Chemistry

SEVENTH EDITION

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PEARSON

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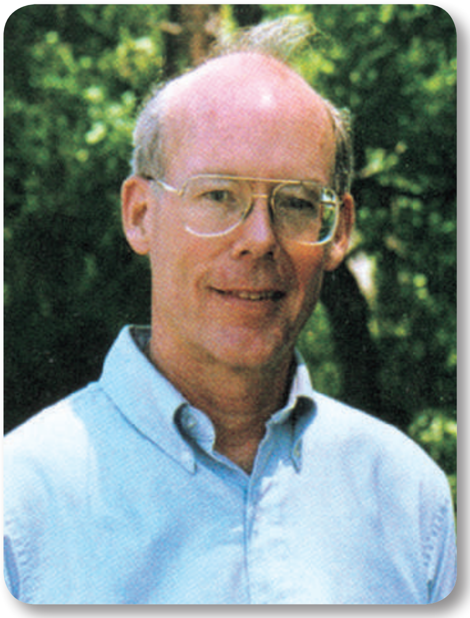

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Preface

FOR THE STUDENT

Francie came away from her first chemistry lecture in a glow. In one hour she found out that everything was made up of atoms which were in continual motion. She grasped the idea that nothing was ever lost or destroyed. Even if something was burned up or rotted away, it did not disappear from the face of the earth; it changed into something else—gases, liquids, and powders. Everything, decided Francie after that first lecture, was vibrant with life and there was no death in chemistry. She was puzzled as to why learned people didn't adopt chemistry as a religion.

—**Betty Smith,** *A Tree Grows in Brooklyn*

OK, not everyone has such a breathless response to their chemistry lectures, and few would mistake chemistry as a religion, yet chemistry *is* a subject with great logical beauty. We love chemistry because it explains the "why" behind many observations of the world around us and we use it every day to help us make informed choices about our health, lifestyle, and politics. Moreover, chemistry is the fundamental, enabling science that underlies many of the great advances of the last century that have so lengthened and enriched our lives. Chemistry provides a strong understanding of the physical world and will give you the foundation you need to go on and make important contributions to science and humanity.

HOW TO USE THIS BOOK

You no doubt have experience using textbooks and know they are not meant to read like a novel. We have written this book to provide you with a clear, cohesive introduction to chemistry in a way that will help you, as a new student of chemistry, understand and relate to the subject. While you *could* curl up with this book, you will greatly benefit from continually formulating questions and checking your understanding as you *work* through each section. The way this book is designed and written will help you keep your mind active, thus allowing you to digest big ideas as you learn some of the many principles of chemistry. Features of this book and how you should use them to maximize your learning are described below.

1. **Narrative:** As you read through the text, always challenge yourself to understand the "why" behind the concept. For example, you will learn that carbon forms four bonds, and the narrative will give the reason why. By gaining a conceptual understanding, you will *not need to memorize* a large collection of facts, making learning and retaining important principles much easier!
2. **Figures:** Figures are not optional! Most are carefully designed to summarize and convey important points. *Figure It Out* questions are included to draw your attention to a key principle. Answer the question by examining the figure and perhaps rereading the related narrative. Answers to *Figure It Out* questions are provided near the figure.
3. **Worked Examples:** Numerous worked examples are given throughout the text to show the approach for solving a certain type of problem. A stepwise procedure is used within each worked example.

    Identify—The first step in problem solving is to identify key information and classify it as a known or unknown quantity. This step also involves translating between words and chemical symbols. Listing knowns on one side and unknowns on the other organizes the information and makes the process of identifying the correct strategy more visual. The *Identify* step will be used in numerical problems.

    Strategy—The strategy describes how to solve the problem without actually solving it. Failing to articulate the needed strategy is a common pitfall; too often students start manipulating numbers and variables without first identifying key equations or making a plan. Articulating a strategy will develop conceptual understanding and is highly preferable to simply memorizing the steps involved in solving a certain type of problem.

Solution—Once the plan is outlined, the key information can be used and the answer obtained.

Check—A problem is not completed until you have thought about whether the answer makes sense. Use both your practical knowledge of the world and knowledge of chemistry to evaluate your answer. For example, if heat is added to a sample of liquid water and you are asked to calculate the final temperature, you should critically consider your answer: Is the final temperature lower than the original? Shouldn't adding heat raise the temperature? Is the new temperature above 100 °C, the boiling point of water? The ***Check*** step will be used in problems when the magnitude and sign of a number can be estimated or the physical meaning of the answer verified based on familiar observations.

To test your mastery of the concept explored in worked examples, two problems will follow. **PRACTICE** problems are similar in style and complexity to the worked example and will test your basic understanding. Once you have correctly completed this problem, tackle the **APPLY** problem, in which the concept is used in new situation. Video tutorials explaining some of the APPLY problems illustrate the process of expert thinking and point out how the same principle can be used in multiple ways.

4. **Conceptual Problems:** Conceptual understanding is a primary focus of this book. Conceptual problems are intended to help you with the critical skill of visualizing the structure and interactions of atoms and molecules while probing your understanding of key principles rather than your ability to correctly use numbers in an equation. The time you spend mastering these problems will provide high long-term returns by solidifying main ideas.
5. **Inquiries:** Inquiry sections connect chemistry to the world around you by highlighting useful links in the future careers of many science students. Typical themes are materials, medicine, and the environment. The goal of these sections is to deepen your understanding and aid in retention by tying concepts to memorable applications. These sections can be considered as a capstone for each chapter because *Inquiry* problems review several main concepts and calculations. These sections will also help you prepare for professional exams because they were written in the same style as new versions of these exams. For example, starting in 2015 the MCAT will provide a reading passage about a medical situation and you will be required to apply physical and chemical principles to interpret the system.
6. **End-of-Chapter Study Guide and Problem Sets:** The end-of-chapter study guide can be used either during active study of the chapter or to prepare for an exam. The concept summary provides the central idea for each section, and learning objectives specify key skills needed to solve a variety of problems. Learning objectives are linked to end-of-chapter problems so that you can assess your mastery of that skill.

   Working problems is essential for success in chemistry! The number and variety of problems at the end of chapter will give you the practice needed to gain mastery of specific concept. Answers to every other problem are given in the "Answers" section at the back of the book so that you can assess your understanding.

For Instructors

NEW TO THIS EDITION

One of the biggest challenges for general chemistry students is that they are often overwhelmed by the number of topics and massive amount information in the course. Frequently, they do not see connections between new material and previous content, thus creating barriers to learning. ***Therefore, the table of contents was revised to create more uniform themes*** within chapters and a coherent progression of concepts that build on one another.

