

Silberberg | Amateis

CHEMISTRY

The Molecular Nature of Matter and Change

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CHEMISTRY: THE MOLECULAR NATURE OF MATTER AND CHANGE, NINTH EDITION

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This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 LWI 24 23 22 21 20

ISBN 978-1-260-24021-4 (bound edition)

MHID 1-260-24021-5 (bound edition)

ISBN 978-1-260-47740-5 (loose-leaf edition)

MHID 1-260-47740-1 (loose-leaf edition)

Executive Portfolio Manager: *Michelle Hentz*

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Design: *Jessica Cuevas*

Content Licensing Specialist: *Lorraine Buczek*

Cover Image: *OliveTree/Shutterstock*

Compositor: *Aptara[®], Inc.*

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Library of Congress Cataloging-in-Publication Data

Names: Silberberg, Martin S. (Martin Stuart), 1945- author. | Amateis, Patricia, author.

Title: Chemistry : the molecular nature of matter and change / [Martin S.] Silberberg, [Patricia G.] Amateis.

Description: [Ninth edition]. | Dubuque : McGraw-Hill Education, [2021] | Includes index.

Identifiers: LCCN 2019033353 (print) | LCCN 2019033354 (ebook) | ISBN 9781260240214 (hardcover) | ISBN 9781260477405 (spiral bound) | ISBN 9781260477375 (ebook)

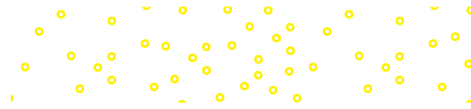
Subjects: LCSH: Chemistry—Textbooks.

Classification: LCC QD33.2 .S55 2021 (print) | LCC QD33.2 (ebook) | DDC 540—dc23

LC record available at <https://lcn.loc.gov/2019033353>

LC ebook record available at <https://lcn.loc.gov/2019033354>

The Internet addresses listed in the text were accurate at the time of publication. The inclusion of a website does not indicate an endorsement by the authors or McGraw-Hill Education, and McGraw-Hill Education does not guarantee the accuracy of the information presented at these sites.

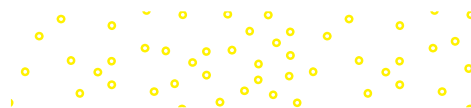


To Ruth and Daniel, with all my love and gratitude.

MSS

To Ralph, Eric, Samantha, and Lindsay:
you bring me much joy.

PGA



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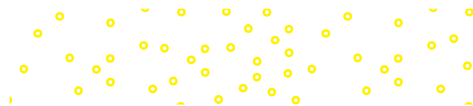
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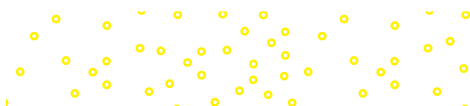
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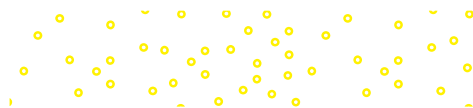
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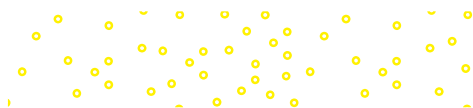
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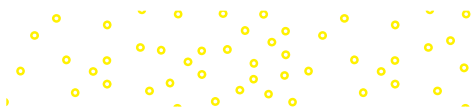
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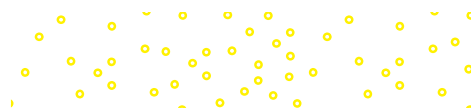
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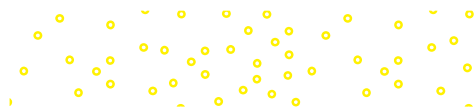
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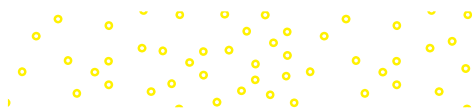
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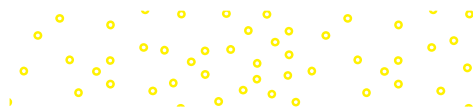
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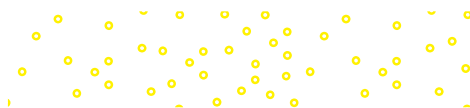
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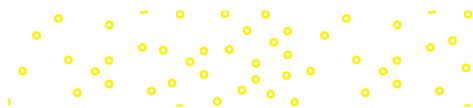
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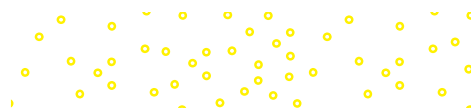
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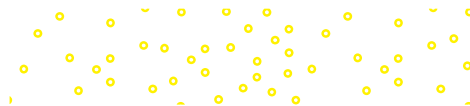
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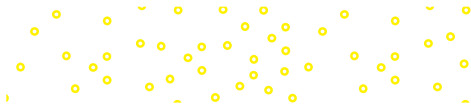
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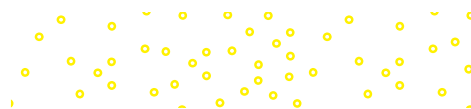
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- 23.3 Finding the Coordination Number and Charge of the Central Metal Ion in a Coordination Compound 1061
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ABOUT THE AUTHORS



Courtesy of Ruth Melnick

Martin S. Silberberg received a B.S. in Chemistry from the City University of New York and a Ph.D. in Chemistry from the University of Oklahoma. He then accepted a position as research associate in analytical biochemistry at the Albert Einstein College of Medicine in New York City, where he developed methods to study neurotransmitter metabolism in Parkinson's disease and other neurological disorders. Following six years in neurochemical research, Dr. Silberberg joined the faculty of Bard College at Simon's Rock, a liberal arts college known for its excellence in teaching small classes of highly motivated students. As head of the Natural Sciences Major and Director of Premedical Studies, he taught courses in general chemistry, organic chemistry, biochemistry, and liberal-arts chemistry. The small class size and close student contact afforded him insights into how students learn chemistry, where they have difficulties, and what strategies can help them succeed. Dr. Silberberg decided to apply these insights in a broader context and established a textbook writing, editing, and consulting company. Before writing his own texts, he worked as a consulting and development editor on chemistry, biochemistry, and physics texts for several major college publishers. He resides with his wife, Ruth, in the Pioneer Valley near Amherst, Massachusetts, where he enjoys the rich cultural and academic life of the area and relaxes by traveling, gardening, and singing.



