bacteria—living organisms. Because the chemical environment of a radioactive isotope does not affect its radioactivity, boiling alone will not make water containing a radioactive isotope safe to drink. Distillation, a process involving boiling and condensation in another place, may separate the isotope from the water, making the water safe to drink.

- 21.51** (a) At least half of the neutrons must escape or be absorbed.
 (b) At least two thirds of the neutrons must escape or be absorbed.

- 21.52** The number of moles of each isotope is calculated first:

$$3.01 \times 10^{-4} \text{ g } {}^{235}\text{U} \left(\frac{1 \text{ mol } {}^{235}\text{U}}{235 \text{ g } {}^{235}\text{U}} \right) = 1.281 \times 10^{-6} \text{ mol } {}^{235}\text{U}$$

$$7.93 \times 10^{-4} \text{ g } {}^{207}\text{Pb} \left(\frac{1 \text{ mol } {}^{207}\text{Pb}}{207 \text{ g } {}^{207}\text{Pb}} \right) = 3.831 \times 10^{-6} \text{ mol } {}^{207}\text{Pb}$$

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The total number of moles of ^{235}U originally present was 5.112×10^{-6} mol.

The fraction remaining is

$$\frac{1.28I \times 10^{-6} \text{ mol}}{5.112 \times 10^{-6} \text{ mol}} = 0.25 = \frac{1}{4}$$

Two half-lives have passed, or 1.43×10^9 years has elapsed.

21.53 The number of moles of each isotope is calculated first:

$$1.58 \times 10^{-3} \text{ g } ^{238}\text{U} \left(\frac{1 \text{ mol}}{238 \text{ g}} \right) = 6.639 \times 10^{-6} \text{ mol } ^{238}\text{U}$$

$$2.49 \times 10^{-4} \text{ g } ^{206}\text{Pb} \left(\frac{1 \text{ mol}}{206 \text{ g}} \right) = 1.209 \times 10^{-6} \text{ mol } ^{206}\text{Pb}$$

The total number of moles of ^{238}U when the rock solidified is the sum of these, 7.847×10^{-6} mol.

$$\ln\left(\frac{n_o}{n}\right) = \left(\frac{0.693}{t_{1/2}}\right)t$$

$$\ln\left(\frac{7.847 \times 10^{-6} \text{ mol}}{6.639 \times 10^{-6} \text{ mol}}\right) = \left(\frac{0.693}{4.51 \times 10^9 \text{ years}}\right)t$$

$$t = 1.09 \times 10^9 \text{ years}$$

21.63 Algebraically, (a) $\ln(a/b) = -\ln(b/a)$ (b) $\ln a = [\ln(10)] [\log a] = 2.303 \log a$ (c) $\log(a/b) = -\log(b/a)$. The equation given in the book might be easier since neither the minus sign nor the additional factor 2.303 needs to be remembered.

Appendix 1

A.1 Be sure to distinguish between equations and expressions when simplifying.

- (a) $x = 11$ (b) $3.0x/y$
 (c) $x = 0.50$ (d) $0.80x$
 (e) $x = 18.8$ (f) $-x - 18$

A.2 (a) P_1
 (b) The expression cannot be simplified.
 (c) $T_2 = 3T_1$

A.3 $x = +8$

A.4 $x = -28$

A.5 (a) 1.2 (b) 7.5 (c) 1.2

A.6 The exponent 3 outside the parentheses indicates that the 3.0, as well as the unit (centimeter), is to be cubed. The values are 3.0 cm^3 and 27 cm^3 .

A.7 (a) 13.0 lb (b) 55.5 gal

A.8 (a) g/mL (b) kg/mL (c) mg/mL

A.9 (a) All three expressions are equal.

- (b) The first two expressions are equal; the third is not.
 (c) None of the expressions is equal to any of the others.

A.10 (a) 9.0 (b) 300

A.11 (a) -6 (b) -2 (c) -0.5

A.12 (a) -10 (b) 9 (c) +4

A.13 (a) Equal: $\frac{1}{50} = \frac{1}{50}$

(b) Not equal: $\frac{1}{15} \neq \frac{3}{10}$

(c) Not equal: $\frac{1}{5} \neq -\frac{1}{10}$

A.14 The total mass is 14.44 g.

$$\%S = \frac{5.78 \text{ g S}}{14.44 \text{ g total}} \times 100\% = 40.0\% \text{ S}$$

$$\text{A.15} \quad 13.7 \text{ g C} \left(\frac{100 \text{ g CO}}{42.9 \text{ g C}} \right) = 31.9 \text{ g CO}$$

APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems

A.16 (a) They are not equal: $-d$ times $-f$ is equal to $+df$, not $-df$.
 (b) They are equal.

$$\text{A.17} \quad 2.0 \times 10^3 \text{ m}^{-1} = 2.0 \times 10^3/\text{m}$$

$$\text{A.18} \quad 81 \quad (3^4)$$

$$\text{A.19} \quad (\text{a}) \text{ kg/cm}^3 \quad (\text{b}) \text{ kg/L} \quad (\text{c}) \text{ kg/m}^3$$

$$\text{A.20} \quad V = lwt = (7.00 \text{ cm})(1.80 \text{ cm})(0.750 \text{ cm}) = 9.45 \text{ cm}^3$$

$$\text{A.21} \quad (\text{a}) 4.11 \times 10^5 \quad (\text{b}) 4.11 \times 10^{-5} \\ (\text{c}) -4.11 \times 10^5 \quad (\text{d}) -4.11 \times 10^{-5} \\ (\text{e}) 2.3 \times 10^9$$

$$\text{A.23} \quad (\text{a}) 3.0 \quad (\text{b}) -3.0 \quad (\text{c}) 3.0 \quad (\text{d}) -3.0 \times 10^{-20} \\ (\text{e}) 3.0 \times 10^{20}$$

$$\text{A.24} \quad (\text{a}) \text{ g/mL} \quad (\text{b}) \text{ g/cm}^3 \quad (\text{c}) \text{ kg/L} \quad (\text{d}) \text{ kg/m}^3$$

$$\text{A.25} \quad (\text{a}) \text{ Dollars} \quad (\text{b}) \text{ cm}^2 \quad (\text{c}) \text{ cm} \quad (\text{d}) \text{ cm}^2$$

$$\text{A.26} \quad (\text{a}) \text{ cm} \quad (\text{b}) \text{ cm}^2 \quad (\text{c}) \text{ cm}^3 \quad (\text{d}) \text{ cm}^2$$

$$\text{A.28} \quad 14.7 \text{ g O} \left(\frac{100 \text{ g CO}}{57.1 \text{ g O}} \right) = 25.7 \text{ g CO}$$

$$\text{A.29} \quad \frac{21 \text{ children}}{50 \text{ people}} \times 100\% = 42\% \text{ children}$$

A.31 Specific gravity has *no units*. The units of the density of the substance cancel the units of the density of water. For example, the specific gravity of gold is

$$\frac{19.3 \text{ g/mL}}{1.00 \text{ g/mL}} = 19.3$$

The units cancel each other.

$$\text{A.32} \quad (\text{a}) \quad T_1 = \frac{T_2 P_1 V_1}{P_2 V_2} \quad (\text{b}) \quad n = \frac{\pi V}{RT} \quad (\text{c}) \quad R = \frac{PV}{nT} \\ (\text{d}) \quad n = MV \quad (\text{e}) \quad V = m/d$$

$$\text{A.33} \quad (\text{a}) \quad T_1 = \frac{P_1 V_1 T_2}{P_2 V_2} \quad (\text{b}) \quad v = E/h \quad (\text{c}) \quad k_f = \Delta t/m \\ (\text{d}) \quad P_2 = \frac{P_1 T_2}{T_1} \quad (\text{e}) \quad V = nRT/\pi \quad (\text{f}) \quad V = nRT/P \\ (\text{g}) \quad V = n/M \quad (\text{h}) \quad m = dV$$

$$\text{A.34} \quad (\text{a}) \quad n = \frac{PV}{RT} = \frac{(1.25 \text{ atm})(15.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(315 \text{ K})} = 0.725 \text{ mol}$$

$$\text{A.34} \quad (\text{b}) \quad V = n/M = 0.750 \text{ mol} \left(\frac{1 \text{ L}}{1.25 \text{ mol}} \right) = 0.600 \text{ L}$$

$$\text{A.34} \quad (\text{c}) \quad m = dV = (2.20 \text{ g/mL})(2.75 \text{ mL}) = 6.05 \text{ g}$$

$$\text{A.34} \quad (\text{d}) \quad T_1 = \frac{P_1 T_2}{P_2} = \frac{(836 \text{ torr})(273 \text{ K})}{760 \text{ torr}} = 300 \text{ K}$$