- The focus of Chapter 1 has been changed to experimentation and measurements. In this 7th edition, the periodic table and element properties are covered in Chapter 2 (Chemistry Fundamentals: Elements, Molecules, and Ions).
- Coverage of nuclear reactions, radioactivity, and nuclear stability has been consolidated in this edition. Copy on nuclear reactions formerly found in Chapter 2 has been moved to Chapter 19 to keep all nuclear chemistry within one chapter.
- Solution stoichiometry and titrations were moved from Chapter 3 (Mass Relationships in Chemical Reactions) to Chapter 4 (Reactions in Aqueous Solutions).
- At the suggestion of instructors who used the last edition, coverage of redox stoichiometry now appears in the electrochemistry chapter where it is most needed. This change simplifies Chapter 4, which now serves as an introduction to aqueous reactions.
- The new edition features a chapter dedicated to main group chemistry. Main group chemistry sections formerly appearing in Chapter 6: Ionic Compounds: Periodic Trends and Bonding Theory are now incorporated into Chapter 22: The Main Group Elements.
- Covalent bonding and molecular structure are now covered in two chapters (7 and 8) to avoid having to cover an overwhelming amount of material in one chapter. The topic of intermolecular forces was added to Chapter 8 to reinforce its connection to polarity.
- Nuclear chemistry has been moved forward in the table of contents because of its relevance in energy production, medicine, and the environment.
- The chapter on hydrogen and oxygen has been omitted, but key chemical properties and reactions of hydrogen and oxygen are now covered in Chapter 22: The Main Group Elements.
- Chapter 10 dealing with gases now includes content on air pollution and climate change.
- Chapter 23 has been heavily revised to review important general chemistry principles of bonding and structure as they apply to organic and biological molecules. This chapter may be covered as a standalone chapter or sections may be incorporated into earlier chapters if an instructor prefers to cover organic and biological chemistry throughout the year.

NEW! All Worked Examples have been carefully revisited in the context of newly articulated Learning Outcomes.

Worked examples are now tied to Learning Outcomes listed at chapter end and to representative EOC problems so that students can test their own mastery of each skill.

Select worked examples now contain a section called **Identify**, which lays out the known and unknown variables for students. Listing knowns on one side and unknowns on the other organizes the information and makes the process of identifying the correct strategy more visual. The *Identify* step will be used in numerical problems with equations.

Worked examples in the 7th edition now conclude with two problems, one called **Practice** and the other called **Apply**, to help students see how the same principle can be used in different types of problems with different levels of complexity.

To discourage a plug-and-chug approach to problem solving, related Worked Examples from the previous edition have been consolidated, giving students a sense of how different approaches are related.

The number of in-chapter problems has increased by 20% to encourage the students to work problems actively immediately after reading.

NEW! Inquiry Sections have been updated and integrated conceptually into each chapter.

Inquiry sections highlight the importance of chemistry, promote student interest, and deepen the students understanding of the content. The new Inquiry sections include problems that revisit several chapter concepts and can be covered in class, recitation sections, or assigned as homework in MasteringChemistry.

NEW! Chapter Study Guide offers a modern and innovative way for students to review each chapter.

Prepared in a grid format, the main lessons of each chapter are reiterated and linked to learning objectives, associated worked examples, and representative end-of-chapter problems.

NEW! Figure It Out questions promote active learning.

Selected figures are tagged with questions designed to prompt students to look at each illustration more carefully, and interpret graphs and recognize key ideas.

NEW! Looking Forward Notes are now included.

Looking Forward Notes, in addition to Remember Notes, are included to underscore and reiterate connections between topics in different chapters.

NEW! Over 600 new problems have been written for the 7th edition.

New problems ensure there is a way to assess each learning objective in the Study Guide, all of which are suitable for use in MasteringChemistry.

The seventh edition was extensively revised. Here is a list of some of the key changes made in each chapter:

Chapter 1 Chemical Tools: Experimentation and Measurement

- Chapter 1 focuses on experimentation, the scientific method, and measurement and offers a new, robust Inquiry on nanotechnology.
- The scientific method is described in the context of a case study for the development of an insulin drug.

Chapter 2 Atoms, Molecules, and Ions

- Material on the elements and periodic table previously found in Chapter 1 has been relocated here, and nuclear chemistry has been moved to the nuclear chemistry chapter.
- Coverage of the naming of binary molecular compounds was moved to a later point in the chapter to consolidate coverage of the naming of ionic compounds.
- A new Inquiry on green chemistry, focusing on the concept of atom economy, revisits the Law of Conservation of Mass.

Chapter 3 Mass Relationships in Chemical Reactions

- Section 3.2 includes a revised Worked Example on balancing chemical reactions to give students a chance to use the method in simple and complex problems.
- New coverage of mass spectrometry in Section 3.8 explains how molecular weights are measured and mass spectral data is utilized in problems. The topic of mass spectrometry is connected to crime scene analysis and offers a good example of how the new edition presents chemistry in a modern way.
- A new Inquiry explores CO_2 emissions from various alternative fuels using concepts of stoichiometry.

Chapter 4 Reactions in Aqueous Solution

- Section order and coverage were revised to keep the focus on solution chemistry.
- Problems and worked examples are rearranged so that conceptual worked examples lead off the discussion rather than wrap it up.
- The new Inquiry on sports drinks applies the concepts of electrolytes, solution concentration, and solution stoichiometry.

Chapter 5 Periodicity and Electronic Structure of Atoms

- Section 5.3 on line spectra has been revised to better show how spectral lines of the elements are produced.
- Sections 5.7–5.10 offer a more continuous description of how orbitals can be described using quantum numbers.
- The Inquiry on fluorescent lights was revised to include problems that require students to write electron configurations and interpret line spectra.

Chapter 6 Ionic Compounds: Periodic Trends and Bonding Theory

- As this is the first of three chapters on bonding, it now includes some introduction to topic sequence in Chapters 6–8.
- Every chapter problem is now preceded by a Worked Example and followed by Practice and Apply problems.
- New figures in Section 6.2 help visualize why creating an ion changes the size of an atom.
- Updated Inquiry on ionic liquids includes problems on writing ion electron configurations and relating ion size to properties of the ionic compound.
- Main group chemistry now appears in Chapter 22 (Main Group Chemistry).

Chapter 7 Covalent Bonding and Electron-Dot Structures

- Chapter 7 is now dedicated to covalent bonding using the Lewis electron-dot model. Valence shell electron pair repulsion theory, molecular shape, and molecular orbital theory now appear in Chapter 8.
- Section 7.6 summarizes a general procedure for drawing electron-dot structures and applies the procedure in new Worked Examples.
- The coverage of resonance includes an introduction to the use of curved arrows to denote rearrangement of electrons, a practice that is commonly used in organic chemistry courses.
- The new Inquiry, "How do we make organophosphate insecticides less toxic to humans?," builds on several concepts introduced in this chapter, including polar covalent bonds, electron-dot structures, and resonance.
- The chapter includes many new figures. Much of the new art appears in revised Worked Examples, replacing and/or embellishing Worked Examples appearing in the prior edition.

Chapter 8 Covalent Compounds: Bonding Theories and Molecular Structure

- The focus of Chapter 7 is covalent bonds and electron-dot structures, whereas the focus of Chapter 8 is quantum mechanical theories of covalent bonding, molecular shape, polarity, and intermolecular forces. Polarity and intermolecular forces are a direct extension of molecular shape and have been moved from Chapter 10 to Chapter 8.
- Section 8.1 on the VSEPR model explains use of solid wedges and dashed lines to draw the 3-D structure of molecules.
- Many Worked Examples in this chapter were substantively revised to reflect the chapter's new emphasis. New figures for Worked Examples 8.3 and 8.4 illustrate orbital overlap involved in each type of bond.
- Section 8.5 includes new Figure 8.8: A flowchart to show the strategy for determining molecular polarity. Worked Example 8.6 was revised to follow this flowchart.
- A New Conceptual Worked Example on drawing hydrogen bonds and new end of chapter problems were developed.
- The Inquiry for this chapter was expanded to include intermolecular forces in biomolecular binding. Two new figures were added to illustrate how the mirror image has a different geometric arrangement of atoms and how this can lead to discrimination between these two molecules by a receptor site. New cumulative problems were added that include all topics in the chapter thus far: geometry, hybridization, polarity, intermolecular forces, and mirror images.

