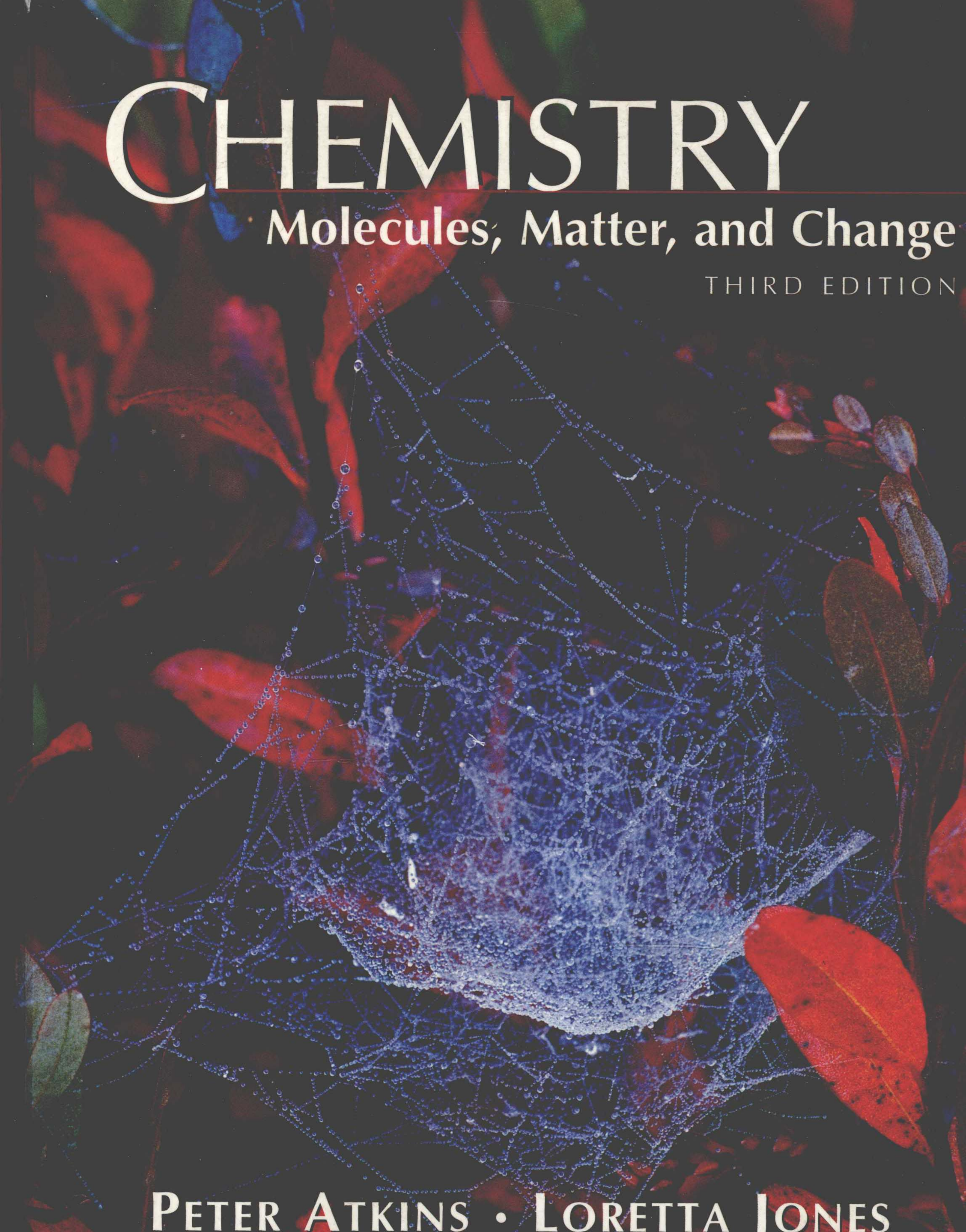
CHEMISTRY

Molecules, Matter, and Change

THIRD EDITION



PETER ATKINS • LORETTA JONES

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Molecules, Matter, and Change