$$\text{A.34} \quad (\text{e}) \quad n = \frac{\pi V}{RT} = \frac{(1.05 \text{ atm})(6.27 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.269 \text{ mol}$$

$$\text{A.34} \quad (\text{f}) \quad V_2 = \frac{P_1 V_1}{P_2} = \frac{(1.11 \text{ atm})(6.10 \text{ L})}{(2.34 \text{ atm})} = 2.89 \text{ L}$$

$$\text{A.34} \quad (\text{g}) \quad v = E/h = (8.00 \times 10^{-18} \text{ J})/(6.63 \times 10^{-34} \text{ J} \cdot \text{s}) = 1.21 \times 10^{16}/\text{s}$$

$$\text{A.34} \quad (\text{h}) \quad k_f = \Delta t/m = (0.484^\circ\text{C})/(0.903 \text{ m}) = 0.536^\circ\text{C/m}$$

$$\text{A.35} \quad (\text{a}) \quad 0.0333 \quad (\text{b}) \quad 0.0481$$

$$\text{A.35} \quad (\text{c}) \quad 4.33 \times 10^{-15} \quad (\text{d}) \quad 4.49 \times 10^{-15}$$

$$\text{A.35} \quad (\text{e}) \quad 3.00 \quad (\text{f}) \quad 2.19$$

$$\text{A.35} \quad (\text{g}) \quad 0.0333 \quad (\text{h}) \quad 0.0481$$

(i) The first of each pair of answers is an approximation of the second with easier numbers to manipulate without a calculator. Use this method to check the final answers when working the chemistry problems.

$$\text{A.36} \quad (\text{a}) \quad 7650 \quad (\text{b}) \quad -76.8 \quad (\text{c}) \quad 6.75 \\ (\text{d}) \quad 2.47 \quad (\text{e}) \quad -0.64 \quad (\text{f}) \quad -48.3 \\ (\text{g}) \quad 3.58 \quad (\text{h}) \quad 14$$

APPENDIX 5 ■ Answers to Selected End-of-Chapter Problems

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A.39 (a) 18 (b) 36 (c) -9 (d) 81

A.41 (a) 4.50×10^4 (b) 0.800

A.42 (a) 4.14 (b) 515
(c) $4.00/x = 40.7$ (d) $1.73/x = 1.74$
 $x = 0.098$ $x = 0.993$
(e) $x/2.50 = 0.0474$ (f) $4.00 - x = 22.26$
 $x = 0.12$ $x = -18.3$

A.43 (a) 1.428 (b) 4.644 (c) 10.701
(d) -6.365 (e) 460 (f) 1.0473

A.47 (a) 3.5×10^{12} (b) 3×10^{-8} (c) 3.0×10^3
(d) 2.5×10^3 (e) 6.0×10^{10} (f) -5.0×10^{-4}
(g) -5.0×10^{12}

A.48 (a) $(a - b) - c - d$ (b) $(a/b) - c$
(c) $(ab)/c$ or $a(b/c)$ (d) $a/(bc)$

A.49 (a) $d = 12.6 \text{ cm}$ (b) $V = 3.45 \times 10^{-29} \text{ m}^3$
A.50 (a) -4.808×10^4 (b) 149

A.51 The volume of the cube, and thus the sphere, is

$$(4.00 \text{ cm})^3 = 64.0 \text{ cm}^3$$

$$V = \frac{4}{3}\pi r^3$$

$$64.0 \text{ cm}^3 = \frac{4}{3}\pi r^3$$

$$r^3 = \frac{3(64.0 \text{ cm}^3)}{4\pi} = 15.29 \text{ cm}^3$$

$$r = 2.48 \text{ cm}$$

A.53 $V = \frac{4}{3}\pi r^3 = \frac{4}{3}(3.14)(6.12 \times 10^{-10} \text{ m})^3$
 $= 9.60 \times 10^{-28} \text{ m}^3$

A.54 $r = d/2 = (3.88 \times 10^{-10} \text{ m})/2 = 1.94 \times 10^{-10} \text{ m}$
 $V = \frac{4}{3}\pi r^3 = \frac{4}{3}(3.14)(1.94 \times 10^{-10} \text{ m})^3$
 $= 3.06 \times 10^{-29} \text{ m}^3$

A.55 Exponentiation is done right to left. Thus, first square x , yielding 9, and then raise the 4 to the ninth power, yielding 262 thousand.

A.56 (a) 4.642 (b) 1.3512

A.60 *a* *b* *c* *x*
(a) 1 1 -6 -3 and +2
(b) 1 -5 6 2 and 3
(c) 1 4 4 -2 and -2
(d) 1 -8 16 +4 and +4
(e) 2 1 -21 3 and $-\frac{7}{2}$

The equations of parts (f)–(j) may be rearranged to give the same equations as in parts (a)–(e), respectively, and so the answers are the same.

A.61 5.19 years

Glossary

The section numbers in which the terms are explained are given in parentheses.

absolute temperature (12.3) A temperature, measured on the Kelvin scale, that must be used for gas law and certain other types of calculations.

absolute zero (12.3) 0 K, the lowest possible temperature.

accuracy (2.4) The closeness of a measurement or set of measurements to the correct value.

acetone (20.3) CH_3COCH_3 , propanone, the simplest ketone.

acetylene (20.1) $\text{HC}\equiv\text{CH}$, ethyne, the simplest alkyne.

acid (6.3, 8.4) A compound that provides H^+ ions to water solutions. (See also *Brønsted acid* and *organic acid*.)

acid carbonate (8.4) A compound containing the HCO_3^- ion.

acid dissociation constant (19.2) The equilibrium constant that controls the extent of ionization of a weak acid in water; symbolized by K_a .

acid salt (6.3, 8.4) A partially neutralized acid that originally contained two or more ionizable hydrogen atoms per molecule; for example, HSO_4^- is partially neutralized H_2SO_4 .

acid strength (19.1) The tendency for a certain percentage of acid molecules to ionize in water; the higher the acid strength, the higher is the percent ionization.

acidic anhydride (8.4) A nonmetal oxide that can react with water to form an acid.

active (8.3) Having a high tendency to react; reactive.

alcohol (20.3) An organic compound with the $-\text{OH}$ functional group.

aldehyde (20.3) An organic compound with the $-\text{CHO}$ functional group.

alkali metal (1.5) A metal in group IA of the periodic table: Li, Na, K, Rb, Cs, or Fr.

alkaline earth metal (1.5) A metal in group IIA of the periodic table: Be, Mg, Ca, Sr, Ba, or Ra.

alkane (20.1) A hydrocarbon containing only single bonds.

alkene (20.1) A hydrocarbon containing one double bond per molecule.

alkyl radical (20.3) A portion of an alkane formed by loss of one hydrogen atom.

alkyne (20.1) A hydrocarbon containing one triple bond per molecule.

allotrope (5.1) One of two or more forms of an uncombined element; for example, diamond and graphite are allotropes of carbon.

alpha particle (21.1) A helium nucleus generated in a nuclear reaction; a stream of such particles is referred to as an alpha ray.

amide (20.3) An organic compound with the $-\text{CONH}-$ functional group.

amine (20.3) An organic compound with the $-\text{NR}_2$ functional group, in which either or both R groups can be hydrogen atoms.

ammonia (6.1) The covalent compound NH_3 .

ammonium ion (6.2) The NH_4^+ ion.

amorphous solid (14.1) A solid with an internal structure that does not repeat over many molecules and that therefore has a large melting range.

amphotropic (19.1) The ability of a molecule or ion to react with both acids and bases.

analytical chemistry (Chapter 1, Introduction) The branch of chemistry dealing with the composition of samples.

angular molecule (13.4) A three-atom molecule in which the atoms do not lie on a line.

angular momentum quantum number (4.3) The quantum number (ℓ) that governs the shape of the space occupied by an electron in an atom.

anhydride (8.4) A compound resulting from loss of water by another compound; for example, the CaO resulting from strong heating of $\text{Ca}(\text{OH})_2$.

anhydrous (5.1) Without water; for example, CuSO_4 resulting from loss of water from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is said to be anhydrous.

anion (5.2) A negatively charged ion.

anode (5.2) The electrode where oxidation occurs in an electrochemical reaction.

aqueous solution (8.2) Any solution in which water is the solvent.

aromatic hydrocarbon (20.1) A hydrocarbon containing one or more benzene rings.

Arrhenius acid (8.4) A compound that provides H^+ ions to water.

Arrhenius base (8.4) A compound that provides OH^- ions to water.