Chapter 9 Thermochemistry: Chemical Energy

- Section 9.2, Internal Energy and State Function, includes a new figure to illustrate ΔE in an example of the caloric content of food.
- Section 9.4, Energy and Enthalpy, has a new figure illustrating energy transfer as heat and work in a car's engine to help students grasp the meaning of internal energy.
- Section 9.5, entitled "Thermochemical Equations and the Thermodynamic Standard State," covers all aspects of writing and manipulating thermochemical equations (standard state, stoichiometry, reversibility, and importance of specifying phases).
- Section 9.6 on Enthalpy of Chemical and Physical Change offers improved definitions of endothermic and exothermic phenomena, including new Worked Examples and problems on classifying reactions and identifying direction of heat transfer.

Chapter 10 Gases: Their Properties and Behavior

- Chapter 10 is revised to include three new sections on atmospheric chemistry (air pollution, the greenhouse effect, and climate change) and a new Inquiry on greenhouse gases.
- There are thirty new end-of-chapter problems that require students to describe atmospheric chemistry and utilize many chemistry skills covered thus far in the book.

Chapter 11 Liquids, Solids, and Phase Changes

- Worked Example 11.2 is new and describes how to calculate the energy change associated with heating and phase changes.
- New Section 11.5 now includes two new images to enhance discussion of X-ray diffraction experiments.
- The Inquiry on decaffeination is new and builds on the topics of phase diagrams and energy of phase changes.

Chapter 12 Solutions and Their Properties

- Section 12.2 on Energy Changes and the Solution Process includes a new figure illustrating the hydrogen bonding interactions between solute and solvent (added emphasis on chemical structure and visual explanation of solubility).
- Section 12.3 on Concentration Units for Solutions has refined coverage of concentration units and a new Worked Example on ppm and ppb.
- Section 12.6 on Vapor-Pressure Lowering includes new Worked Examples on the van't Hoff factor and on vapor pressure lowering with a volatile solute.
- The Inquiry on dialysis was expanded and improved through the addition of an illustration of dialysis and follow-up problems dealing with solution concentration and colligative properties.

Chapter 13 Chemical Kinetics

- The first section includes a generic introduction to the concept of a reaction rate, which is now used in problems throughout the chapter instead of reaction rates specific to a reactant or product.
- A new section on Enzyme Catalysis (Section 13.14) has been added, along with new end-of-chapter problems on this topic.
- Coverage of radioactive decay formerly included in this chapter has been moved to the nuclear chemistry chapter.
- The new Inquiry on ozone depletion builds on various kinetics concepts including activation energy determination, calculation of rate, reaction mechanisms, catalysis.

Chapter 14 Chemical Equilibrium

- Section 14.2 on The Equilibrium Constant K_c has an expanded discussion and new Worked Examples dealing with manipulating equations and calculating new values of K_c.
- Section 14.4 on Heterogeneous Equilibria has been revised to clarify when concentrations of pure solids and liquids present in a chemical equation are not included in the equilibrium constant.
- Section 14.5 on Using the Equilibrium Constant has been enhanced by the addition of a new worked example on Judging the Extent of a Reaction.
- Figure 14.6, entitled Steps in Calculating Equilibrium Concentrations, was modified to include the important first step of determining reaction direction.
- The Inquiry on equilibrium and oxygen transport now includes several follow-up problems that give students practice with various equilibrium concepts.

Chapter 15 Aqueous Equilibria: Acids and Bases

- Section 15.3, Factors that Affect Acid Strength, now appears earlier in the chapter to explain *why* chemical structure affects acid strength, and is bolstered by new Worked Example 15.4 entitled 'Evaluating Acid Strength Based Upon Molecular Structure' as well as new end-of-chapter problems.
- Section 15.5 on the pH scale includes new problems exploring environmental issues.
- The Inquiry on acid rain has been updated to include new statistics and a new figure illustrating changes in acid rainfall over time.

Chapter 16 Applications of Aqueous Equilibria

- Coverage of the Henderson-Hasselbalch Equation has been reworked so that students progress from simpler problems to more complex ones.
- Reaction tables are now routinely included in titration problems to help students see what species remain at the end of the neutralization reaction. New Worked Examples are included.
- Section 16.12 on Factors that Affect Solubility has been enhanced with relevant new examples (e.g., tooth decay).
- The new and highly pertinent Inquiry for Chapter 16 on ocean acidification revisits key concepts such as acid-base reactions, buffers, and solubility equilibria in a meaningful environmental context.

Chapter 17 Thermodynamics: Entropy, Free Energy, and Equilibrium

- Section 17.3 on Entropy and Probability is enhanced with a new Worked Example and follow-up problems on the expansion of an ideal gas.
- Different signs of enthalpy and entropy in are broken down on a case-by-case basis in Section 17.7.
- The Inquiry on biological complexity was heavily revised to describe why some biological reactions are spontaneous. The Inquiry now includes concrete examples of the thermodynamics of living systems and four relevant follow-up problems.

Chapter 18 Electrochemistry

- Section on balancing redox reactions using the half-reaction method was taken out of Chapter 4 and placed in Chapter 18 based on reviewer feedback.
- Coverage of fuel cells has been streamlined and incorporated into the Inquiry. New Inquiry problems revisit core thermodynamic and electrochemical concepts.

Chapter 19 Nuclear Chemistry

- All the nuclear chemistry content is now contained in Chapter 19.
- Coverage on balancing a nuclear reaction was revised to more clearly show that mass number and atomic number are equal on both sides of the equation.
- Figure 19.3 was added to illustrate the concept of a radioactive decay series.
- Several improvements were made in Section 19.6 on Fission and Fusion: the difference between nuclear fuel rods used in a reactor and weapons-grade nuclear fuel has been clarified; Figure 19.8 has been updated to include 2013 figures for nuclear energy output.
- New end-of-chapter problems dealing with aspects of nuclear power and nuclear weapons have been added.

Chapter 20 Transition Elements and Coordination Chemistry

- Worked Example 20.5, Identifying Diastereomers, has been revised and moved earlier so that students begin with a conceptual problem.
- Worked Example 20.6, Drawing Diastereomers for Square Planar and Octahedral Complexes, was rewritten to promote conceptual understanding and discourage rote memorization.
- A new Inquiry on the mechanism of action of the antitumor drug cisplatin reinforces several concepts covered in the chapter, including nomenclature, chirality, the formation of coordination compounds, and crystal field theory.

Chapter 21 Metals and Solid-State Materials

- Band theory in metals has been clarified by
  - describing the formation of band from MOs in more detail in the text
  - revising Figure 21.6 to show that bands contain many closely spaced MOs
  - the addition of Figure It Out questions that require extension of band theory to different systems.
- New Figure 21.10 on doping of semiconductors correlates molecular picture with energy level diagrams.