Courtesy of Ralph L. Amateis

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PREFACE

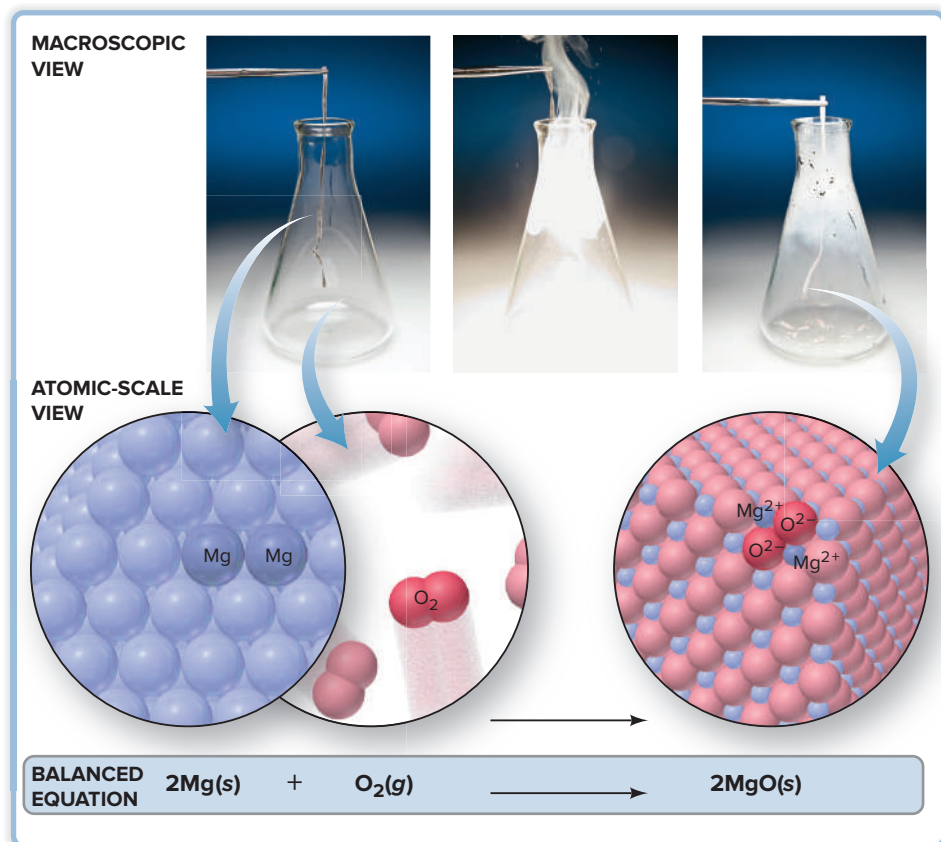
Chemistry is so crucial to an understanding of medicine and biology, environmental science, and many areas of engineering and industrial processing that it has become a requirement for an increasing number of academic majors. Furthermore, chemical principles lie at the core of some of the key societal issues we face in the 21st century—dealing with climate change, finding new energy options, and supplying nutrition and curing disease on an ever more populated planet.

SETTING THE STANDARD FOR A CHEMISTRY TEXT

The ninth edition of *Chemistry: The Molecular Nature of Matter and Change* maintains its standard-setting position among general chemistry textbooks by evolving further to meet the needs of professor and student. The text still contains the most accurate molecular illustrations, consistent step-by-step worked problems, and an extensive collection of end-of-chapter problems. And changes throughout this edition make the text more readable and succinct, the artwork more teachable and modern, and the design more focused and inviting. The three hallmarks that have made this text a market leader are now demonstrated in its pages more clearly than ever.

Visualizing Chemical Models—Macroscopic to Molecular

Chemistry deals with observable changes caused by unobservable atomic-scale events, requiring an appreciation of a size gap of mind-boggling proportions. One of the text's goals coincides with that of so many instructors: to help students visualize chemical events on the molecular scale. Thus, concepts are explained first at the macroscopic level and then from a molecular point of view, with pedagogic illustrations always placed next to the discussions to bring the point home for today's visually oriented students.

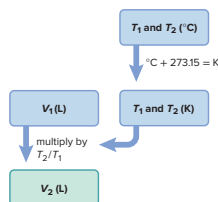


Charles D. Winters/McGraw-Hill Education

Thinking Logically to Solve Problems

The problem-solving approach, based on the four-step method widely accepted by experts in chemical education, is introduced in Chapter 1 and employed *consistently* throughout the text. It encourages students to *plan* a logical approach to a problem, and only then proceed to *solve* it. Each sample problem includes a *check*, which fosters the habit of “thinking through” both the chemical and the quantitative reasonableness of the answer. Finally, for *practice* and reinforcement, each sample problem is followed immediately by *two* similar follow-up problems. And *Chemistry* marries problem solving to visualizing models with molecular-scene problems, which appear not only in homework sets, as in other texts, but also in the running text, where they are worked out stepwise.

Road Map



SAMPLE PROBLEM 5.3 Applying the Volume-Temperature and Pressure-Temperature Relationships

Problem A balloon is filled with 1.95 L of air at 25°C and then placed in a car sitting in the sun. What is the volume of the balloon when the temperature in the car reaches 90°C?

Plan We know the initial volume (V_1) and the initial (T_1) and final (T_2) temperatures of the gas; we must find the final volume (V_2). The pressure of the gas is fixed, since the balloon is subjected to atmospheric pressure, and n is fixed, since air cannot escape or enter the balloon. We convert both T values to kelvins, rearrange the ideal gas law, and solve for V_2 (see the road map).

Solution Summarizing the gas variables:

$$\begin{array}{ll} V_1 = 1.95 \text{ L} & V_2 = \text{unknown} \\ T_1 = 25^\circ\text{C (convert to K)} & T_2 = 90^\circ\text{C (convert to K)} \\ P \text{ and } n \text{ remain constant} & \end{array}$$

Converting T from °C to K:

$$T_1 (\text{K}) = 25^\circ\text{C} + 273.15 = 298 \text{ K} \quad T_2 (\text{K}) = 90^\circ\text{C} + 273.15 = 363 \text{ K}$$

Rearranging the ideal gas law and solving for V_2 : at fixed n and P , we have

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = V_1 \times \frac{T_2}{T_1} = 1.95 \text{ L} \times \frac{363 \text{ K}}{298 \text{ K}} = 2.38 \text{ L}$$

Check Let's predict the change to check the math: because $T_2 > T_1$, we expect $V_2 > V_1$. Thus, the temperature ratio should be greater than 1 (T_2 in the numerator). The T ratio is about 1.2 ($363/298$), so the V ratio should also be about 1.2 ($2.4/2.0 \approx 1.2$).

FOLLOW-UP PROBLEMS

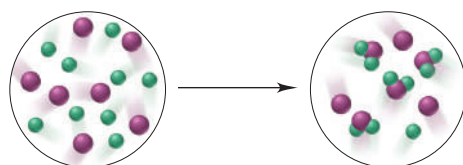
5.3A A steel tank used for fuel delivery is fitted with a safety valve that opens if the internal pressure exceeds 1.00×10^3 torr. The tank is filled with methane at 23°C and 0.991 atm and placed in boiling water at 100°C. What is the pressure in the heated tank? Will the safety valve open?

5.3B A sample of nitrogen occupies a volume of 32.5 L at 40°C. Assuming that the pressure remains constant, what temperature (in °C) will result in a decrease in the sample's volume to 28.6 L?

SOME SIMILAR PROBLEMS 5.26–5.29

SAMPLE PROBLEM 2.3 Visualizing the Mass Laws

Problem The scenes below represent an atomic-scale view of a chemical reaction:



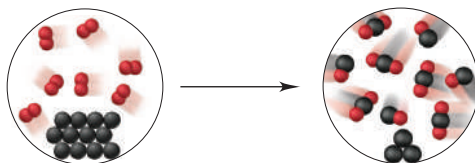
Which of the mass laws—mass conservation, definite composition, and/or multiple proportions—is (are) illustrated?