Arrhenius theory (8.4) The fundamental theory of acids and bases. (Contrast with *Brønsted theory*.)

atmosphere (12.1) A unit equal to 760 torr and abbreviated atm that is the pressure of the atmosphere on a “normal” day at sea level; the envelope of air surrounding the Earth.

atmospheric pressure (12.1) The pressure of the atmosphere.

atom (3.2) The smallest particle that retains the characteristic composition of an element.

atom smasher (21.3) A machine designed to initiate nuclear reactions.

atomic bomb (21.3) A nuclear bomb; a bomb in which matter is converted to energy for destructive purposes.

atomic mass (3.4, 7.1) The weighted average of the masses of the naturally occurring isotopes of an element, compared with one twelfth of the mass of a ^{12}C atom.

atomic mass scale (3.4) A relative scale of masses based on the mass of ^{12}C being the standard and having a mass defined as exactly 12 amu.

atomic mass unit (3.4) A mass equal to one twelfth of the mass of a ^{12}C atom; abbreviated amu.

atomic number (3.3) The number of protons in the nucleus of each atom of an element.

atomic size (13.1) The size of an atom.

atomic theory See *Dalton's atomic theory*.

atomic weight See *atomic mass*.

atomic weight scale (3.4) Atomic mass scale.

autoionization (19.3) A reaction of molecules of a single substance to produce both positive and negative ions; for example, water molecules react to produce both H_3O^+ and OH^- ions.

autooxidation-reduction See *disproportionation*.

average kinetic energy (12.10) The total kinetic energy of all the molecules of a sample, divided by the number of molecules; the average kinetic energy is dependent on temperature only.

Avogadro's number (7.3) 6.02×10^{23} , which is the number of ^{12}C atoms in exactly 12 g of ^{12}C (as well as the number of atomic mass units in exactly 1 g).

balanced equation (8.1) A written representation of a chemical reaction in which formulas of the reactants and products appear on two sides of an arrow, with coefficients to make the numbers of atoms of each element the same on both sides.

barometer (12.1) An instrument for measuring the pressure of a gas, especially the atmosphere.

barometric pressure (12.1) The pressure of the atmosphere.

base (6.3, 8.4) A compound that provides OH^- ions to water solutions. (See also *Brønsted base*.)

base (2.2) The number that is raised to a power and multiplied by a coefficient in an exponential number; for example, the 10 in 1.5×10^2 .

base dissociation constant (19.2) The equilibrium constant that controls the extent of ionization of a weak base in water; symbolized K_b .

base strength (19.1) The tendency for a certain percentage of molecules of a base to ionize in water; the higher the base strength, the higher is the percent ionization.

basic anhydride (8.4) A metal oxide that can react with water to form a base.

battery (17.1) A combination of two or more galvanic cells.

bent molecule (13.4) See *angular molecule*.

benzene (20.1) C_6H_6 , the simplest aromatic hydrocarbon.

beta particle (21.1) A high-energy electron emitted from a nucleus in a nuclear reaction; a stream of such particles is called a beta ray.

binary compound (5.1) A compound composed of two elements.

biochemistry (Chapter 1, Introduction) The branch of chemistry dealing with living things.

Bohr theory (4.2) The first theory of the atom to propose that electrons in atoms were in definite energy levels.

boiling point (14.2) The temperature at which a liquid changes to a gas at the prevailing pressure.

boiling-point elevation (15.6) An increase in the boiling point of a solvent due to the presence of a solute.

bond See *covalent bond* and *ionic bond*.

bond order See *total bond order*.

Boyle's law (12.2) At constant temperature, the volume of a given sample of gas is inversely proportional to its pressure.

Brønsted acid (19.1) A proton donor.

Brønsted base (19.1) A proton acceptor.

Brønsted theory (19.1) A theory of acids and bases that is broader than the Arrhenius theory in that it does not limit acids and bases to water solutions and it defines ions as acids or bases depending on their tendency to react with water.

buffer solution (19.4) A solution of a weak acid and its conjugate base or a weak base and its conjugate acid, which resists changes in its acidity even on addition of a moderate quantity of strong acid or strong base.

build-up principle (4.4) The addition of an electron to the configuration of an atom of the preceding element on the periodic table allows determination of the electronic configuration of an atom of a given element.

buret (11.3) A piece of laboratory glassware calibrated for measuring the volume of liquid delivered.

carbohydrate (20.5) A compound containing carbon plus hydrogen and oxygen in a mole ratio of 2 : 1; the general formula is $\text{C}_x\text{H}_{2y}\text{O}_y$.

carbonate (8.4) An ionic compound containing the CO_3^{2-} ion.

catalyst (8.3, 18.1) A material that affects the speed of a chemical reaction without any permanent change in its own composition.

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cathode (5.2) The electrode where reduction occurs in an electrochemical reaction.

cation (5.2) A positively charged ion.

cell (Chapter 17, Introduction) An electrochemical apparatus in which an oxidation half-reaction occurs at the anode and at the same time a reduction half-reaction occurs at the cathode resulting in (1) a chemical reaction creating electricity (voltaic cell), or (2) electricity creating a chemical reaction (electrolytic cell).

Celsius scale (2.6) The temperature scale defined with 0° as the freezing point of water and 100° as the normal boiling point of water; the centigrade scale.

centered dot (5.1) An indication that water of hydration is part of a compound, as in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

centigrade scale (2.6) The Celsius scale.

central atom (13.4) The atom in a molecule or ion to which (most of) the other atoms are covalently bonded.

chain reaction (21.3) A nuclear reaction whose products cause the same reaction to occur again.

charge (17.5) A quantity of electricity, measured in coulombs or faradays.

Charles' law (12.3) At constant pressure, the volume of a given sample of gas is directly proportional to its absolute temperature.

chemical change (1.1) A chemical reaction.

chemical property (1.2) A property having to do with possible changes in the composition of a substance.

chemical reaction (1.1) A change in which the composition (or structure) of one or more substances is altered.

chemistry (1.3) The study of the interaction of matter and energy and the changes that matter undergoes.

circuit (17.1) A closed path that electric charge can follow and get back to its original location. The word is related to the word *circle*, because if you follow the path from any point you get back where you started. In electrochemistry, the circuit is composed of solutions (through which ions carry the charge) and wires (through which electrons carry the charge).

coefficient (2.2) The number that is multiplied by a base raised to a certain power in a number written in exponential notation, such as the 1.5 in 1.5×10^2 .

coefficient (8.1) The number placed before a formula in a chemical equation to balance the equation.

coinage metal (1.5) An element of periodic group IB: Cu, Ag, or Au.

colligative properties (15.6) Characteristics of solutions that are dependent on the concentration of solute particles and the nature of the solvent but not on the nature of the solute.

combination reaction (8.3) A reaction in which two substances combine to form one.

combined gas law (12.4) For a given sample of gas, the volume is directly proportional to the absolute temperature and inversely proportional to the pressure.

combustion (8.3) A reaction of an element or compound with oxygen at high temperature.

completion (10.4) The condition a reaction has reached when the limiting quantity of reactant has been used up.

compound (1.1) A chemical combination of elements that has a definite composition and its own set of properties.

concentration (11.1, 15.3) The quantity of solute per unit volume of solution or per unit mass of solvent.

condensation (14.2) A change of phase from gaseous to liquid or solid.

condensed formula (20.1) A formula that shows bonded groups of atoms in a molecule or polyatomic ion rather than the atoms individually (as in a structural formula) but is not limited to a single line (as is a line formula).

conjugate acid (19.1) The cation (or molecule) that results from the reaction of a base with a proton.

conjugate acid-base pair (19.1) A Brønsted acid and base that differ from each other by H^+ .

conjugate base (19.1) The anion (or molecule) that results from the loss of a proton by an acid.

constant composition See *law of constant composition*.

“control” of shared electrons (16.1) Assignment of the electrons in a covalent bond to the more electronegative atom of the bond.

control rod (21.3) A neutron-absorbing rod used to slow down nuclear reactions in reactors.

controlled experiment (13.1) An experiment in which only one of several variables is altered at a time.

conversion factor (2.1) A ratio equal to 1, which can be multiplied by a quantity to change the form of the quantity without changing its value.

covalent bond (5.5) A bond resulting from electron sharing.

critical mass (21.3) The smallest mass capable of sustaining a nuclear chain reaction.

crystalline solid (14.1) A solid with a regular internal structure of repeating units and a definite melting point.

cubic meter (2.3) The volume equal to that of a cube that measures 1 m on each edge; the basic unit of volume in SI.

Dalton's atomic theory (3.2) The theory that matter is made up of small particles (atoms) that have properties characteristic of an element.