- The connection between LED color and periodic trends is described in Section 21.6. New problems are included.
- The Inquiry on quantum dots was heavily revised to more clearly connect with chapter content on band theory and semiconductors.

Chapter 22 The Main-Group Elements

- Main group chemistry is consolidated into one chapter. The content has been trimmed and key concepts related to periodic trends, bonding, structure, and reactivity are reviewed in the context of main group chemistry.
- The Inquiry Section dealing with barriers to a hydrogen economy describes hydrogen production and storage methods including recent development in photocatalysts.

Chapter 23 Organic and Biological Chemistry

- This chapter was revised so that the focus is on important concepts of structure and bonding that organic chemistry instructors would like students to master in general chemistry.
- Over 50 end-of-chapter problems are completely new.
- Section 23.1 offers an introduction to skeletal structures (line drawings) commonly used as a shorthand method for drawing organic structures.
- Coverage of the alkanes is consolidated in Section 23.1 (the cycloalkanes were formerly covered in Section 23.5 in 6e.).
- Coverage of the naming of organic compounds was shortened in 7e Section 23.3 because the primary focus of the new chapter is on bonding and structure.
- Section 23.4, entitled "Carbohydrates: A Biological Example of Isomers" offers a good example of how the applied chapters at the end of the book explore key concepts (isomerism) in a relevant context (carbohydrates).
- Section 23.4 also offers a good example of how key concepts from other chapters are revisited in the applied chapters at book end. Here chirality is revisited, a subject first presented in the Chapter 8 Inquiry.
- Section 23.5 considers cis-trans isomerism in the context of valence bond theory. Two new Worked Examples are included that describe orbital overlap in organic molecules.
- The theme of cis-trans isomerism is revisited in Section 23.6 with the introduction of the lipids. New Figure 23.6, for example, shows the difference in packing of saturated and unsaturated fats and the role played by intermolecular forces.
- Section 23.5 revisits the concepts of formal charge and resonance first introduced in Ch 7. Problems in this section give students additional practice in the drawing of electron-dot structures and electron "pushing." Common patterns of resonance in organic molecules are introduced as well.
- Section 23.8 is new to the 7th edition, covering conjugated systems in the context of resonance and orbital diagrams. New worked examples tie the section together, offering problems on drawing conjugated π systems, and exploring how to recognize localized vs delocalized electrons.
- Section 23.9, entitled "Proteins: A Biological Example of Conjugation" follows logically from Section 23.8 to look at conjugation in the peptide bond and proteins.
- Section 23.10, new to the 7th edition, considers aromatic compounds in the context of molecular orbital theory. Building on students' understanding of conjugation, molecular orbital theory is invoked to describe the stability of benzene.
- Section 23.11 on the nucleic acids expands on the discussion of aromaticity in describing how aromaticity makes base stacking in the interior of the DNA molecule possible.

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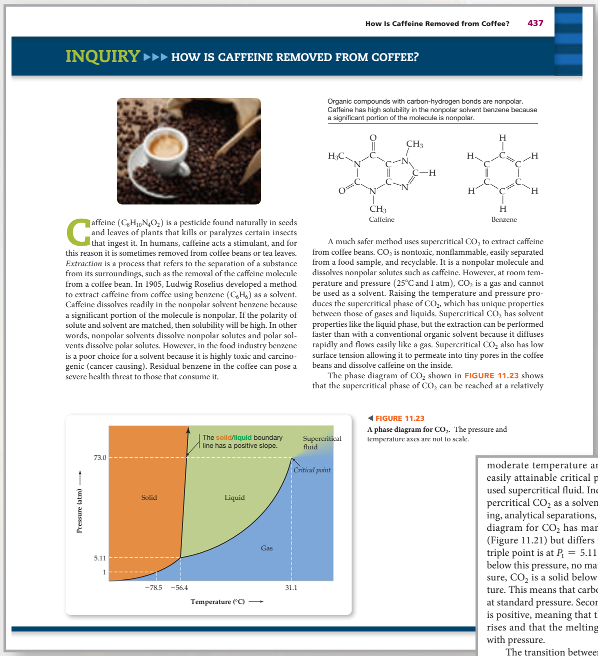
Showing Students the Connections in Chemistry and Why They Matter

McMurry/Fay/Robinson's Chemistry, Seventh Edition provides a streamlined presentation that blends the quantitative and visual aspects of chemistry, organizes content to highlight connections between topics and emphasizes the application of chemistry to students lives and careers. New content provides a better bridge between organic and biochemistry and general chemistry content, and new and improved pedagogical features make the text a true teaching tool and not just a reference book.

New MasteringChemistry features include conceptual worked examples and integrated Inquiry sections that help make critical connections clear and visible and increase students' understanding of chemistry. The Seventh Edition fully integrates the text with new MasteringChemistry content and functionality to support the learning process before, during, and after class.


How Is Caffeine Removed from Coffee? 437

INQUIRY ▸▸▸ HOW IS CAFFEINE REMOVED FROM COFFEE?

Caffeine ($C_8H_{10}N_4O_2$) is a pesticide found naturally in seeds and leaves of plants that kills or paralyzes certain insects that ingest it. In humans, caffeine acts a stimulant, and for this reason it is sometimes removed from coffee beans or tea leaves. *Extraction* is a process that refers to the separation of a substance from its surroundings, such as the removal of the caffeine molecule from a coffee bean. In 1905, Ludwig Roselius developed a method to extract caffeine from coffee using benzene (C_6H_6) as a solvent. Caffeine dissolves readily in the nonpolar solvent benzene because a significant portion of the molecule is nonpolar. If the polarity of solute and solvent are matched, then solubility will be high. In other words, nonpolar solvents dissolve nonpolar solutes and polar solvents dissolve polar solutes. However, in the food industry benzene is a poor choice for a solvent because it is highly toxic and carcinogenic (cancer causing). Residual benzene in the coffee can pose a severe health threat to those that consume it.

Organic compounds with carbon-hydrogen bonds are nonpolar. Caffeine has high solubility in the nonpolar solvent benzene because a significant portion of the molecule is nonpolar.

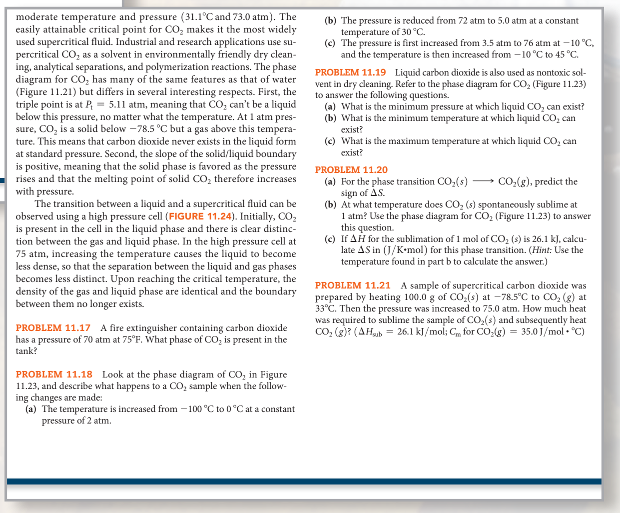
Caffeine   Benzene

A much safer method uses supercritical CO_2 to extract caffeine from coffee beans. CO_2 is nontoxic, nonflammable, easily separated from a food sample, and recyclable. It is a nonpolar molecule and dissolves nonpolar solutes such as caffeine. However, at room temperature and pressure (25°C and 1 atm), CO_2 is a gas and cannot be used as a solvent. Raising the temperature and pressure produces the supercritical phase of CO_2, which has unique properties between those of gases and liquids. Supercritical CO_2 has solvent properties like the liquid phase, but the extraction can be performed faster than with a conventional organic solvent because it diffuses rapidly and flows easily like a gas. Supercritical CO_2 also has low surface tension allowing it to permeate into tiny pores in the coffee beans and dissolve caffeine on the inside.