Plan From the depictions, we note the numbers, colors, and combinations of atoms (spheres) to see which mass laws pertain. If the numbers of each atom are the same before and after the reaction, the total mass did not change (mass conservation). If a compound forms that always has the same atom ratio, the elements are present in fixed parts by mass (definite composition). If the same elements form different compounds and the ratio of the atoms of one element that combine with one atom of the other element is a small whole number, the ratio of their masses is a small whole number as well (multiple proportions).

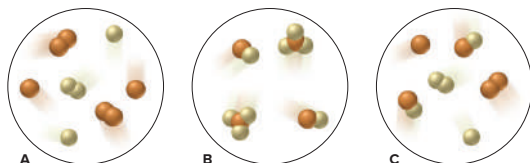
Solution There are seven purple and nine green atoms in each circle, so mass is conserved. The compound formed has one purple and two green atoms, so it has definite composition. Only one compound forms, so the law of multiple proportions does not pertain.

FOLLOW-UP PROBLEMS

2.3A The following scenes represent a chemical change. Which of the mass laws (are) illustrated?



2.3B Which sample(s) best display(s) the fact that compounds of bromine (orange) and fluorine (yellow) exhibit the law of multiple proportions? Explain.



SOME SIMILAR PROBLEMS 2.14 and 2.15

SAMPLE PROBLEM 5.4 Applying the Volume-Amount and Pressure-Amount Relationships

Problem A scale model of a blimp rises when it is filled with helium to a volume of 55.0 dm³. When 1.10 mol of He is added to the blimp, the volume is 26.2 dm³. How many more grams of He must be added to make it rise? Assume constant T and P .

Plan We are given the initial amount of helium (n_1), the initial volume of the blimp (V_1), and the volume needed for it to rise (V_2), and we need the additional mass of helium to make it rise. So, we first need to find n_2 . We rearrange the ideal gas law to the appropriate form, solve for n_2 , subtract n_1 to find the additional amount (n_{add}), and then convert moles to grams (see the road map).

Applying Ideas to the Real World

As the most practical science, chemistry should have a textbook that highlights its countless applications. Moreover, today's students may enter emerging chemistry-related hybrid fields, like biomaterials science or planetary geochemistry, and the text they use should point out the relevance of chemical concepts to such related sciences. The *Chemical Connections* and *Tools of the Laboratory* boxed essays (which include problems for added relevance), the more pedagogic margin notes, and the many applications woven into the chapter content are up-to-date, student-friendly features that are directly related to the neighboring content.

CHEMICAL CONNECTIONS TO ENVIRONMENTAL ENGINEERING

Solutions and Colloids in Water Purification

Water Treatment Plants

Most water destined for human use comes from lakes, rivers, reservoirs, or groundwater. Present in this essential resource may be soluble toxic organic compounds and high concentrations of NO_3^- and Fe^{2+} , colloidal clay and microbes, and suspended debris. Let's see how water is treated to remove these dissolved, dispersed, and suspended particles.

Step 1. Screening and settling. As water enters the facility, screens remove debris, and settling removes sand and other particles.

Step 2. Coagulating. This step and the next two remove colloids. These particles have negative surfaces that repel each other. Added aluminum sulfate [cake alum, $\text{Al}_2(\text{SO}_4)_3$] or iron(III) chloride (FeCl_3), which supply Al^{3+} or Fe^{3+} ions that neutralize the charges, coagulates the particles through intermolecular forces.

Step 3. Flocculating and sedimenting. Mixing water and flocculating agents in large basins causes a fluffy floc to form. Added cationic polymers form long-chain bridges between floc particles, which grow bigger and flow into other basins, where they form a sediment and are removed. Some plants use dissolved air flotation (DAF) instead: bubbles forced through the water attach to the floc, and the floating mass is skimmed.

Step 4. Filtering. Various filters remove remaining particles. In *slow sand filters*, the water passes through sand and/or gravel of increasing particle size. In *rapid sand filters*, the sand is backwashed with water, and the colloidal mass is removed. Membrane filters (not shown) with pore sizes of 0.1–10 μm are thin tubes bundled together inside a vessel. The water is forced into these

Step 5. Disinfecting. Water sources often contain harmful microorganisms that are killed by one of three agents:

- Chlorine, as aqueous bleach (ClO^-) or Cl_2 , is most common, but carcinogenic chlorinated organic compounds can form.
- UV light emitted by high-intensity fluorescent tubes disinfects by disrupting microorganisms' DNA.
- Ozone (O_3) gas is a powerful oxidizing agent.

Sodium fluoride (NaF) to prevent tooth decay and phosphate salts to prevent leaching of lead from pipes may then be added.

Step 6 (not shown). Adsorbing onto granular activated carbon (GAC). Petroleum and other organic contaminants are removed by adsorption. GAC is a highly porous agent formed by "activating" wood, coal, or coconut shells with steam: 1 kg of GAC has a surface area of 275 acres!

Water Softening via Ion Exchange

Water with large amounts of $2+$ ions, such as Ca^{2+} and Mg^{2+} , is called **hard water**. Combined with fatty-acid anions in soap, these cations form solid deposits on clothes, washing machines, and sinks:

$$\text{Ca}^{2+}(\text{aq}) + 2\text{C}_{17}\text{H}_{33}\text{COONa}(\text{aq}) \rightarrow (\text{C}_{17}\text{H}_{33}\text{COO})_2\text{Ca}(\text{s}) + 2\text{Na}^+(\text{aq})$$

When a large amount of HCO_3^- is present, the cations form *scale*, a carbonate deposit in boilers and hot-water pipes that interferes with the transfer of heat:

$$\text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$

Wastewater Treatment

Wastewater, used domestic or industrial water, is treated in several ways before being returned to a natural source:

- In *primary treatment*, the water enters a settling basin to remove particles.
- In *biological treatment*, bacteria metabolize organic compounds and are then removed by settling.
- In *advanced treatment*, a process is tailored to remove a specific pollutant. For example, ammonia, which causes excessive growth of plants and algae, is removed in two steps:
 - Nitrification.** Certain bacteria oxidize ammonia (electron donor) with O_2 (electron acceptor) to form nitrate ion:

$$\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$$
 - Denitrification.** Other bacteria oxidize an added compound, like methanol (CH_3OH), using the NO_3^- :

$$5\text{CH}_3\text{OH} + 6\text{NO}_3^- \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^-$$

Thus, the process converts NH_3 in wastewater to N_2 , which is released to the atmosphere.

Membrane Processes and Reverse Osmosis

Membranes with 0.0001–0.01 μm pores can remove unwanted ions from water. Recall that solutions of different concentrations separated by a semipermeable membrane create osmotic pressure. In **reverse osmosis**, a pressure greater than the osmotic pressure is applied to the more concentrated solution to force water back through the membrane and filter out ions. In homes, toxic *heavy-metal ions*, such as Pb^{2+} , Cd^{2+} , and Hg_2^{2+} , are removed this way. On a large scale, reverse osmosis is used for **desalination**, which can convert seawater (40,000 ppm of ions) to drinking water (400 ppm) (Figure B13.3). There are over 18,000 desalination plants worldwide, providing water for 300 million people.