Dalton's law of partial pressures (12.6) The total pressure of a gas mixture is equal to the sum of the partial pressures of its components.

Daniell cell (17.1) A cell with zinc and copper electrodes.

daughter isotope (21.1) The large product of a natural radioactive decay event.

decay See *radioactive decay*.

decomposition reaction (8.3) A reaction in which one compound is broken down into two or more substances.

definite composition (1.1) The given ratio by mass of each element in a compound to any other element in the compound.

definite proportions See *law of definite proportions*.

degenerate (4.4) Having the same energy.

density (2.5) The mass per unit volume of a sample of matter.

deuterium (21.4) The isotope of hydrogen with mass number 2; symbolized ^2H or D.

deutron (21.4) A deuterium (^2H) nucleus; symbolized d.

diatomic molecule (5.1) A molecule containing two atoms.

dimensional analysis See *factor label method*.

dipole (13.5) See *dipole moment*.

dipole moment (13.5) An unequal distribution of charge in a molecule resulting from unsymmetrical orientation of polar bonds; also referred to as a dipole.

direct proportionality (12.3) The relationship in which one variable changes by the same factor as another.

disaccharide (20.5) A sugar containing two simple sugar molecules.

discrete energy levels (4.2) Atomic energy levels that have specific energies.

disintegration (21.1) A reaction of an unstable nucleus.

disproportionation (16.4) The reaction of a species with itself to produce products having higher and lower oxidation numbers; also called autooxidation-reduction.

dissociation (Chapter 9, Introduction, 19.2) Separation of ions from their close proximity in a solid lattice to a distance when dissolved in a solvent.

dissolve (1.2) To go into solution, making a homogeneous mixture.

distillation (14.2) The conversion of a liquid to a gas and then back to a liquid to separate it from impurities.

double bond (5.5) The sharing of two pairs of electrons between two atoms.

double displacement reaction (8.3) The reaction of two compounds in which two other compounds are produced, as a result of a trade of the anions by the cations.

double substitution reaction (8.3) A double displacement reaction.

ductile (1.5) Capable of being drawn into a wire.

duet (5.2) A pair of electrons associated with a hydrogen, helium, lithium, or beryllium atom, resulting in the stable configuration of a noble gas (helium).

dynamic state (18.2) A state in which two opposite processes occur at equal rates.

Einstein's equation (21.3) The equation $E = mc^2$, which relates the energy produced to the mass of matter converted to energy in a nuclear reaction.

electrochemistry (Chapter 17, Introduction) The branch of chemistry dealing with the interaction of chemical reactions and electricity.

electrode (5.2) The solid portion of an electrochemical reaction apparatus at which a change from electron conduction to ion conduction, or vice versa, takes place.

electrolysis (17.4) Production of a chemical reaction by means of an electric current.

electrolysis cell (17.4) An apparatus in which electric energy can be used to produce chemical reactions.

electromagnetic radiation (21.1) Any form of light energy: visible light, ultraviolet light, X-rays, gamma rays, infrared radiation, or microwaves.

electromagnetic spectrum (4.1) The complete collection of electromagnetic waves, including visible light, infrared, ultraviolet, X-rays, gamma rays, and microwaves.

electron (3.3) A negatively charged subatomic particle; a fundamental particle of nature.

electron affinity (13.2) The energy liberated when a gaseous atom acquires an electron to form a gaseous anion.

electron group (13.4) A single electron pair, the 4 or 6 electrons in a double or triple bond, or rarely, a single electron, which are attached to a central atom of a molecule or polyatomic ion.

electron sharing (5.5) The sharing of electrons between atoms to form covalent bonds.

electronegative (5.1) A large tendency of an atom to attract electrons in the formation of a compound.

electronegativity (5.1, 13.3) A semiquantitative measure of the tendency of an atom to attract electrons in the formation of a compound.

electronic charge (3.3) The charge on one electron, 1.60×10^{-19} coulomb.

electronic configuration (4.5) The arrangement of the electrons in an atom, ion, or molecule.

electronic structure See *electronic configuration*.

electropositive (5.1) Having only a small tendency to attract electrons.

element (1.1) A substance that cannot be broken down into simpler substances by chemical means; one of the basic building blocks of which all matter is composed.

elemental (5.1) Existing as an element; not combined into any compound.

empirical formula (7.4) The simplest formula for a compound that shows the atomic ratio of elements in the compound.

end point (11.3) The point in a titration when the indicator signals that the reaction is complete.

endothermic process (14.3) A process in which energy is absorbed from outside the system.

energy (1.3) The capacity to do work.

energy level diagram (4.7) A graph in which horizontal lines represent the orbitals of an atom, those with higher energies toward the top, and in which arrows may be used to represent electrons.

enthalpy change (14.4) The heat (under certain familiar conditions) involved in a process; symbolized ΔH .

enthalpy of formation (14.4) The enthalpy change in the formation of a substance from its elements in their standard states; symbolized ΔH_f .

enthalpy of fusion See *heat of fusion*.

enthalpy of vaporization See *heat of vaporization*.

enzyme (18.1) A biochemical catalyst.

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equation (8.1) A written representation of a chemical reaction, using formulas for the reactants and products and coefficients to indicate the mole ratios involved.

equilibrium (18.2) The situation in which the reactants and the products are producing each other *at the same rate*.

equilibrium constant (18.4) A constant that tells how far a reaction will proceed until it reaches equilibrium.

equilibrium constant expression (18.4) The ratio of the product of the concentrations of the products divided by the product of the concentrations of the reactants, each raised to the power corresponding to its coefficient in the balanced equation: for $a A + b B \rightleftharpoons c C + d D$,

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Erlenmeyer flask (11.3) A flask designed to allow swirling of the liquid contents without spillage.

ester (20.3) An organic compound with the $-\text{COO}-\text{R}$ functional group.

ether (20.3) An organic compound with the $-\text{O}-$ functional group.

ethylene (20.1) Ethene, $\text{H}_2\text{C}=\text{CH}_2$.

evaporation (14.2) A change of phase from liquid to gaseous.

event (21.1) A nuclear reaction involving one nucleus.

excess (10.4) The quantity of a reactant that exceeds that which can react with the limiting quantity of another reactant.

excited state (4.3) The state of an atom that has more energy than its lowest energy state. Electrons in higher than normal energy positions are the cause in the discussions in this text.

exothermic process (14.3) A process in which energy is transferred to the surroundings.

exponent (2.2) The number of times the base is multiplied by the coefficient; for example, in 1.5×10^3 , the 1.5 is multiplied by 10 three times, where 3 is the exponent.

exponential notation (2.2) The format for writing large or small numbers that consists of the coefficient times a base raised to a power; for example, 1.5×10^3 .

exponential part (2.2) The base raised to a power in an exponential number.

extensive property (1.2) A characteristic that depends on the quantity of the sample.

factor label method (2.1) A system that involves the use of units to indicate the proper arithmetic operation to perform; also called dimensional analysis.

Fahrenheit scale (2.6) A temperature scale in common use in the United States on which the freezing point of water is defined as 32°F and the normal boiling point of water is defined as 212°F.

family (1.5) In the periodic table, a column that includes elements with similar chemical properties; a periodic group.

faraday (17.5) The charge on 1 mol of electrons.

fat (20.5) A compound formed by the reaction of glycerine with long-chain fatty acids.

feeble acid (19.1) An acid that has no tendency to react with water; the conjugate of a strong base.

feeble base (19.1) A base that has no tendency to react with water; the conjugate of a strong acid.

fluidity (14.1) The characteristic of a gas or liquid that allows it to flow.

force (12.1) A push or a pull.

formaldehyde (20.3) Methanal, HCHO .

formula (1.4, 5.1) A combination of symbols and subscripts that identifies the composition of an element, compound, or ion.

formula mass (7.1) The relative mass of one formula unit compared to the mass of a ^{12}C atom, which is defined as exactly 12 amu.

formula unit (5.1) The collection of atoms described by a chemical formula—an atom of an uncombined element, a molecule of a molecular compound, or the set of ions in the formula of an ionic compound.

formula weight (7.1) Formula mass.

forward reaction (18.2) A reaction that goes as the equation is written.

freezing (14.2) Changing from a liquid to a solid.

freezing-point depression (15.6) A lowering of the freezing point of a solvent due to the presence of a solute.

frequency (4.1) The number of times a wave passes a certain point per second.

functional group (20.3) The characteristic group of atoms attached to a radical that gives a class of organic compounds its characteristic properties.

fusion (14.2) Melting, or changing from a solid to a liquid as a result of heating; see also *nuclear fusion*.

galvanic cell (17.1) A voltaic cell.

gamma particle (21.1) A particle (photon) of high-energy electromagnetic radiation (light) emitted from a nucleus in a nuclear reaction; a stream of such particles is often referred to as a gamma ray.

gas (12.1) A state of matter; a sample of matter that has its volume and shape determined by the volume and shape of its container.