The phase diagram of CO_2 shown in FIGURE 11.23 shows that the supercritical phase of CO_2 can be reached at a relatively

The solid/liquid boundary line has a positive slope.
Supercritical fluid
Critical point
Solid
Liquid
Gas
73.0
5.11
1
Pressure (atm)
−78.5 −56.4 31.1
Temperature (°C)

◂ FIGURE 11.23
A phase diagram for CO_2. The pressure and temperature axes are not to scale.


moderate temperature and pressure (31.1°C and 73.0 atm). The easily attainable critical point for CO_2 makes it the most widely used supercritical fluid. Industrial and research applications use supercritical CO_2 as a solvent in environmentally friendly dry cleaning, analytical separations, and polymerization reactions. The phase diagram for CO_2 has many of the same features as that of water (Figure 11.21) but differs in several interesting respects. First, the triple point is at $P_t = 5.11$ atm, meaning that CO_2 can't be a liquid below this pressure, no matter what the temperature. At 1 atm pressure, CO_2 is a solid below −78.5 °C but a gas above this temperature. This means that carbon dioxide never exists in the liquid form at standard pressure. Second, the slope of the solid/liquid boundary is positive, meaning that the solid phase is favored as the pressure rises and that the melting point of solid CO_2 therefore increases with pressure.

The transition between a liquid and a supercritical fluid can be observed using a high pressure cell (FIGURE 11.24). Initially, CO_2 is present in the cell in the liquid phase and there is clear distinction between the gas and liquid phase. In the high pressure cell at 75 atm, increasing the temperature causes the liquid to become less dense, so that the separation between the liquid and gas phases becomes less distinct. Upon reaching the critical temperature, the density of the gas and liquid phase are identical and the boundary between them no longer exists.

PROBLEM 11.17 A fire extinguisher containing carbon dioxide has a pressure of 70 atm at 75°F. What phase of CO_2 is present in the tank?

PROBLEM 11.18 Look at the phase diagram of CO_2 in Figure 11.23, and describe what happens to a CO_2 sample when the following changes are made:

(a) The temperature is increased from −100 °C to 0 °C at a constant pressure of 2 atm.

(b) The pressure is reduced from 72 atm to 5.0 atm at a constant temperature of 30 °C.

(c) The pressure is first increased from 3.5 atm to 76 atm at −10 °C, and the temperature is then increased from −10 °C to 45 °C.

PROBLEM 11.19 Liquid carbon dioxide is also used as nontoxic solvent in dry cleaning. Refer to the phase diagram for CO_2 (Figure 11.23) to answer the following questions.

(a) What is the minimum pressure at which liquid CO_2 can exist?

(b) What is the minimum temperature at which liquid CO_2 can exist?

(c) What is the maximum temperature at which liquid CO_2 can exist?

PROBLEM 11.20

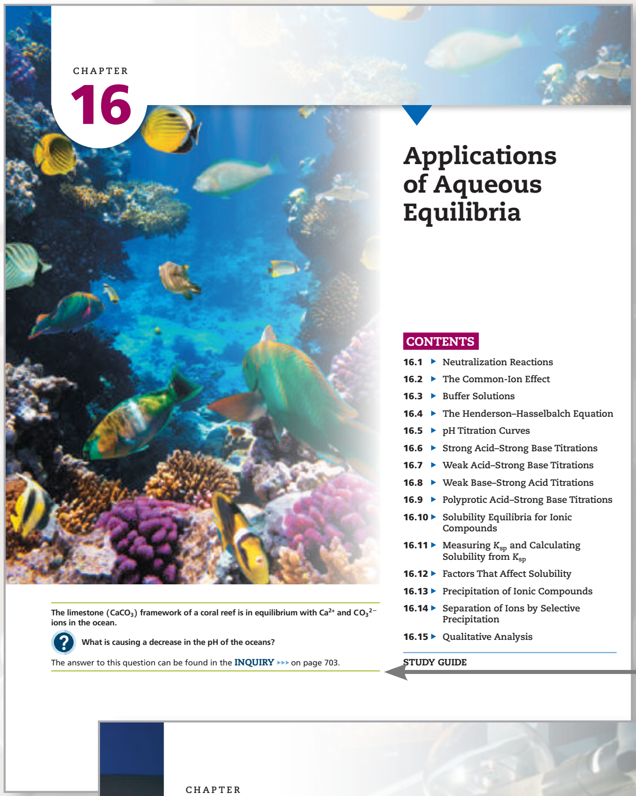
(a) For the phase transition $CO_2(s) \longrightarrow CO_2(g)$, predict the sign of ΔS.

(b) At what temperature does $CO_2(s)$ spontaneously sublime at 1 atm? Use the phase diagram for CO_2 (Figure 11.23) to answer this question.

(c) If ΔH for the sublimation of 1 mol of $CO_2(s)$ is 26.1 kJ, calculate ΔS in (J/K•mol) for this phase transition. (*Hint:* Use the temperature found in part b to calculate the answer.)

PROBLEM 11.21 A sample of supercritical carbon dioxide was prepared by heating 100.0 g of $CO_2(s)$ at −78.5°C to $CO_2(g)$ at 33°C. Then the pressure was increased to 75.0 atm. How much heat was required to sublime the sample of $CO_2(s)$ and subsequently heat $CO_2(g)$? ($\Delta H_{sub} = 26.1$ kJ/mol; C_m for $CO_2(g) = 35.0$ J/mol • °C)

Inquiry Updated inquiry sections now include worked examples and practice problems so that students can apply concepts and skills to scenarios that have relevance to their daily lives. These sections not only highlight the importance of chemistry and promote interest but also deepen students understanding of the content.



CHAPTER

16

Applications of Aqueous Equilibria

CONTENTS

The limestone ($CaCO_3$) framework of a coral reef is in equilibrium with Ca^{2+} and CO_3^{2-} ions in the ocean.

? What is causing a decrease in the pH of the oceans?

The answer to this question can be found in the INQUIRY ▸▸▸ on page 703.

Chapter Openers introduce a topic and question, related to the content in the chapter that will be further discussed in the Inquiry section. The goal is to provide students with a central topic to serve as a waypoint for why the content matters to them beyond what they need to pass the next exam.