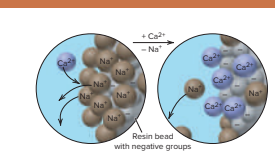


Figure B13.2 Ion exchange to remove hard-water cations.

anionic groups, such as $-\text{SO}_3^-$ or $-\text{COO}^-$, and Na^+ ions for charge balance (Figure B13.2). The hard-water cations displace the Na^+ ions and bind to the anionic groups. When all resin sites are occupied, the resin is regenerated with concentrated Na^+ solution that exchanges Na^+ ions for bound Ca^{2+} and Mg^{2+} .

Problems

B13.1 Briefly answer each of the following:

- Why is cake alum [$\text{Al}_2(\text{SO}_4)_3$] added during water purification?
- Why is water that contains large amounts of Ca^{2+} and Mg^{2+} difficult to use for cleaning?
- What is the meaning of *reverse* in reverse osmosis?
- Why might a water treatment plant use ozone as a disinfectant instead of chlorine?
- How does passing a saturated NaCl solution through a "spent" ion-exchange resin regenerate the resin?

B13.2 Wastewater discharged into a stream by a sugar refinery contains 335 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per liter. A government-sponsored study is testing the feasibility of removing the sugar by reverse osmosis. What pressure must be applied to the wastewater solution at 20.°C to produce pure water?

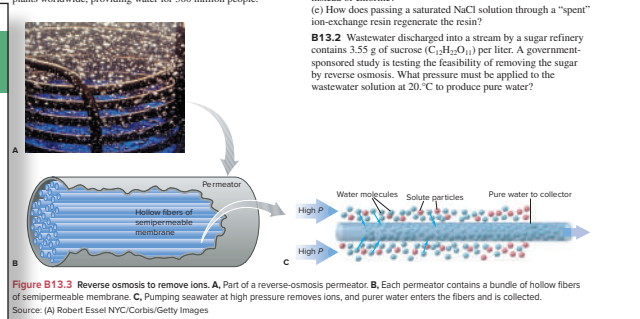


Figure B13.3 Reverse osmosis to remove ions. A, Part of a reverse-osmosis permeator. B, Each permeator contains a bundle of hollow fibers of semipermeable membrane. C, Pumping seawater at high pressure removes ions, and purer water enters the fibers and is collected.

TOOLS OF THE LABORATORY

Nuclear Magnetic Resonance (NMR) Spectroscopy

In addition to mass spectrometry (Chapter 2) and infrared (IR) spectroscopy (Chapter 9), one of the most useful tools for analyzing organic and biochemical structures is **nuclear magnetic resonance (NMR) spectroscopy**, which measures the molecular environments of certain nuclei in a molecule.

Like electrons, several types of nuclei, such as ^{13}C , ^{19}F , ^{31}P , and ^1H , act as if they spin in either of two directions, each of which creates a tiny magnetic field. In this discussion, we focus primarily on ^1H -NMR spectroscopy, which measures changes in the nuclei of the most common isotope of hydrogen. Oriented randomly, the magnetic fields of all the ^1H nuclei in a sample of compound, when placed in a strong external magnetic field (B_0), become aligned either with the external field (parallel) or against it (antiparallel). Most nuclei adopt the parallel orientation, which is slightly lower in energy. The energy difference (ΔE) between the two energy states (spin states) lies in the radio-frequency (rf) region of the electromagnetic spectrum (Figure B15.1).

When an ^1H (blue arrow) in the lower energy (parallel) spin state absorbs a photon in the radio-frequency region with an energy equal to ΔE , it "flips," in a process called *resonance*, to the higher energy (antiparallel) spin state. The system then re-emits that energy, which is detected by the rf receiver of the ^1H -NMR spectrometer. The ΔE between the two states depends on the actual magnetic field acting on each ^1H nucleus, which is affected by the tiny magnetic fields of the *electrons* of atoms adjacent to that nucleus. Thus, the ΔE required for resonance of each ^1H nucleus depends on its specific molecular environment—the C atoms, electronegative atoms, multiple bonds, and aromatic rings around it. ^1H nuclei in different molecular environments produce different peaks in the ^1H -NMR spectrum.

An ^1H -NMR spectrum, which is unique for each compound, is a series of peaks that represents the resonance of a function of the changing magnetic field. The *chemical shift* of the ^1H nuclei in a given environment is where a peak appears. Chemical shifts are shown relative to that of an added standard, tetramethylsilane [(CH_3) $_4\text{Si}$, or TMS]. TMS has 12 ^1H nuclei bonded to four C atoms that are bonded to one Si atom in a tetrahedral arrangement, so all 12 are in identical environments and produce only one peak.

Figure B15.2 shows the ^1H -NMR spectrum of acetone. The six ^1H nuclei of acetone have identical environments: all six are bonded to two C atoms that are each bonded to the C atom involved in the C=O bond. So one peak is produced, but at a different position from the TMS peak. The spectrum of dimethylmethane in Figure B15.3 shows two peaks in addition to the TMS peak, since the ^1H nuclei have two different environments. The taller peak is due to the six ^1H nuclei in the two CH_3 groups, and the shorter peak is due to the two ^1H nuclei in the CH_2 group. The area under each peak (given as a number of chart-paper grid spaces) is proportional to the number of ^1H nuclei in a given environment. Note that the area ratio is 20.3/6.8 \approx 3/1, the same as the ratio of six nuclei in the CH_3 groups to two in the CH_2 group. Thus, by analyzing the chemical shifts and peak areas, the chemist learns the type and number of hydrogen atoms in the compound.

(continued)

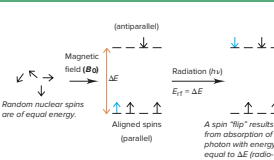


Figure B15.1 The basis of ^1H spin resonance.

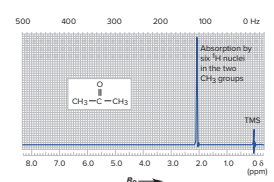


Figure B15.2 The ^1H -NMR spectrum of acetone.

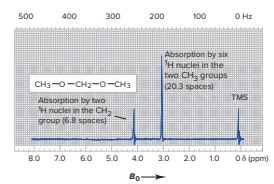


Figure B15.3 The ^1H -NMR spectrum of dimethylmethane.

A Purple Mule, Not a Blue Horse and a Red Donkey

A mule is a genetic mix, a hybrid, of a horse and a donkey; it is not a horse one instant and a donkey the next. Similarly, the color purple is a mix of red and blue. In the same sense, a resonance hybrid is one molecular species, not one resonance form this instant and another resonance form the next. The problem is that we cannot depict the actual species, the hybrid, accurately with a single Lewis structure.

Blue horse Red donkey

|||

Purple mule

Reinforcing through Review and Practice

A favorite feature, the section summaries that conclude every section restate the major ideas concisely and immediately (rather than postponing such review until the end of the chapter).