Gay-Lussac's law of combining volumes (12.9) At equal temperatures and equal pressures, the volumes of *gases* involved in a chemical reaction are directly proportional to their coefficients in the balanced chemical equation.

Geiger counter (21.1) An instrument for measuring radioactivity.

glycerine (20.5) $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$, a tri alcohol.

gram (2.3) The primary unit of mass in the metric system; one thousandth of the SI standard mass: the kilogram.

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ground state (4.3) The lowest energy state of the set of electrons in an atom.

group (1.5) In the periodic table, a column that includes elements with similar chemical properties; a family.

half-life (21.2) The period of time it takes for half of a radioactive sample to disintegrate naturally.

half-reaction (16.4) The oxidation or reduction half of a redox reaction.

half-reaction method (16.4) The method of balancing oxidation-reduction equations that involves the completion and balancing of the oxidation and reduction half-reactions separately, followed by combination of the two.

halogen (1.5) An element of periodic group VIIA: F, Cl, Br, I, or At.

heat (14.4) A form of energy.

heat capacity See *specific heat*.

heat of formation See *enthalpy of formation*.

heat of fusion (14.3) The heat required to change a given quantity of solid to the liquid state.

heat of vaporization (14.3) The heat required to change a given quantity of liquid to the gas state.

heating curve (14.3) A graph showing the temperature changes of a substance as a function of the quantity of heat added.

Heisenberg uncertainty principle (4.6) It is impossible to know exactly both the energy and the momentum of a subatomic particle at the same time.

Henry's law (15.2) The solubility of a gas in a liquid is directly proportional to its partial pressure.

Hess' law (14.4) When two or more processes combine to give a resulting process, their enthalpy changes add up to give the enthalpy change for the resulting process.

heterogeneous mixture (1.1) A physical combination of substances having distinguishable parts.

homogeneous mixture (1.1) A physical combination of substances whose parts are not distinguishable, even with the best optical microscope; a solution.

Hund's rule (4.7) The electrons in a partially filled subshell in an atom will occupy the orbitals singly as far as possible.

hydrate (5.1) A compound that has water molecules bonded in it.

hydrocarbon (8.3, 20.1) A compound consisting of only carbon and hydrogen.

hydrogen (1.5) The first element in the periodic table.

hydrogen (6.3) Word used in names of acid salts to indicate the hydrogen remaining, as in NaHCO_3 , sodium hydrogen carbonate.

hydrogen bomb (21.4) A thermonuclear device in which the nuclear fusion of a hydrogen isotope is the source of energy.

hydrogen bonding (13.6) The intermolecular force resulting from the attraction of a hydrogen atom on one

molecule to a small, highly electronegative atom (F, O, or N) on another molecule (or the same molecule).

hydronium ion (19.1) The H_3O^+ ion.

hypothesis (1.6) A proposed explanation for a body of observed facts.

ideal gas law (12.5) The pressure, volume, number of moles, and temperature of a sample of gas can be related by the equation $PV = nRT$, where $R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$.

ideal solution (15.6) A solution that obeys Raoult's law exactly.

indicator (11.3) A compound that has different colors in solutions of different acidities and that is used to signal the end of a titration.

inner transition element (1.5) An element with atomic number 58–71 or 90–103; a member of the lanthanide or actinide series.

inorganic chemistry (Chapter 1, Introduction) The branch of chemistry dealing with compounds other than those containing C—C or C—H bonds or both.

intensive property (1.2) A characteristic such as color that does not depend on the quantity of material present.

intermolecular force (13.6) An attraction between molecules.

inverse proportionality (12.2) A relationship in which one variable gets smaller by the same factor as another gets larger, or vice versa.

ion (5.2) A charged atom or group of atoms.

ionic bond (5.2) The attractive force between oppositely charged ions.

ionic equation (9.2) A chemical equation in which soluble, ionic substances are written with their ions separated.

ionic size (13.1) The size of an ion.

ionic solid (14.1) A solid consisting of ions.

ionizable hydrogen atom (6.3) Any of the hydrogen atoms in an acid that are capable of reacting with water to form ions.

ionization (19.2) Reaction of a covalent substance with solvent to produce ions, as, for example, the reaction of a strong acid with water.

ionization constant (19.2) The equilibrium constant for the reaction of a weak acid or base with water to form ions in solution; symbolized K_i .

ionization energy (13.2) The energy required to remove an electron from a gaseous atom to form a gaseous cation.

isomers (20.2) Different compounds having the same molecular formula.

isotopes (3.3, 21.1) Two or more forms of an element whose atoms have the same number of protons but different numbers of neutrons.

joule (14.3) The SI unit of energy; it takes 4.184 J to raise the temperature of 1.000 g of water 1.000°C .

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kelvin (12.3) The unit of the Kelvin temperature scale; abbreviated K.

Kelvin scale (2.6, 12.3) The temperature scale with 273 K as the freezing point of water and 373 K as the normal boiling point of water; the scale required for gas law and certain other scientific calculations.

ketone (20.3) A class of organic compounds with the $\text{C}=\text{O}$ functional group not at the end of a carbon chain.

kilogram (2.2) 1000 g; the standard mass in SI.

kinetic energy (12.10) Energy of motion; $\text{KE} = \frac{1}{2}mv^2$.

kinetic molecular theory (12.10) The theory that explains the gas laws (and other phenomena) in terms of the motions and characteristics of the molecules of a gas.

law (1.6) A generalized statement that summarizes a collection of observations.

law of conservation of energy (1.3) Energy can be neither created nor destroyed in any chemical or physical process.

law of conservation of mass (1.6) Mass can be neither created nor destroyed in any chemical or physical process.

law of constant composition (3.1) The composition of a compound is fixed; also called law of definite proportions.

law of definite proportions (3.1) The composition of a compound is fixed; also called law of constant composition.

law of multiple proportions (3.1) When two or more elements combine to form more than one compound, for a fixed mass of one element, the masses of each of the other elements in the compounds are in a small, whole-number ratio.

lead storage cell (17.1) A cell composed of a lead electrode in contact with lead(II) sulfate and a lead(IV) oxide electrode also in contact with lead(II) sulfate in an electrolyte of sulfuric acid.

LeChâtelier's principle (18.3) When a stress is applied to a system at equilibrium, the equilibrium shifts so as to tend to reduce the stress.

length (2.3) The distance from one end of an object to the other.

Lewis electron dot diagram (5.3) A pictorial model of an atom, molecule, or ion consisting of the symbol(s) for element(s) and dots representing the valence electrons.

light (4.1) In general, any electromagnetic radiation; specifically, visible light—the wave motion that affects the human eye.

light absorption (4.2) Process in which the energy of certain wavelengths of light is converted to energy of electrons in atoms, increasing their energy.

light emission (4.2) Process in which light of specific wavelengths is produced as electrons in atoms fall to lower energy levels.

limiting quantity (10.4) The quantity of the reactant that will be exhausted first in a chemical reaction, limiting the quantity of products that can be produced.

line formula (20.1) A formula for an organic compound that is written on a single line, such as $\text{CH}_3\text{CH}_2\text{COOH}$.

linear molecule (13.4) A molecule whose atoms all lie on a line.

liquid (12.1) A state of matter; a sample of matter that has a definite volume but assumes the shape of its container.

liter (2.3) The primary unit of volume of the metric system, equal to 1 dm³.

lobe (4.6) One portion of an atomic orbital.

lone pair (5.5) An unshared pair of electrons on a bonded atom.

macromolecule (5.5) A molecule containing hundreds of thousands to millions of covalently bonded atoms.

magnetic properties (4.7) The characteristics of substances that make them attracted to or repelled by magnetic fields.

magnetic quantum number (4.3) The quantum number (m_ℓ) that designates the orientation in space of the volume occupied by an electron in an atom.

main group element (1.5) An element of one of the periodic groups labeled A, which extend up to the first or second period of the periodic table.

malleable (1.2) Capable of being pounded into various shapes.

mass (1.3) A fundamental characteristic of a sample of matter that quantifies its attraction to the Earth (weight) and its resistance to a change in its motion (inertia).

mass number (3.3) The sum of the number of protons and the number of neutrons in an atom: the distinguishing difference among isotopes of a given element.

matter (1.3) Anything that has mass and occupies space.

melting (14.2) A change of phase from solid to liquid by heating.