CHAPTER

1

Chemical Tools: Experimentation and Measurement

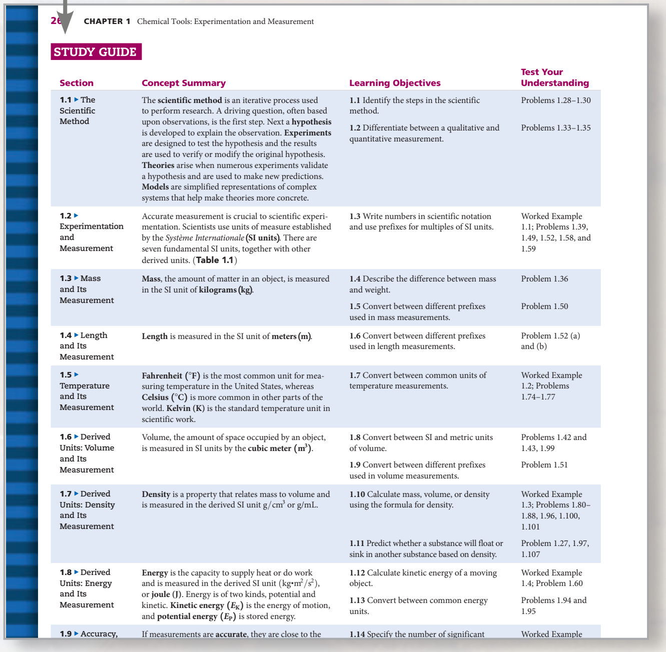
CONTENTS

Instruments for scientific measurements have changed greatly over the centuries. Modern technology has enabled scientists to make images of extremely tiny particles, even individual atoms, using instruments like this atomic force microscope.

? What are the unique properties of nanoscale (1 nm = 10^{-9} m) materials?

The answer to this question can be found in the INQUIRY ▸▸▸ on page 23.

Study Guide The end-of-chapter material now includes a Study Guide to help students review each chapter. Prepared in a grid format, the main lessons of each chapter are laid out and linked to learning objectives, associated worked examples, and representative end-of-chapter problems that allow students to assess their comprehension of the material.



26 CHAPTER 1 Chemical Tools: Experimentation and Measurement

STUDY GUIDE

Section	Concept Summary	Learning Objectives	Test Your Understanding
1.1 ▸ The Scientific Method	The **scientific method** is an iterative process used to perform research. A driving question, often based upon observations, is the first step. Next a **hypothesis** is developed to explain the observation. **Experiments** are designed to test the hypothesis and the results are used to verify or modify the original hypothesis. **Theories** arise when numerous experiments validate a hypothesis and are used to make new predictions. **Models** are simplified representations of complex systems that help make theories more concrete.	**1.1** Identify the steps in the scientific method.	Problems 1.28–1.30
		1.2 Differentiate between a qualitative and quantitative measurement.	Problems 1.33–1.35
1.2 ▸ Experimentation and Measurement	Accurate measurement is crucial to scientific experimentation. Scientists use units of measure established by the *Système Internationale* **(SI units)**. There are seven fundamental SI units, together with other derived units. (**Table 1.1**)	**1.3** Write numbers in scientific notation and use prefixes for multiples of SI units.	Worked Example 1.1; Problems 1.39, 1.49, 1.52, 1.58, and 1.59
1.3 ▸ Mass and Its Measurement	**Mass**, the amount of matter in an object, is measured in the SI unit of **kilograms (kg)**.	**1.4** Describe the difference between mass and weight.	Problem 1.36
		1.5 Convert between different prefixes used in mass measurements.	Problem 1.50
1.4 ▸ Length and Its Measurement	**Length** is measured in the SI unit of **meters (m)**.	**1.6** Convert between different prefixes used in length measurements.	Problem 1.52 (a) and (b)
1.5 ▸ Temperature and Its Measurement	**Fahrenheit (°F)** is the most common unit for measuring temperature in the United States, whereas **Celsius (°C)** is more common in other parts of the world. **Kelvin (K)** is the standard temperature unit in scientific work.	**1.7** Convert between common units of temperature measurements.	Worked Example 1.2; Problems 1.74–1.77
1.6 ▸ Derived Units: Volume and Its Measurement	Volume, the amount of space occupied by an object, is measured in SI units by the **cubic meter** (m^3).	**1.8** Convert between SI and metric units of volume.	Problems 1.42 and 1.43, 1.99
		1.9 Convert between different prefixes used in volume measurements.	Problem 1.51
1.7 ▸ Derived Units: Density and Its Measurement	**Density** is a property that relates mass to volume and is measured in the derived SI unit g/cm^3 or g/mL.	**1.10** Calculate mass, volume, or density using the formula for density.	Worked Example 1.3; Problems 1.80–1.88, 1.96, 1.100, 1.101
		1.11 Predict whether a substance will float or sink in another substance based on density.	Problem 1.27, 1.97, 1.107
1.8 ▸ Derived Units: Energy and Its Measurement	**Energy** is the capacity to supply heat or do work and is measured in the derived SI unit ($kg{\cdot}m^2/s^2$), or **joule (J)**. Energy is of two kinds, potential and kinetic. **Kinetic energy** (E_K) is the energy of motion, and **potential energy** (E_P) is stored energy.	**1.12** Calculate kinetic energy of a moving object.	Worked Example 1.4; Problem 1.60
		1.13 Convert between common energy units.	Problems 1.94 and 1.95
1.9 ▸ Accuracy,	If measurements are **accurate**, they are close to the	**1.14** Specify the number of significant	Worked Example

Helping students relate chemical reasoning to mathematical operations

WORKED EXAMPLE 19.3

Using Half-Life to Calculate an Amount Remaining

Phosphorus-32, a radioisotope used in leukemia therapy, has a half-life of 14.26 days. What percent of a sample remains after 35.0 days?

IDENTIFY

Known	Unknown
$t_{1/2} = 14.26$ days	Percent of sample remaining $(N_t/N_0) \times 100$
$t = 35.0$ days	

STRATEGY

The ratio of remaining (N_t) and initial (N_0) amounts of a radioactive sample at time t is given by the equation

$$\ln\left(\frac{N_t}{N_0}\right) = -kt$$

Taking N_0 as 100%, N_t can then be obtained. The value of the rate constant can be found from the equation $k = 0.693/t_{1/2}$.

SOLUTION

The value of the rate constant is calculated using the half-life.

$$k = \frac{0.693}{14.26 \text{ days}} = 4.860 \times 10^{-2}\ \text{days}^{-1}$$

Substituting values for t and for k into the equation gives

$$\ln\left(\frac{N_t}{N_0}\right) = (-4.860 \times 10^{-2}\ \text{days}^{-1})(35.0 \text{ days}) = -1.70$$

Taking the natural antilogarithm of -1.70 then gives the ratio N_t/N_0:

$$\frac{N_t}{N_0} = \text{antiln}\,(-1.70) = e^{-1.70} = 0.183$$

Since the initial amount of ^{32}P was 100%, we can set $N_0 = 100\%$ and solve for N_t:

$$\frac{N_t}{100\%} = 0.183 \quad \text{so} \quad N_t = (0.183)(100\%) = 18.3\%$$

After 35.0 days, 18.3% of a ^{32}P sample remains and $100\% - 18.3\% = 81.7\%$ has decayed.

CHECK

We can estimate the answer by considering half-life. Since phosphorus-32 has a half-life of 14.26 days and the time is 35 days, we know the time of the reaction is more than two half-lives. After two half-lives, 75% has reacted and 25% remains. Since the time is over two half-lives, we would estimate that less than 25% remains, which agrees with the answer of 18.3%.