A rich catalog of study aids ends each chapter to help students review the content:

- **Learning Objectives**, with section and/or sample problem numbers, focus on the concepts to understand and the skills to master.
- **Key Terms**, boldfaced and defined within the chapter, are listed here by section (with page numbers), as well as being defined in the *Glossary*.
- **Key Equations and Relationships** are highlighted and numbered within the chapter and listed here with page numbers.
- **Brief Solutions to Follow-up Problems** triple the number of worked problems by providing multistep calculations at the end of the chapter, rather than just numerical answers at the back of the book.

Summary of Section 9.1

- Nearly all naturally occurring substances consist of atoms or ions bonded to others. Chemical bonding allows atoms to lower their energy.
- Ionic bonding occurs when metal atoms transfer electrons to nonmetal atoms, and the resulting ions attract each other and form an ionic solid.
- Covalent bonding is most common between nonmetal atoms and usually results in individual molecules. Bonded atoms share one or more pairs of electrons that are localized between them.
- Metallic bonding occurs when many metal atoms pool their valence electrons into a delocalized electron "sea" that holds all the atoms in the sample together.
- The Lewis electron-dot symbol of a main-group atom shows valence electrons as dots surrounding the element symbol.
- The octet rule says that, when bonding, many atoms lose, gain, or share electrons to attain a filled outer level of eight (or two) electrons.

CHAPTER REVIEW GUIDE			
Learning Objectives Relevant section (S) and/or sample problem (SP) numbers appear in parentheses.			
Understand These Concepts			
1. The quantitative meaning of solubility (§13.1)	16. The four colligative properties and their dependence on number of dissolved particles (§13.6)	17. Ideal solutions and the importance of Raoult's law (§13.6)	18. How the phase diagram of a solution differs from that of the pure solvent (§13.6)
2. The major types of intermolecular forces in solution and their relative strengths (§13.1)	19. Why the vapor over a solution of a volatile nonelectrolyte is richer in the more volatile component (§13.6)	20. Why strong electrolyte solutions are not ideal and the meanings of the van't Hoff factor and ionic atmosphere (§13.6)	21. How particle size distinguishes suspensions, colloids, and solutions (§13.7)
3. How the like-dissolves-like rule depends on intermolecular forces (§13.1)	22. How colloidal behavior is demonstrated by the Tyndall effect and Brownian motion (§13.7)	Master These Skills	
4. Why gases have relatively low solubilities in water (§13.1)	1. Predicting relative solubilities from intermolecular forces (SP 13.1)	2. Calculating the heat of solution for an ionic compound (SP 13.2)	3. Using Henry's law to calculate the solubility of a gas (SP 13.3)
5. General characteristics of solutions formed by various combinations of gases, liquids, and solids (§13.1)	4. Expressing concentration in terms of molality, parts by mass, parts by volume, and mole fraction (SPs 13.4, 13.5)	5. Interconverting among the various terms for expressing concentration (SP 13.6)	6. Using Raoult's law to calculate the vapor pressure lowering of a solution (SP 13.7)
6. How intermolecular forces stabilize the structures of proteins, the cell membrane, and DNA (§13.2)	7. Determining boiling and freezing points of a solution (SP 13.8)	8. Using a colligative property to calculate the molar mass of a solute (SP 13.9)	9. Calculating the composition of vapor over a solution of volatile nonelectrolyte (§13.6)
7. The enthalpy components of a solution cycle and their effect on ΔH_{sol} (§13.3)	10. Calculating the van't Hoff factor (<i>i</i>) from the magnitude of a colligative property (§13.6)	11. Using a depiction to determine colligative properties (SP 13.10)	
8. The dependence of ΔH_{sol} on ionic charge density and the factors that determine whether ionic solution processes are exothermic or endothermic (§13.3)			
9. The meaning of entropy and how the balance between the change in enthalpy and the change in entropy governs the solution process (§13.3)			
10. The distinctions among saturated, unsaturated, and supersaturated solutions, and the equilibrium nature of a saturated solution (§13.4)			
11. The relation between temperature and the solubility of solids (§13.4)			
12. Why the solubility of gases in water decreases with a rise in temperature (§13.4)			
13. The effect of gas pressure on solubility and its quantitative expression as Henry's law (§13.4)			
14. The meaning of molarity, molality, mole fraction, and parts by mass or by volume of a solution, and how to convert among them (§13.5)			
15. The distinction between electrolytes and nonelectrolytes in solution (§13.6)			
Key Terms Page numbers appear in parentheses.			
alloy (540)	dipole-induced dipole force (537)	heat (enthalpy) of hydration (ΔH_{hyd}) (547)	immiscible (536)
amino acid (541)	double helix (545)	heat (enthalpy) of solution (ΔH_{sol}) (546)	ion exchange (573)
boiling point elevation (ΔT_b) (562)	entropy (<i>S</i>) (550)	Henry's law (554)	ion-induced dipole force (536)
charge density (547)	fractional distillation (567)	hydration (547)	like-dissolves-like rule (536)
colligative property (560)	freezing point depression (ΔT_f) (563)	hydration shell (536)	lipid bilayer (544)
colloid (571)	hard water (573)	ideal solution (561)	mass percent [% (w/w)] (557)
desalination (574)			miscible (536)
			molality (<i>m</i>) (556)
			mole fraction (<i>X</i>) (557)
			mononucleotide (545)
			nonelectrolyte (560)
			nucleic acid (544)
			osmosis (565)
			osmotic pressure (Π) (565)
			protein (544)
			Raoult's law (561)
			reverse osmosis (574)
			saturated solution (552)
			semipermeable membrane (565)
			soap (543)
			solubility (<i>S</i>) (536)
			solute (535)
			solvation (547)
			solvent (535)
			strong electrolyte (560)
			supersaturated solution (552)
			suspension (571)
			osmosis (565)
			osmotic pressure (Π) (565)
			solubility (<i>S</i>) (536)
			solute (535)
			solvation (547)
			solvent (535)
			strong electrolyte (560)
			supersaturated solution (552)
			suspension (571)
			Tyndall effect (572)
			unsaturated solution (552)
			vapor pressure lowering (ΔP) (561)
			volume percent [% (v/v)] (557)
			wastewater (574)
			water softening (573)
			weak electrolyte (560)
Key Equations and Relationships Page numbers appear in parentheses.			
13.1 Dividing the general heat of solution into component enthalpies (546):			
$\Delta H_{\text{sol}} = \Delta H_{\text{solvent}} + \Delta H_{\text{ionization}} + \Delta H_{\text{hydration}}$			
13.2 Dividing the heat of solution of an ionic compound in water into component enthalpies (548):			
$\Delta H_{\text{sol}} = \Delta H_{\text{ionization}} + \Delta H_{\text{hydration of the ions}}$			
13.3 Relating gas solubility to its partial pressure (Henry's law) (554):			
$S_{\text{gas}} = k_H \times P_{\text{gas}}$			
13.4 Defining concentration in terms of molarity (555):			
$\text{Molarity (} M \text{)} = \frac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$			
13.5 Defining concentration in terms of molality (556):			
$\text{Molality (} m \text{)} = \frac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$			
13.6 Defining concentration in terms of mass percent (557):			
$\text{Mass percent [\% (w/w)]} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$			
13.7 Defining concentration in terms of volume percent (557):			
$\text{Volume percent [\% (v/v)]} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$			
BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS			
13.1A (a) 1-Butanol has one —OH group/molecule, whereas 1,4-butanediol has two —OH groups/molecule. 1,4-Butanediol is more soluble in water because it can form more H bonds.			
(b) Chloroform is more soluble in water because of dipole-dipole forces between the polar CHCl ₃ molecules and water. The forces between nonpolar CCl ₄ molecules and water are weaker dipole-induced dipole forces, which do not effectively replace H bonds between water molecules.			
13.1B (a) Chloroform dissolves more chloromethane due to similar dipole-dipole forces between the polar molecules of these two substances. CH ₂ Cl ₂ molecules do not exhibit H bonding and, so, do not effectively replace H bonds between methanol molecules.			
(b) Hexane dissolves more pentanol due to dispersion forces between the hydrocarbon chains in each molecule.			
13.2B Due to its smaller size, Na ⁺ should have a greater charge density and thus a larger ΔH_{hyd} than CN ⁻ . From Equation 13.2, we have			
$\Delta H_{\text{hyd}} \text{ of NaCN} = \Delta H_{\text{ionization}} \text{ of NaCN} + (\Delta H_{\text{hyd}} \text{ of Na}^+ + \Delta H_{\text{hyd}} \text{ of CN}^-)$			
$1.21 \text{ kJ/mol} = 766 \text{ kJ/mol} + (-410. \text{ kJ/mol} + \Delta H_{\text{hyd}} \text{ of CN}^-)$			
$\Delta H_{\text{hyd}} \text{ of CN}^- = 1.21 \text{ kJ/mol} - 766 \text{ kJ/mol} + 410. \text{ kJ/mol} = -355 \text{ kJ/mol}$			
13.3A The partial pressure of N ₂ in air is the volume percent divided by 100 times the total pressure (Dalton's law, Section 5.4):			
$P_{\text{N}_2} = 0.78 \times 1 \text{ atm} = 0.78 \text{ atm.}$			
$S_{\text{gas}} = k_H \times P_{\text{gas}}$			
$S_{\text{N}_2} = (7 \times 10^{-4} \text{ mol/L} \cdot \text{atm})(0.78 \text{ atm}) = 5 \times 10^{-4} \text{ mol/L.}$			