metal (1.5) An element on the left of the stepped line in the periodic table, or a mixture of such elements.

metallic solid (14.1) A solid consisting of atoms of one or more elemental metals.

metalloid (1.5) An element near the dividing line between metals and nonmetals on the periodic table and that has properties of both metals and nonmetals.

metathesis reaction (8.3) A double displacement reaction.

meter (2.3) The primary unit of length in the metric system and SI.

metric system (2.3) A system of measurement whose units have subunits and multiples that are based on powers of 10.

mixture (1.1) A physical combination of substances that has an arbitrary composition and properties characteristic of its components.

molal (15.4) The unit of molality, abbreviated m.

molality (15.4) A measure of concentration defined as the number of moles of solute per kilogram of solvent; symbolized m .

molar (11.1) The unit of molarity; abbreviated M.

molar mass (7.3) The mass in grams of 1 mol of a substance.

molarity (11.1) A measure of concentration defined as the number of moles of solute per liter of solution; symbolized M .

mole (7.3) The chemical unit of quantity for any substance; equal to 6.02×10^{23} individual atoms, molecules, or formula units of the substance; abbreviated mol.

mole fraction (15.5) The ratio of the number of moles of a component (A) of a solution to the total number of moles in the solution; symbolized X_A .

molecular formula (7.5) The formula of a molecular substance that gives the ratio of atoms of each element to the substance's molecules.

molecular mass (7.1) The relative mass of a molecule of a substance compared to the mass of a ^{12}C atom.

molecular shape (13.4) The spatial arrangement of the atoms in a molecule.

molecular solid (14.1) A solid consisting of (relatively small) molecules.

molecular weight (7.1) Molecular mass.

molecule (3.2, 5.1) An uncharged, covalently bonded group of atoms.

molten (8.3) Melted: in a liquid state without being dissolved.

monatomic ion (5.2) An ion consisting of one atom only.

monomer (20.4) A molecule that is capable of reacting with other similar molecules to form a polymer.

monosaccharide (20.5) A simple sugar, such as glucose, $\text{C}_6\text{H}_{12}\text{O}_6$.

multiple bond (5.5) A double or triple bond.

$n + \ell$ rule (4.4) The electron with the lower value for the sum of quantum numbers n and ℓ is lower in energy.

natural logarithm (A.2) Logarithm to the base e ; abbreviated ln.

Nernst equation (17.3) An equation relating the potential of a cell or half-cell to the concentrations or pressures of its reagents.

net ionic equation (9.2) An ionic equation in which the ions that do not change (the spectator ions) are omitted.

network solid (14.1) A solid consisting of macromolecules.

neutral (3.3) Neither positively nor negatively charged.

neutral (8.4) Neither acidic nor basic.

neutralization reaction (8.4) A reaction of an acid and a base.

neutron (3.3) A subatomic particle that has no charge and a mass slightly greater than 1 amu.

noble gas (1.5) An element of periodic group 0: He, Ne, Ar, Kr, Xe, or Rn.

noble gas configuration (5.2) An electronic configuration like that of a noble gas, with 8 electrons (or 2 for very light elements) in the outermost shell.

nomenclature (Chapter 6, Introduction) The systematic naming of chemical substances.

nonelectrolyte (9.1) A compound that is not ionized at all, even in aqueous solution.

nonoctet structure (5.5) Any electronic structure in which an atom in a molecule or ion contains more or fewer than eight electrons in its valence shell.

nonlinear molecule (13.4) See *angular molecule*.

nonmetal (1.5) Hydrogen or any element on the right of the stepped line in the periodic table.

nonpolar bond (13.3) A covalent bond in which the electrons are shared equally.

nonpolar molecule (13.5) A molecule in which the centers of positive and negative charge lie at the same place.

nonvolatile (15.6) Not easily vaporized.

normal boiling point (14.2) The boiling point of a substance at a pressure of 1 atm.

nuclear fission (21.3) The splitting of a nucleus into two more or less equal sized smaller nuclei, plus some subatomic particles.

nuclear fusion (21.4) Combination of nuclei in a nuclear reaction.

nuclear radiation (21.1) Alpha, beta, or gamma particles; particles emitted in nuclear reactions.

nucleus (3.3) The center of an atom, consisting of the protons and neutrons.

nylon (20.4) A polymer of a diacid and a diamine.

octet (5.2) A set of 8 electrons in the outermost shell of an atom or ion.

octet rule (5.2) Atoms or ions with an octet are stable.

orbit (4.2) As described by Bohr, the circular path for electrons in an atom, the most important characteristic of which is its energy.

orbital (4.5) A part of a subshell of an atom having a given set of n , ℓ , and m_ℓ quantum numbers.

orbital shape (4.6) The shape of the volume of space that can be occupied by an electron in an atom.

organic acid (20.3) An organic compound containing the $-\text{COOH}$ functional group.

organic chemistry (Chapter 1, Introduction) The branch of chemistry dealing with organic compounds.

organic compound (Chapter 20, Introduction) A compound containing at least one carbon-carbon or carbon-hydrogen bond.

organic halide (20.3) An organic compound that has at least one halogen atom per molecule.

osmotic pressure (15.6) The difference in pressure between a solution and the pure solvent separated by a semipermeable membrane.

outermost shell (5.2) The highest shell that contains electrons.

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overall equation See *total equation*.

oxidation (16.4) An increase in oxidation number.

oxidation number (16.1) The difference in the number of electrons in a neutral atom and the number “controlled” by the atom in a compound, in which control is assigned to the more electronegative atom of a covalent bond.

oxidation-reduction reaction (16.4) A reaction in which the oxidation number of one element is raised and the oxidation number of another element (or the same element) is lowered.

oxidation state (16.1) The oxidation number.

oxidizing agent (16.4) A species that can increase the oxidation number of another reactant.

oxoacid (6.3) An acid of a nonmetal covalently bonded to one or more oxygen atoms; such as HClO_3 .

oxoanion (6.2) An anion containing oxygen covalently bonded to another element.

ozone (5.1) O_3 , an allotrope of oxygen.

parent isotope (21.1) The isotope that is the reactant in natural radioactive decay.

partial pressure (12.6) The pressure of one gas in a mixture of gases.

Pauli exclusion principle (4.3) The rule that prohibits more than one electron in an atom from having the same set of four quantum numbers.

percent (3.1, 15.3, A.1) Parts per hundred parts.

percent by mass (15.3) One hundred percent times the ratio of the mass of an element in a compound divided by the mass of the compound.

percent composition (7.2) The percentages by mass of all elements in a compound.

percent yield (10.5) The ratio of actual yield to theoretical yield, expressed as a percentage.

perfectly elastic collision (12.10) A collision that occurs with no loss of kinetic energy.

period (1.5) One of the seven horizontal rows of the periodic table.

periodic table (1.5) An assemblage of elements in order of atomic number, with elements having similar chemical properties aligned in vertical columns.

periodicity of electronic configuration (4.8) The regularity of the change in the outermost electronic configuration of the elements in the groups of the periodic table.

peroxide ion (6.2) The O_2^{2-} ion.

pH (19.3) A measure of the acidity of a solution, defined as $-\log [\text{H}_3\text{O}^+]$.

phase (12.1) A state of matter: solid, liquid, or gas.

phase change (14.2) A transition from one to another of the three states of matter, for example, from gas to liquid.

photon (4.1) A particle of light.

physical change (1.1) A process in which no change in composition occurs.

physical chemistry (Chapter 1, Introduction) The branch of chemistry dealing with the properties of substances.

physical equilibrium (14.2) A situation in which two exactly opposite physical processes are occurring at the same rate in the same system.

physical property (1.2) Property unrelated to possible changes in the composition of a substance.

pipet (11.3) A piece of laboratory glassware designed to deliver an exact volume of liquid.

polar bond (13.3) A covalent bond in which there is unequal sharing of electrons.

polar molecule (13.5) A molecule that has a permanent dipole.

polyatomic ion (5.5) An ion composed of two or more atoms.

polyester (20.4) A polymer of a diacid and a dialcohol.

polymer (20.4) A molecule built from many (thousands or even more) smaller molecules (monomers) or parts of molecules.

polyprotic acid (19.5) An acid with more than one ionizable hydrogen atom.

polysaccharide (20.5) A complex carbohydrate composed of more than one monosaccharide.

positron (21.3) A subatomic particle created in a nuclear reaction that has the same properties as an electron except for being *positively charged*.

postulate (3.2) A proposed explanation for an observation or set of observations.

potential (17.2) Voltage, the driving force of electric current.

precipitate (8.3) A solid formed from substances in solution.

precision (2.4) The degree of reproducibility of measurements.