▶ **PRACTICE 19.7** What percentage of $^{14}_{6}$C ($t_{1/2} = 5715$ years) remains in a sample estimated to be 16,230 years old?

▶ **APPLY 19.8** Cesium-137 is a radioactive isotope released as a result of the Fukushima Daiichi nuclear disaster in Japan in 2011. If 89.2% remains after 5.00 years, what is the half-life?

Worked Examples Numerous Worked Examples show the approach for solving different types of problems using a stepwise procedure.

Identify The first step helps students identify key information and classify the known or unknown variables. This step frequently involves translating between words and chemical symbols.

Strategy The strategy describes how to solve the problem without actually solving it. Failing to articulate the needed strategy is a common pitfall; this step involves outlining a plan for solving the problem.

Solution Once the plan is outlined, the key information can be used and the answer obtained.

Check Uses both your practical knowledge of the world and knowledge of chemistry to evaluate your answer.

WORKED EXAMPLE 9.2

Calculating Internal Energy Change (ΔE) for a Reaction

The reaction of nitrogen with hydrogen to make ammonia has $\Delta H = -92.2$ kJ. What is the value of ΔE in kilojoules if the reaction is carried out at a constant pressure of 40.0 atm and the volume change is -1.12 L?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \quad \Delta H = -92.2 \text{ kJ}$$

IDENTIFY

Known	Unknown
Change in enthalpy ($\Delta H = -92.2$ kJ)	Change in internal energy (ΔE)
Pressure ($P = 40.0$ atm)	
Volume Change ($\Delta V = -1.12$ L)	

STRATEGY

We are given an enthalpy change ΔH, a volume change ΔV, and a pressure P and asked to find an energy change ΔE. Rearrange the equation $\Delta H = \Delta E + P\Delta V$ to the form $\Delta E = \Delta H - P\Delta V$ and substitute the appropriate values for ΔH, P, and ΔV.

SOLUTION

$$\Delta E = \Delta H - P\Delta V$$

where $\Delta H = -92.2$ kJ

$$P\Delta V = (40.0 \text{ atm})(-1.12 \text{ L}) = -44.8 \text{ L}\cdot\text{atm}$$

$$= (-44.8 \text{ L}\cdot\text{atm})\left(101 \frac{\text{J}}{\text{L}\cdot\text{atm}}\right) = -4520 \text{ J} = -4.52 \text{ kJ}$$

$$\Delta E = (-92.2 \text{ kJ}) - (-4.52 \text{ kJ}) = -87.7 \text{ kJ}$$

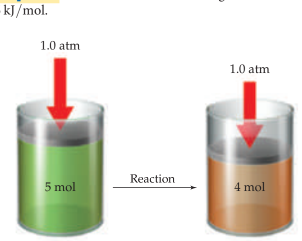
CHECK

The sign of ΔE is similar in size and magnitude ΔH, which is to be expected because energy transfer as work is usually small compared to heat.

▶ **PRACTICE 9.3** The reaction between hydrogen and oxygen to yield water vapor has $\Delta H = -484$ kJ. How much PV work is done, and what is the value of ΔE in kilojoules for the reaction of 2.00 mol of H_2 with 1.00 mol of O_2 at atmospheric pressure if the volume change is -24.4 L?

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \quad \Delta H° = -484 \text{ kJ}$$

▶ **Conceptual APPLY 9.4** The following reaction has $\Delta E = -186$ kJ/mol.

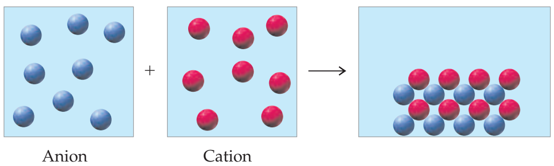


(a) Is the sign of $P\Delta V$ positive or negative? Explain.
(b) What is the sign and approximate magnitude of ΔH? Explain.

Conceptual WORKED EXAMPLE 4.7

Visualizing Stoichiometry in Precipitation Reactions

When aqueous solutions of two ionic compounds are mixed, the following results are obtained:



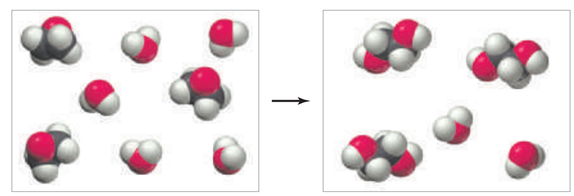
(Only the anion of the first compound, represented by blue spheres, and the cation of the second compound, represented by red spheres, are shown.) Which cation and anion combinations are compatible with the observed results?

Anions: NO_3^-, Cl^-, CO_3^{2-}, PO_4^{3-}

Cations: Ca^{2+}, Ag^+, K^+, Cd^{2+}

Conceptual Worked Examples and Conceptual Questions

Worked Conceptual Examples are included throughout each chapter to emphasize the conceptual nature of problem solving, often using molecular illustrations. Conceptual problems are now always preceded by Conceptual Worked Examples.



(a) Identify the limiting and the excess reactant.
(b) How many molecules of excess reactant are left over after the reaction occurs?
(c) How many molecules of product can be made?

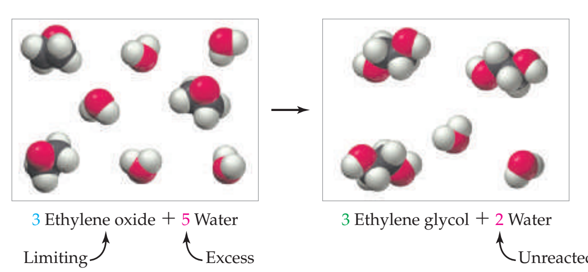
STRATEGY

Count the numbers of reactant and product molecules and use coefficients from the balanced equation to relate them to one another.

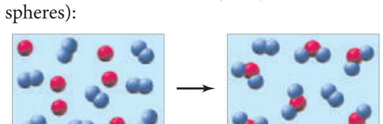
SOLUTION

(a) Count the number of each type of molecule in the box on the reactant side of the equation. There are 3 ethylene oxide molecules and 5 water molecules. According to the balanced equation the stoichiometry between the reactants is 1:1. Therefore, 5 ethylene oxide molecules would be needed to react with 5 water molecules. Since there are only 3 ethylene oxide molecules, it is the limiting reactant, and water is in excess.
(b) Count the number of water molecules on the product side of the equation. There are 2 water molecules that have not reacted, and water is called the excess reactant.
(c) Count the number of ethylene glycol molecules on the product side of the equation. There are 3 ethylene glycol molecules present.

Therefore, the reaction of 3 ethylene oxide molecules with 5 water molecules results in 3 ethylene glycol molecules with 2 water molecules left over.



▶ **Conceptual PRACTICE 3.13** The following diagram represents the reaction of A (red spheres) with B_2 (blue spheres):



(a) Write a balanced equation for the reaction.
(b) Identify the limiting and excess reactant.
(c) How many molecules of product are made?

Conceptual Practice and Apply questions located at the end of selected Worked Examples assess understanding of principles rather than the ability to simply plug numbers into a formula.