Finally, an exceptionally large number of qualitative, quantitative, and molecular-scene problems end each chapter. Four types of problems are presented—three by chapter section, with comprehensive problems following:

- **Concept Review Questions** test qualitative understanding of key ideas.
- **Skill-Building Exercises** are grouped in similar pairs, with one of each pair answered in the back of the book. A group of similar exercises may begin with explicit steps and increase in difficulty, gradually weaning the student from the need for multistep directions.
- **Problems in Context** apply the skills learned in the skill-building exercises to interesting scenarios, including realistic examples dealing with industry, medicine, and the environment.
- **Comprehensive Problems**, mostly based on realistic applications, are more challenging and rely on material from any section of the current chapter or any previous chapter.

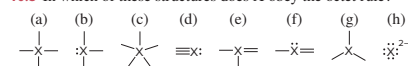
PROBLEMS

Problems with colored numbers are answered in Appendix E and worked in detail in the Student Solutions Manual. Problem sections match those in the text and give the numbers of relevant sample problems. Most offer Concept Review Questions, Skill-Building Exercises (grouped in pairs covering the same concept), and Problems in Context. The Comprehensive Problems are based on material from any section or previous chapter.

Depicting Molecules and Ions with Lewis Structures (Sample Problems 10.1 to 10.5)

Concept Review Questions

- 10.1** Which of these atoms *cannot* serve as a central atom in a Lewis structure: (a) O; (b) He; (c) F; (d) H; (e) P? Explain.
- 10.2** When is a resonance hybrid needed to adequately depict the bonding in a molecule? Using NO_2 as an example, explain how a resonance hybrid is consistent with the actual bond length, bond strength, and bond order.
- 10.3** In which of these structures does X obey the octet rule?



- 10.4** What is required for an atom to expand its valence shell? Which of the following atoms can expand its valence shell: F, S, H, Al, Se, Cl?

Skill-Building Exercises (grouped in similar pairs)

- 10.5** Draw a Lewis structure for (a) SiF_4 ; (b) SeCl_2 ; (c) COF_2 (C is the central atom).
- 10.6** Draw a Lewis structure for (a) PH_4^+ ; (b) C_2F_4 ; (c) SbH_3 .
- 10.7** Draw a Lewis structure for (a) PF_3 ; (b) H_2CO_3 (both H atoms are attached to O atoms); (c) CS_2 .
- 10.8** Draw a Lewis structure for (a) CH_4S ; (b) S_2Cl_2 ; (c) CHCl_3 .
- 10.9** Draw Lewis structures of all the important resonance forms of (a) NO_2^- ; (b) NO_2F (N is central).
- 10.10** Draw Lewis structures of all the important resonance forms of (a) HNO_3 (HONO_2); (b) HASO_4^{2-} (HOAsO_3^{2-}).
- 10.11** Draw Lewis structures of all the important resonance forms of (a) N_3^- ; (b) NO_2^- .
- 10.12** Draw Lewis structures of all the important resonance forms of (a) HCO_3^- (H is attached to C); (b) HBrO_4 (HOBrO_3).
- 10.13** Draw the Lewis structure with lowest formal charges, and determine the charge of each atom in (a) IF_5 ; (b) AlH_4^- .
- 10.14** Draw the Lewis structure with lowest formal charges, and determine the charge of each atom in (a) IF_5 ; (b) NO .

- 10.15** Draw the Lewis structure with lowest formal charges, and determine the charge of each atom in (a) CN^- ; (b) ClO^- .

- 10.16** Draw the Lewis structure with lowest formal charges, and determine the charge of each atom in (a) ClF_2^+ ; (b) ClNO .

- 10.17** Draw a Lewis structure for a resonance form of each ion with the lowest possible formal charges, show the charges, and give oxidation numbers of the atoms: (a) BrO_3^- ; (b) SO_3^{2-} .

- 10.18** Draw a Lewis structure for a resonance form of each ion with the lowest possible formal charges, show the charges, and give oxidation numbers of the atoms: (a) AsO_4^{3-} ; (b) ClO_2^- .

- 10.19** These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception: (a) BH_3 (b) AsF_4^- (c) SeCl_4

- 10.20** These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception: (a) PF_6^- (b) ClO_3 (c) H_3PO_3 (one P—H bond)

- 10.21** These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception: (a) BrF_3 (b) ICl_2^- (c) BeF_2

- 10.22** These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception: (a) O_3^- (b) XeF_2 (c) SbF_4^-

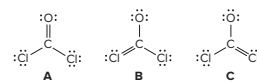
Problems in Context

- 10.23** Molten beryllium chloride reacts with chloride ion from molten NaCl to form the BeCl_4^{2-} ion, in which the Be atom attains an octet. Show the net ionic reaction with Lewis structures.

- 10.24** Despite many attempts, the perbromate ion (BrO_7^-) was not prepared in the laboratory until about 1970. (In fact, articles were published explaining theoretically why it could never be prepared!) Draw a Lewis structure for BrO_7^- in which all atoms have lowest formal charges.