prefix (6.1) A word fragment placed before another part of a word to impart a special meaning.

pressure (12.1) Force divided by area.

principal quantum number (4.3) The main quantum number (n) of an electron in an atom, which is the major factor determining the energy of the electron and its mean distance from the nucleus.

proceed to the left (18.2) A phrase used to indicate that the products of a chemical equation (as written) will yield the reactants.

proceed to the right (18.2) A phrase used to indicate that the reactants of a chemical equation (as written) will yield the products.

product (8.1) Any substance produced in a reaction and appearing on the right-hand side of a chemical equation.

property (1.2) A characteristic of a substance.

proportion (3.1, A.1) The ratio of the number of a certain item divided by the total number of items. (Compare to percent.)

propylene (20.1) Propene, $\text{CH}_2=\text{CHCH}_3$.

protein (20.4) A polymer formed from amino acids.

proton (3.3) A subatomic particle with a mass slightly greater than 1 amu and a charge of $1+$.

proton (19.1) In the Brønsted sense, the nucleus of the hydrogen atom.

proton acceptor (19.1) A molecule or ion that accepts a proton; a Brønsted base.

proton donor (19.1) A molecule or ion that donates a proton; a Brønsted acid.

pure substance (1.1) An element or compound.

quantitative property (1.2) A property that is measurable.

quantum numbers (4.3) Four numbers assigned to each electron in an atom that describe the energy and other properties of the electron.

radiation See *electromagnetic radiation* or *nuclear radiation*.

radical (20.3) The hydrocarbon portion of an organic molecule that has a functional group.

radioactive dating (21.2) The determination of the age of an object from the measurement of the radioactivity of an isotope it contains.

radioactive decay (21.1) Disintegration of nuclei of an isotope.

radioactive series (21.1) A parent isotope and the successive daughters of its natural decay.

radioactivity (21.1) Spontaneous reaction of nuclei.

random motion (12.10) Motion of molecules in arbitrary directions.

Raoult's law (15.6) The vapor pressure of a solute in a solution is equal to its mole fraction in the solution times the vapor pressure of the pure solute: $P_A = X_A P_A^0$.

rate (18.1) The number of moles per liter produced or used up in a chemical reaction per unit time.

reactant (8.1) Any substance that undergoes a reaction and thus appears on the left-hand side of a chemical equation.

reacting ratio (10.1) A ratio of coefficients from a balanced equation, which represents the ratio of moles of reactants or products involved in the reaction.

reaction See *chemical reaction*.

reactive (8.3) Having a high tendency to undergo chemical reaction.

reagent (8.1) A reactant.

recrystallization (15.2) A purification process carried out by dissolving a substance in a solvent at one temperature and changing the temperature so that the (purified) substance crystallizes out.

redox reaction (16.4) An abbreviation for *oxidation-reduction reaction*.

reducing agent (16.4) A species that reduces the oxidation number of another reactant.

reduction (16.4) The lowering of oxidation number.

relative scale (3.4) A scale based on an arbitrarily chosen standard; the atomic mass scale is a relative scale of masses based on the mass of ^{12}C .

resonance structures (5.5) Two or more structures of a given molecule differing only in the locations of the electrons.

reverse reaction (18.2) A reaction in which the products of an equation as written actually produce the reactants.

rounding (2.4) Reducing the number of digits in a calculated result to the proper number of significant digits.

salt (6.3, 8.4) An ionic compound that does not contain H^+ , OH^- , or O^{2-} ions.

salt bridge (17.1) A solution of an inert electrolyte that connects two half-cells in order to complete the circuit in a voltaic cell.

saturated fat (20.5) A fat that contains no carbon-carbon multiple bonds.

saturated hydrocarbon (20.1) A compound containing only carbon and hydrogen linked only by single bonds.

saturated solution (15.2) A solution that holds as much solute as it is capable of holding stably at a given temperature.

scientific method (1.6) The method employed by scientists consisting of (1) collection of data by observation and experimentation; (2) generalization of much data into a statement, known as a law; (3) proposal of an explanation for the law, called a hypothesis; and (4) acceptance of the hypothesis as a theory if the hypothesis can be substantiated by all additional experiments.

scientific notation (2.2) A format for writing large and small numbers, using a coefficient with one (nonzero) integer digit times 10 to an integral exponent.

second ionization energy (13.2) The energy required to remove an electron from a gaseous, monopositive ion to form a gaseous, dipositive ion.

shell (4.5) A set of energy levels for electrons in an atom that is characterized by a given value of the principal quantum number, n .

shift (18.3) A net reaction of a system at equilibrium in response to a stress—a change in the conditions on the system.

SI (2.3) Système International d'Unités; the modern form of the metric system.

significant digit (2.4, A.2) Any digit that reflects the accuracy with which a measurement was made.

significant figure (2.4) A significant digit.

single bond (5.5) A covalent bond formed by a single pair of shared electrons.

single displacement reaction (8.3) The reaction of an element with a compound to produce another element and another compound.

single substitution reaction (8.3) A reaction in which an uncombined element reacts with a compound to produce a new compound and a different uncombined element. A single displacement reaction.

soap (20.5) A salt of a fatty acid, such as sodium stearate, $\text{Na}^+ \text{C}_{17}\text{H}_{35}\text{COO}^-$.

sodium chloride structure (5.2) The three-dimensional lattice containing alternating positive and negative ions that is characteristic of sodium chloride and many other ionic compounds.

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solid (12.1) A state of matter; a sample of matter that has a definite shape and volume.

solubility (8.3, 15.2) The concentration of a saturated solution at a given temperature.

solute (11.1) The component of a solution that is dissolved in another component—the solvent.

solution (1.1) A homogeneous mixture.

solvent (11.1) The component of a solution that does the dissolving.

specific heat (14.3) The quantity of heat required to raise the temperature of 1 g of a substance by 1°C; the specific heat capacity, symbolized *c*.

spectator ion (9.2) An ion that is present but does not change during a chemical reaction.

spin quantum number (4.3) The quantum number (m_s) that determines electron pairings.

stability (8.3) Resistance to reaction; relative lack of reactivity.

standard (2.3) A basis for comparison, such as the mass of ^{12}C .

standard atmosphere (12.1) A pressure of 760 torr.

standard cell potential (17.2) The potential of a cell in its standard state.

standard exponential form (2.2) A format in which a number is expressed as a coefficient with one (nonzero) integer digit times 10 to an integral exponent.

standard half-cell potential (17.2) The potential of a half-cell in its standard state.

standard state (14.4) The normal state for a substance at 1 atm and the temperature involved; for example, the standard state for oxygen at 25°C is gaseous O₂ molecules.

standard state of a system (17.2) A condition of a system in which all solutes are at 1 M and all gases are at 1 atm.

standard temperature and pressure (12.4) 0°C and 1 atm, abbreviated STP; used in gas law problems.

state (8.2, 12.1) A phase in which matter exists: solid, liquid, or gas.

state function (14.4) A variable that depends only on the initial and final states of a system and not on the path between them.

state of subdivision (18.1) The particle size of a sample of a solid.

Stock system (6.2, 16.2) The nomenclature system for inorganic compounds in which the oxidation state (or charge for a monatomic cation) is represented as a Roman numeral in the name of the compound.

stoichiometry (10.1) The determination of how much a reactant can produce or how much of a product can be produced from a given quantity of another substance in a reaction.

stress (18.3) Any change in conditions affecting a system at equilibrium.

strong acid (8.4) An acid that reacts completely with water to form ions in solution.

strong base (8.4) A base that is fully ionized in water solution.

strong electrolyte (9.1) A compound that is fully ionized in aqueous solution.

structural formula (5.5) A formula in which lines represent electron pairs shared by covalently bonded atoms.

structural isomers (20.2) Compounds with the same molecular formula but differing in structural arrangement of their atoms; that is, having some atoms bonded to different atoms from one molecule to the other(s), as CH₃CH₂OH and CH₃OCH₃.

subatomic particle (3.3) A proton, neutron, electron, deuteron, positron, alpha particle, etc.

sublimation (13.6) A phase change in which a solid goes directly into the gas phase.

subscript (5.1) A number following the symbol of an element (or a closing parenthesis) that denotes the number of atoms of the element (or the number of groups) in the formula unit.

subshell (4.5) The portion of a shell characterized by the same principal quantum number and the same angular momentum quantum number.

substance See *pure substance*.

sugar (20.5) A carbohydrate consisting of a monosaccharide or a combination of them, for example, sucrose.

superoxide ion (16.1) The O₂⁻ ion.

supersaturated solution (15.2) A solution holding more solute than it can hold stably at a given temperature.

surroundings (12.2) Anything outside of the system under investigation.

symbol (1.4) A one- or two-letter representation of an element.

synthetic fiber (20.4) A polymer, such as nylon, that has the form of a fiber.