THIRD EDITION

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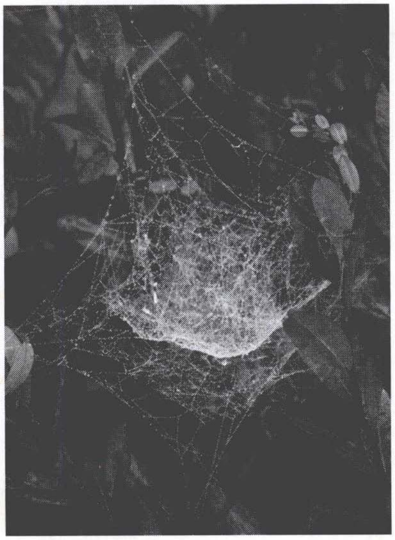
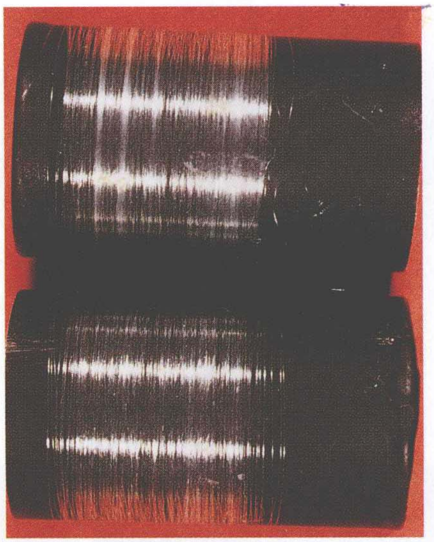
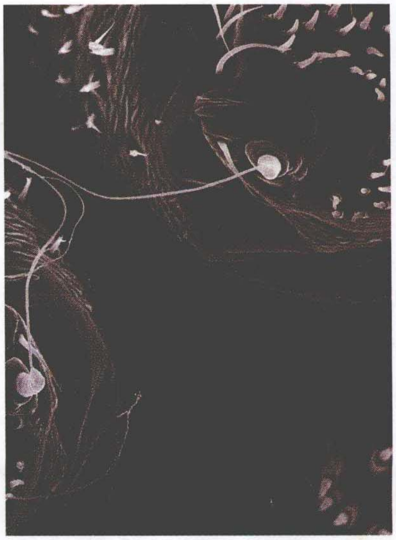


ABOUT THE COVER

Chemistry can be compared to a spider's web. Its interlinked ideas offer an astounding diversity—and a single, fascinating whole. The strength of a spider's web is also an inspiration to chemists, who have determined the structure of its material. Artificial spider's silk can now be made in bulk. It can be spun into thin, tough thread, as on the spools shown here, or wound into cables strong enough to support suspension bridges. It is a new synthetic polymer, a class of materials you will meet in Chapter 11.

Wherever we look, we find chemistry at work. In this textbook, we shall lead you through its intricate but rewarding paths. Before you are through, you will learn to see a spider's web, the color of leaves on a forest floor, and the rest of your world with a chemist's careful but penetrating eye.





PREFACE

Our principal aim is to impart *chemical insight*. From our many years of teaching experience, we know the difficulties students face as they begin to acquire a chemist's view of the world. We strongly believe that a textbook must connect observations—in the everyday world and in the laboratory—to the principles of chemistry. Our approach is always anchored in a student's experience and then goes beyond the perceived, to help students visualize entities they cannot see directly. It is essential to build a bridge between these realms of observation and imagination, so that students can understand phenomena in terms of atoms, molecules, and energy.

Our second major theme is how qualitative concepts lead to quantitative results. Stating and solving problems quantitatively is more than a basic skill in general chemistry. It is also part of the scientific method, and we believe that it too should be guided by chemical insight. These two aims—to convey chemical insight and to build quantitative skills—have remained constant over three editions.

Although this edition builds on the strengths of previous ones, we have introduced important changes to make chemistry more meaningful to students and to help them understand its principles. Most obvious is a new coauthor. Our two backgrounds have given us unique experience with a wide range of students, and we have developed material that works at very different institutions. Together, we have tried to make this edition more helpful to students than ever. We have changed the order of the chapters, rewritten them all, provided a completely new set of drawings and a great many new photographs, relied on important new technologies coming to use in today's classroom, and added many other features designed to make learning chemistry the exciting and rewarding experience we believe it can and should be. We wanted a third edition that is a pleasure to read, yet also is an efficient, innovative resource for teaching and learning.

When we look at changes in the natural world, from the germination of a seed through the unfurling of a leaf to the decay of fall leaves, we may be amazed by the variety of processes that can take place. Yet chemists have discovered that all chemical reactions can be classified into a limited number of types. These shoots of the bloodroot plant (Sanguinaria canadensis), *a member of the poppy family, make use of the reactions described in this chapter as they convert the debris of the forest floor into new living cells. The sap of the bloodroot was once used as a dye, and it contains medically active compounds.*

A DESIGN FOR LEARNING

We have kept in mind what it is like to be a student grappling with chemistry. We have retained two widely praised features of past editions—the problem-solving *Strategies* and the *Case Studies*. We have also rewritten most of the text to highlight succinctly and clearly the essential principles of the subject, and we have introduced many new features to develop a student's insight into chemistry.

CHAPTER OPENINGS

We typically open chapters by raising observations and applications of current interest. These first paragraphs, NEW to this edition, orient the student and suggest the purpose of the concepts to come. Where appropriate, we return to that opening theme throughout the chapter. We think our readers will see more easily how their accumulating knowledge and developing problem-solving skills help in resolving the important issues that they face every day.