- 10.25** Cryolite (Na_3AlF_6) is an indispensable component in the electrochemical production of aluminum. Draw a Lewis structure for the AlF_6^{3-} ion.

- 10.26** Phosgene is a colorless, highly toxic gas that was employed against troops in World War I and is used today as a key reactant in organic syntheses. From the following resonance structures, select the one with the lowest formal charges:



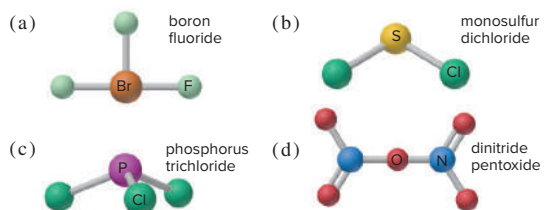
Comprehensive Problems

- 2.121** Helium is the lightest noble gas and the second most abundant element (after hydrogen) in the universe.
- (a) The radius of a helium atom is 3.1×10^{-11} m; the radius of its nucleus is 2.5×10^{-15} m. What fraction of the spherical atomic volume is occupied by the nucleus (V of a sphere = $\frac{4}{3}\pi r^3$)?
- (b) The mass of a helium-4 atom is 6.64648×10^{-24} g, and each of its two electrons has a mass of 9.10939×10^{-28} g. What fraction of this atom's mass is contributed by its nucleus?

- 2.122** From the following ions (with their radii in pm), choose the pair that forms the strongest ionic bond and the pair that forms the weakest:

Ion:	Mg^{2+}	K^+	Rb^+	Ba^{2+}	Cl^-	O^{2-}	I^-
Radius:	72	138	152	135	181	140	220

- 2.123** Give the molecular mass of each compound depicted below, and provide a correct name for any that are named incorrectly.



OPTIMIZING THE TEXT

The modern chemistry student's learning experience is changing dramatically. To address the changes that students face, a modern text partnered with a suite of robust digital tools must continue to evolve. With each edition, students and instructors alike have been involved in refining this text. From one-on-one interviews, focus groups, and symposia, as well as extensive chapter reviews and class tests, we learned that everyone praises the pioneering molecular art; the stepwise problem-solving approach; the abundant mix of qualitative, quantitative, and applied end-of-chapter problems; and the rigorous *and* student-friendly coverage of mainstream topics.

Global Changes to Every Chapter

Our revision for the ninth edition focused on continued optimization of the text. To aid us in this process, we were able to use data from literally thousands of student responses to questions in SmartBook probes, the adaptive learning system that assesses student knowledge of course content. The data, such as average time spent answering each question and the percentage of students who correctly answered the question on the first attempt, revealed the learning objectives that students found particularly difficult. We utilized several approaches to present these difficult concepts in a clear, straightforward way in the ninth edition of *Chemistry: The Molecular Nature of Matter and Change*.

Making the concepts clearer through digital learning resources. Students will be able to access digital learning resources throughout this text's SmartBook. These learning resources present summaries of concepts and worked examples, including videos of chemistry instructors solving problems or modeling concepts that students can view over and over again. Thus, students can have an "office hour" moment at any time.

Student Hot Spots

We are very pleased to incorporate real student data points and input, derived from thousands of our SmartBook users, to help guide our revision. SmartBook Heat Maps provided a quick visual snapshot of usage of portions of the text and the relative difficulty students experienced in mastering the content. With these data, we were able to both hone our text content when needed and, for particularly challenging concepts, point students to the learning resource videos that can elucidate and reinforce those concepts. You'll see these marginal features throughout the text. Students should log into Connect and view the resources through our SmartBook.

Applying ideas with enhanced problems throughout the chapters. The much admired four-part problem-solving format (plan, solution, check, follow-up) is retained in the ninth edition, in both data-based and molecular-scene *Sample Problems*. Two *Follow-up Problems* are included with each sample problem, as well as a list of *Similar Problems* within the end-of-chapter problem set. *Brief Solutions* for all of the follow-up problems appear at the end of each chapter (rather than providing just a numerical answer in a distant end-of-book appendix, as is typical). The ninth edition has over 250 sample problems and over 500 follow-up problems. In many chapters, several sample and follow-up problems (and their brief solutions) were revised in this edition with two goals in mind. We sought to provide students with a variety of problems that would clearly elucidate concepts and demonstrate problem-solving techniques, while giving students the opportunity to be challenged and gain competence. We also included more intermediate steps in the solutions to both sample and follow-up problems so that students could more easily follow the solutions.

Re-learning ideas with annotated illustrations. The innovative three-level figures and other art that raised the bar for molecular visualization in chemistry textbooks is still present. Several existing figures have been revised and several new ones added to create an even better teaching tool. We continue to streamline figure legends by placing their content into clarifying annotations with the figures themselves.

Mass (kg) of uranium = mass (kg) of pitchblende \times $\frac{\text{mass (kg) of uranium in pitchblende}}{\text{mass (kg) of pitchblende}}$

$$= 102 \text{ kg pitchblende} \times \frac{71.4 \text{ kg uranium}}{84.2 \text{ kg pitchblende}} = 86.5 \text{ kg uranium}$$

Converting the mass of uranium from kg to g:

$$\text{Mass (g) of uranium} = 86.5 \text{ kg uranium} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 8.65 \times 10^4 \text{ g uranium}$$

Finding the mass (in kg) of oxygen in 102 kg of pitchblende:

$$\text{Mass (kg) of oxygen} = \text{mass (kg) of pitchblende} - \text{mass (kg) of uranium}$$

$$= 102 \text{ kg} - 86.5 \text{ kg} = 15.5 \text{ kg oxygen}$$

Converting the mass of oxygen from kg to g:

$$\text{Mass (g) of oxygen} = 15.5 \text{ kg oxygen} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 1.55 \times 10^4 \text{ g oxygen}$$

Check The analysis showed that most of the mass of pitchblende is due to uranium, so the large mass of uranium makes sense. Rounding off to check the math gives

$$\sim 100 \text{ kg pitchblende} \times \frac{70}{85} = 82 \text{ kg uranium}$$

FOLLOW-UP PROBLEMS

2.2A The mineral "fool's gold" does not contain any gold; instead, it is a compound composed only of the elements iron and sulfur. A 110.0-g sample of fool's gold contains 51.2 g of iron. What mass of sulfur is in a sample of fool's gold that contains 86.2 g of iron?

2.2B Silver bromide is the light-sensitive compound coated onto black-and-white film. A 26.8-g sample contains 15.4 g of silver, with bromine as the only other element. How many grams of each element are on a roll of film that contains 3.57 g of silver bromide?

SOME SIMILAR PROBLEMS 2.22–2.25

Student Hot Spot

Student data indicate that you may struggle with using mass fraction to calculate the mass of an element in a compound. Access the eBook to view an additional Learning Resource video on this topic.

Mastering the content with abundant end-of-chapter problem sets. New problems were added to several chapter problem sets, providing students and teachers with abundant choices in a wide range of difficulty and real-life scenarios. The problem sets are more extensive than in most other texts.