Système International d'Unités See *SI*.

temperature (2.6) The intensity of heat in a body.

ternary compound (8.3) A compound consisting of three elements.

tetrahedral molecule (13.4) A molecule with bonded atoms oriented toward the corners of a tetrahedron (a solid object with four sides, all of which are identical equilateral triangles).

theoretical yield (10.5) The calculated quantity of product that would result from a chemical reaction based on the laws of stoichiometry.

theory (1.6) A generally accepted explanation for a law (or series of observations).

third ionization energy (13.2) The energy required to remove an electron from a gaseous, dipositive ion to form a gaseous, tripositive ion.

titration (11.3) An experimental technique used to determine the concentration of a solution of unknown concentration or the number of moles in an unknown sample of a substance.

torr (12.1) A unit of pressure equal to 1 mm Hg or $\frac{1}{760}$ atm.

total bond order (20.3) The number of electron pairs shared by an atom in a molecule or ion.

total equation (9.2) The equation representing the complete compounds undergoing reaction, as opposed to an ionic or a net ionic equation.

tracer (21.1) A radioactive isotope of an element used to determine what happens to the element, often in some biochemical system.

transition element (1.5) Any element in the groups that start in the fourth period of the periodic table, having atomic numbers 21–30, 39–48, 57, 72–80, or 104–112.

transmutation (21.3) The conversion of one element into another by a nuclear reaction.

trigonal planar molecule (13.4) A molecule with atoms oriented toward the corners of an equilateral triangle, with the central atom in the same plane.

trigonal pyramidal molecule (13.4) A molecule with atoms oriented toward the corners of an equilateral triangle, with the central atom out of that plane.

triple bond (5.5) A covalent bond consisting of three pairs of electrons shared between two atoms.

tritium (21.4) The isotope ${}^3\text{H}$.

uncertainty principle See *Heisenberg uncertainty principle*.
unit (2.1) A standard division of measure having a certain value; for example, the meter is the primary metric unit of length.

unsaturated fat (20.5) A fat that contains one or more carbon-carbon multiple bonds per molecule.

unsaturated hydrocarbon (20.1) A compound containing only carbon and hydrogen and having one or more multiple bonds per molecule.

unsaturated solution (15.2) A solution that contains less solute than it could hold stably at a given temperature.

unshared pair (5.5) A pair of electrons in a molecule or ion that is not shared between atoms.

urea (Chapter 20, Introduction) NH_2CONH_2 (an organic compound despite its lack of carbon-carbon or carbon-hydrogen bonds).

valence electron (5.2) An electron in or from the outermost electron-containing shell of an uncombined atom.

valence shell (5.2) The outermost shell containing electrons in an uncombined atom, or that same shell even when the atom is combined in a compound.

van der Waals force (13.6) An intermolecular force resulting from instantaneous dissymmetry of charge in otherwise nonpolar molecules.

vapor (14.2) A gas in contact with its liquid (or solid) phase.

vapor pressure (12.6, 14.2) The pressure of the vapor in equilibrium with its liquid (or solid).

vapor-pressure lowering (15.6) A decrease in the vapor pressure of a solvent due to the presence of a solute.

vaporization (14.2) A phase change from liquid to gas (vapor).

volatile (15.6) Easily vaporized.

voltage (17.2) Electric potential.

voltaic cell (17.1) An apparatus that provides a combination of half reactions that can produce an electric current.

volume (2.3) The extent of space occupied by a sample of matter.

volume ratio (12.9) The ratio of volumes of gases involved in a chemical reaction.

water ionization constant (19.3) The equilibrium constant for the autoionization of water; symbolized K_w ; at 25°C, $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$.

wavelength (4.1) The length of a single wave.

weak acid (8.4) An acid that reacts only partially with water to form ions.

weak base (8.4) A base that reacts only partially with water to form ions.

weak electrolyte (9.1) A compound that is only slightly ionized in aqueous solution.

weighted average (3.4) The average value of several types of items, taking into account the number of individual items of each type.

work (14.4) All forms of energy except heat.

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Periodic Table of the Elements

Table of the Elements

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)	Erbium	Er	68	167.26
Aluminum	Al	13	26.9815	Europium	Eu	63	151.96
Americium	Am	95	(243)	Fermium	Fm	100	(253)
Antimony	Sb	51	121.75	Fluorine	F	9	18.9984
Argon	Ar	18	39.948	Francium	Fr	87	(223)
Arsenic	As	33	74.9216	Iron	Fe	26	55.847
Astatine	At	85	(210)	Gadolinium	Gd	64	157.25
Silver	Ag	47	107.868	Gallium	Ga	31	69.72
Gold	Au	79	196.9665	Germanium	Ge	32	72.59
Barium	Ba	56	137.34	Gold	Au	79	196.9665
Berkelium	Bk	97	(249)	Hafnium	Hf	72	178.49
Beryllium	Be	4	9.01218	Hassium	Hs	108	(265)
Bismuth	Bi	83	208.9806	Helium	He	2	4.00260
Bohrium	Bh	107	(262)	Holmium	Ho	67	164.9303
Boron	B	5	10.81	Hydrogen	H	1	1.0080
Bromine	Br	35	79.904	Mercury	Hg	80	200.59
Cadmium	Cd	48	112.40	Indium	In	49	114.82
Calcium	Ca	20	40.08	Iodine	I	53	126.9045
Californium	Cf	98	(251)	Iridium	Ir	77	192.22
Carbon	C	6	12.011	Iron	Fe	26	55.847
Cerium	Ce	58	140.12	Krypton	Kr	36	83.80
Cesium	Cs	55	132.9055	Potassium	K	19	39.102
Chlorine	Cl	17	35.453	Lanthanum	La	57	138.9055
Chromium	Cr	24	51.996	Lawrencium	Lr	103	(257)
Cobalt	Co	27	58.9332	Lead	Pb	82	207.2
Copper	Cu	29	63.546	Lithium	Li	3	6.941
Curium	Cm	96	(247)	Lutetium	Lu	71	174.97
Dubnium	Db	105	(260)	Magnesium	Mg	12	24.305
Dysprosium	Dy	66	162.50	Manganese	Mn	25	54.9380
Einsteinium	Es	99	(254)	Meitnerium	Mt	109	(266)

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Mendelevium	101	(256)	Samarium	Sm	62	150.4	
Mercury	Hg	80	200.59	Scandium	Sc	21	44.9559
Molybdenum	Mo	42	95.94	Seaborgium	Sg	106	(263)
Neodymium	Nd	60	144.24	Selenium	Se	34	78.96
Neon	Ne	10	20.179	Silicon	Si	14	28.086
Neptunium	Np	93	237.0482	Silver	Ag	47	107.868
Nickel	Ni	28	58.71	Sodium	Na	11	22.9898
Niobium	Nb	41	92.9064	Strontium	Sr	38	87.62
Nitrogen	N	7	14.0067	Sulfur	S	16	32.06
Nobelium	No	102	(254)	Antimony	Sb	51	121.75
Sodium	Na	11	22.9898	Tin	Sn	50	118.69
Osmium	Os	76	190.2	Tantalum	Ta	73	180.9479
Oxygen	O	8	15.9994	Technetium	Tc	43	98.9062
Palladium	Pd	46	106.4	Tellurium	Te	52	127.60
Phosphorus	P	15	30.9738	Terbium	Tb	65	158.9254
Platinum	Pt	78	195.09	Thallium	Tl	81	204.37
Plutonium	Pu	94	(242)	Thorium	Th	90	232.0381
Polonium	Po	84	(210)	Thulium	Tm	69	168.9342
Potassium	K	19	39.102	Tin	Sn	50	118.69
Praseodymium	Pr	59	140.9077	Titanium	Ti	22	47.90
Promethium	Pm	61	(145)	Tungsten	W	74	183.85
Protactinium	Pa	91	231.0359	Uranium	U	92	238.029
Lead	Pb	82	207.2	Vanadium	V	23	50.9414
Radium	Ra	88	226.0254	Tungsten	W	74	183.85
Radon	Rn	86	(222)	Xenon	Xe	54	131.30
Rhenium	Re	75	186.2	Ytterbium	Yb	70	173.04
Rhodium	Rh	45	102.9055	Yttrium	Y	39	88.9059
Rubidium	Rb	37	85.4678	Zinc	Zn	30	65.37
Ruthenium	Ru	44	101.07	Zirconium	Zr	40	91.22
Rutherfordium	Rf	104	(257)				