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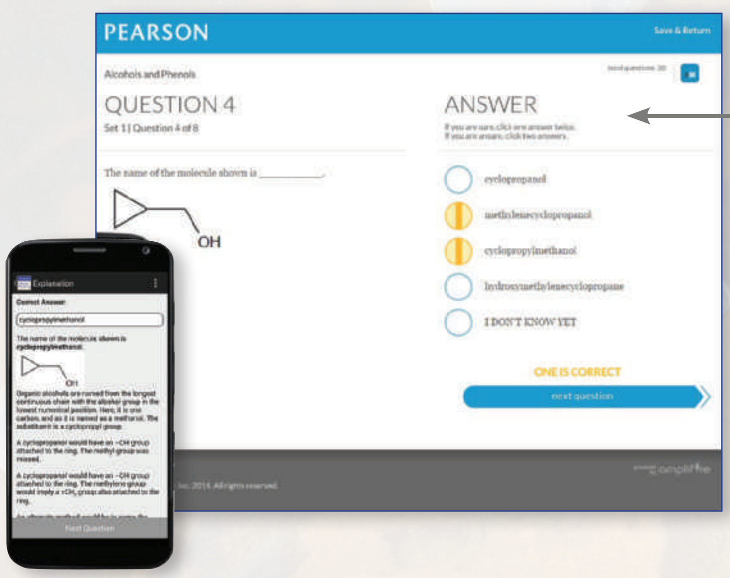

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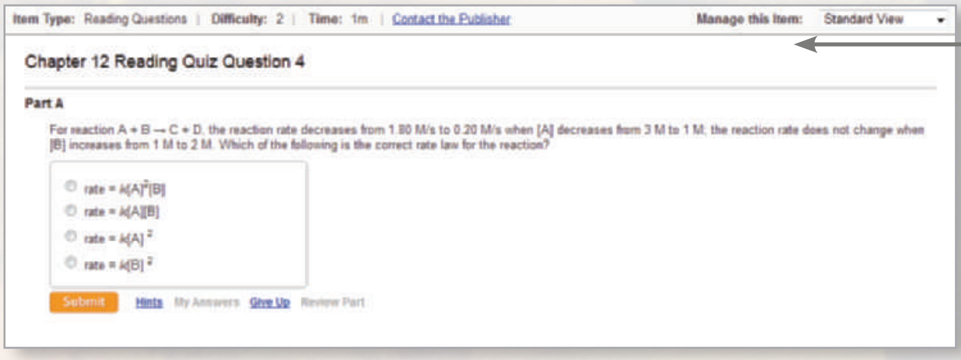
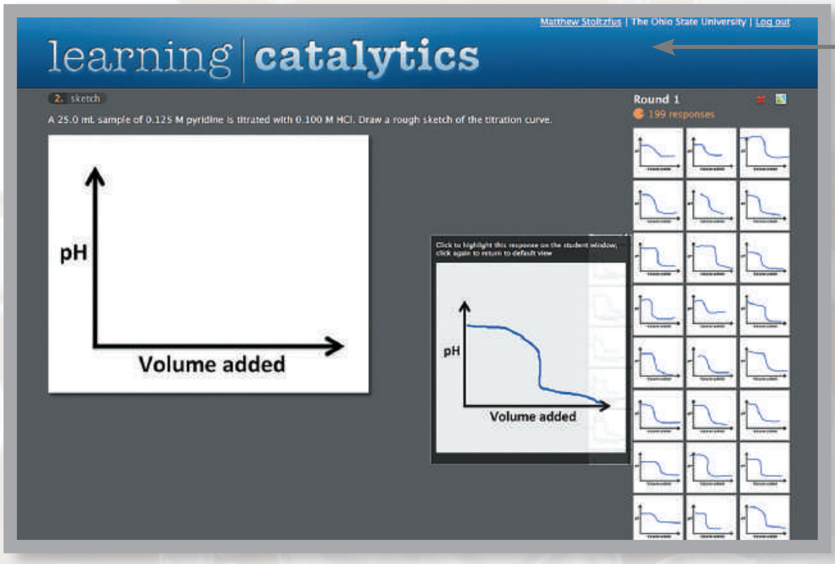


Reading Quizzes give instructors the opportunity to assign reading and test students on their comprehension of chapter content. Reading Quizzes are often useful to provide a common baseline for students prior to coming to class, thereby saving time on lower level content and allowing instructors to use in-class time on more challenging topic.

During Class



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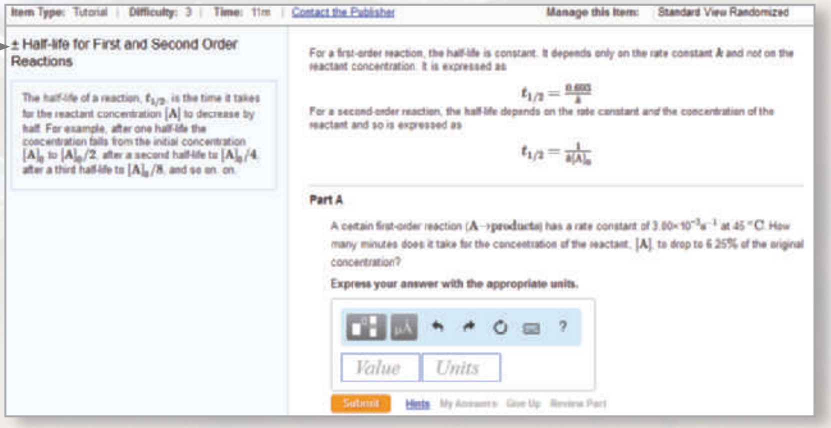

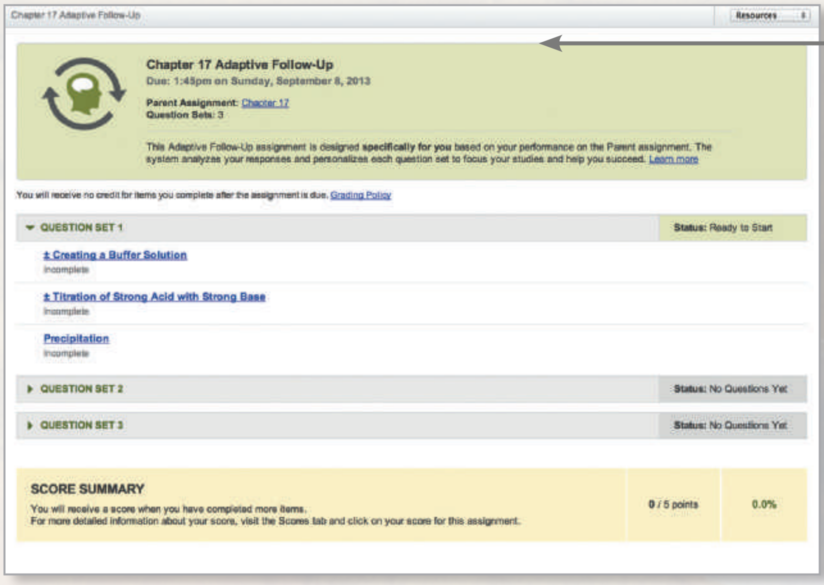

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For Students

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This manual contains worked out solutions to all in-chapter problems and even-numbered end-of-chapter problems.

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For Instructors

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Mark Benvenuto, *University of Detroit Mercy*

This resource contains the following:

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Chemistry

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