Content Changes to Individual Chapters

In addition to the general optimization of concept explanations and problem solutions throughout the text, specific improvements were made to most chapters:

- **Chapter 1** has a revised discussion of significant figures to make this important topic clearer, two revised sample problems on significant figures and rounding in calculations, and a new follow-up problem on using density in calculations.
- **Chapter 2** includes an improved discussion on mass spectrometry, isotopic composition, and atomic mass; five new figures to aid in nomenclature of compounds, including a summary nomenclature decision tree; and two new end-of-chapter problems on naming compounds.
- **Chapter 3** now features two new problem-solving Student Hot Spot resources on mass/moles/molecules conversions and on determination of a molecular formula; and revisions to four sample problems on stoichiometry.
- **Chapter 4** has been reorganized for better flow and clarity; there is a new table on the types of electrolytes, a revised sample problem on the stoichiometry of ions in solution, and a revised sample problem on writing acid-base reactions.
- **Chapter 5** now has three improved sample problems and two revised figures on gas laws.
- **Chapter 6** includes heavily revised sample problems on heat, temperature change, and specific heat capacity; Hess's Law; and calculations with heat of formation values. The Chemical Connections on energy has been updated.
- **Chapter 7** includes a new video to help students understand line spectra, three revised figures, and a revised sample problem on quantum numbers.
- **Chapter 8** incorporates a new figure to illustrate penetration and shielding of $4s$ vs. $3d$ orbitals, four revised figures (on electron spin, orbital filling, element reactivity, and acid-base behavior of oxides), a heavily revised discussion on using the periodic table to write electron configurations, and a new treatment of the concept of assigning quantum numbers to electrons.
- **Chapter 9** has a revised treatment of the Born-Haber cycle and a clearer discussion of the three types of bonding.
- **Chapter 10** includes two new videos: one video demonstrates the process of drawing Lewis structures and one explains the process of determining molecular geometry. There are also improvements in the text explanation about drawing Lewis structures, on assigning and using formal charges, and on determining molecular polarity.
- **Chapter 11** has a revised sample problem and a new follow-up problem on types of orbitals, a revised follow-up problem on hybrid orbitals, and an improved discussion on hybridization and bond angles in molecules.
- **Chapter 12** includes a rewritten section on phase changes, a new discussion on intermolecular forces and boiling points, a revision to a figure that helps students determine the type of intermolecular forces in a sample, and updated discussions in the advanced material section on LEDs, plastic recycling, 3-D printing, and nanomedicine.
- **Chapter 13** incorporates a new video on freezing point depression calculations, a new graphical figure that depicts Henry's law for several gases and connects gas solubility with molar mass and the strength of dispersion forces, a revised figure on the types of intermolecular forces in solution, and revised sample and follow-up problems on predicting charge density.
- **Chapter 14** has two revised figures, one showing silicates and the other showing crystals of a noble gas compound, and an updated discussion, with new figures, on carbon allotropes.
- **Chapter 15** includes a new example and new art to aid in naming organic compounds and new videos on naming alkanes, understanding optical isomers, and recognizing functional groups.
- **Chapter 16** has a newly organized section on rate laws and half-lives for first-, second-, and zero-order reactions, an addition to a sample problem that requires the calculation of rate from rate constant and concentration data, a new follow-up problem on first-order integrated rate law calculations, and several new or revised end-of-chapter problems. The section on collision theory, activation energy, and transition state theory was heavily revised for better flow and clarity. There is a new Student Hot Spot resource on solving first-order integrated rate law problems.
- **Chapter 17** has several revised and new sample problems and follow-up problems, including a new sample problem on the van't Hoff equation for calculating the change in equilibrium constant with a change in temperature, several new end-of-chapter problems, and three new Student Hot Spot resources explaining equilibrium and Le Châtelier's principle. There are two revised figures on equilibrium position.
- **Chapter 18** has a significant rearrangement of topics, introducing conjugate acid-base pairs and the pH scale before the introduction of K_a ; two new figures, one describing the relationship between $[H^+]$ and $[OH^-]$ and the other summarizing K_a and K_b calculations; three revised sample and follow-up problems; and two new videos to help students understand acidic metal cations and how to predict the pH of salts with amphiprotic anions.
- **Chapter 19** includes three new tables, one summarizing buffer pH relative to buffer concentration ratio and the other two summarizing pH calculations for titrations of weak acids and weak bases. There are new Student Hot Spot resources on the calculation of buffer pH, the preparation of a buffer of a specific pH, and the calculation of pH during acid-base titrations.
- **Chapter 20** includes new tables with values of entropy and Gibbs free energy for selected substances, a revised sample problem on the calculation of the standard entropy of reaction, and a new video on spontaneity and temperature.

- **Chapter 21** incorporates a more useful example of balancing a redox reaction in acidic solution and a new Student Hot Spot resource that illustrates the balancing method, new art to explain the function of a salt bridge, a new follow-problem on the relationship between cell potential and equilibrium constant, and an updated discussion on batteries.
- **Chapter 23** has a revised section on nomenclature of coordination compounds, including a revised sample problem on nomenclature; new art on the color of complex ions; and new videos on coordination number, optical isomers, and low-spin vs. high-spin complex ions.
- **Chapter 24** includes a new table on stability of isotopes, a new sample problem on writing transmutation reactions, an updated table on radiation exposure, and updated discussions on PET scans and on fusion.

Innovative Topic and Chapter Presentation

Although the topic sequence coincides with that used in most mainstream courses, built-in flexibility allows a wide range of differing course structures:

For courses that follow their own topic sequence, the general presentation, with its many section and subsection breaks and bulleted lists, allows topics to be rearranged, or even deleted, with minimal loss of continuity.

For courses that present several chapters, or topics within chapters, in different orders:

- Redox balancing by the half-reaction method is covered with electrochemistry in Chapter 21, but it can easily be taught with Chapter 4.
- Gases (Chapter 5) can be covered in sequence to explore the mathematical modeling of physical behavior or, with no loss of continuity, just before liquids and solids (Chapter 12) to show the effects of intermolecular forces on the three states of matter.

For courses that use an atoms-first approach for some of the material, Chapters 7 through 13 move smoothly from quantum theory (7) through electron configuration (8), bonding models (9), molecular shape (10), VB and MO bonding theories (11), intermolecular forces in liquids and solids (12), and solutions (13). Immediate applications of these concepts appear in the discussions of periodic patterns in main-group chemistry (Chapter 14) and in the survey of organic chemistry (Chapter 15). Some instructors have also brought forward the coverage of transition elements and coordination compounds (23) as further applications of bonding concepts. (Of course, Chapters 14, 15, and 23 can just as easily remain in their more traditional placement later in the course.)

For courses that emphasize biological/medical applications, many chapters highlight these topics, including the

role of intermolecular forces in biomolecular structure (12), the chemistry of polysaccharides, proteins, and nucleic acids (including protein synthesis, DNA replication, and DNA sequencing) (15), as well as introductions to enzyme catalysis (16), biochemical pathways (17), and trace elements in protein function (23).

For courses that stress engineering applications of physical chemistry topics, Chapters 16 through 21 cover kinetics (16), equilibrium in gases (17), acids and bases (18), and aqueous ionic systems (19) and entropy and free energy (20) as they apply to electrochemical systems (21), all in preparation for coverage of the elements in geochemical cycles, metallurgy, and industry in Chapter 22.



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