> With every breath we take, we inhale carbon dioxide molecules along with the other gases of the air. Each breath connects us with history. Some of the carbon atoms in the molecules were once exhaled by our ancestors; in fact, some of them were exhaled by virtually everyone who has ever lived. One atom
>
> The progress of carbon atoms through the environment is called the **carbon cycle.** For example, some atmospheric carbon dioxide dissolves in seawater, where it is absorbed into the shells of shellfish. After the death of the animal, it is compressed to form limestone (calcium carbonate, $CaCO_3$). It may remain as
>
> **CHEMICAL EQUATIONS AND CHEMICAL REACTIONS**
> 3.1 Symbolizing chemical reactions
> 3.2 Balancing chemical equations
>
> **PRECIPITATION REACTIONS**
> 3.3 Aqueous solutions
> 3.4 Reactions between strong electrolyte solutions
> 3.5 Ionic and net ionic equations

THE BOTTOM LINE

> ***An aqueous strong electrolyte solution consists of hydrated ions that are free to move through the solvent.***

Each section of the text concludes with a one- or two-sentence summary of its principal points. We have found that these summaries, NEW to this edition, help to focus a student's attention on the "bottom line," and they are especially helpful when preparing for a test.

DRAWINGS OF THE MOLECULAR WORLD

Every drawing is NEW to this edition, and they number more than 700. All of them have been drawn—by us—to convey our understanding of the molecular world. By sharing our vision, we can help students develop their own understanding. Many drawings show molecular models, accurately scaled to help students visualize in three dimensions; each of these models is brought further alive on our accompanying CD-ROM.

ANIMATION SEQUENCES

Among other NEW features, certain illustrations look like screens from an animation. Unique to this book, they each bring vividly to life a dynamic sequence. Taking our cue from our CD-ROM, on which many of these illustrations become actual animations, we indicate the time sequence by a scroll bar across the screen.

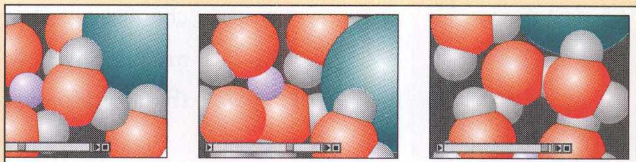


FIGURE 3.9 This animation sequence shows a series of scenes in a solution of sodium chloride. A sodium ion and a chloride ion move together, linger near each other for a time because of the attraction of their opposite charges, and then move apart and meet other partners elsewhere. The loose, transient association of oppositely charged ions is called an ion pair.

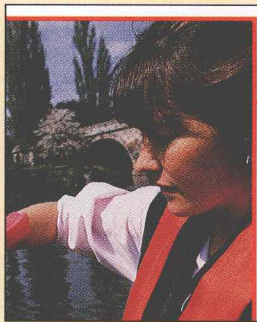
SIDENOTES

Also NEW to this edition, notes in the margin call out further information that might be useful in learning. Sidenotes take readers into our confidence, and they anticipate many of the questions that students often raise. They include the history of terms and ideas, as well as sections to review or anticipate as needed. A thumb button (◀◀ or ▶▶), which also becomes a "hot link" on our accompanying CD-ROM, flags these important cross-references.

▶▶ This definition is due to the Swedish chemist Svante Arrhenius. We shall meet a more general definition in Section 14.1.

CHEMISTRY AT WORK

Among the vast number of photographs NEW to this edition, every chapter highlights *Chemistry at Work*. Many students must take general chemistry courses before they have a clear idea of the relevance of chemistry to their chosen field. We show students that all kinds of people in all kinds of contexts use the techniques that they are struggling to learn. Chemistry, after all, is not just for chemists.



CHEMISTRY AT WORK

A pollution control officer samples water from a river in England. To ensure that the river is safe for drinking, fishing, and recreation, she monitors water quality frequently. She will analyze the acid content of the sample and will add reagents to precipitate heavy metal ions such as lead and mercury. If the pollutant

CASE STUDIES

We have expanded a popular feature of the second edition, the *Case Studies*. A *Case Study* looks in depth at a problem of topical interest, such as water treatment, pollution, the greenhouse effect, and the self-assembling molecules typical of life. We intend *Case Studies* to interest and motivate students, but because they also pull together the concepts of the

CASE STUDY FROM RIVER WATER TO DRINKING WATER

EVERY LARGE RIVER is tapped by cities for drinking water. The used water is then treated and returned to the river as sewage, along with industrial waste. As a result, the water in many rivers is growing more and more polluted. Water flowing through underground aquifers (porous rock layers) is relatively pure, but it is still not free of pollution.

Assuring a potable (consumable) drinking water supply is a major concern of today's cities and is the responsibility of water chemists and sanitary engineers. Domestic

and precipitates Mg^{2+}, Fe^{3+}, and heavy metal ions as hydroxides.

Hard water contains relatively high concentrations of Ca^{2+} and Mg^{2+} ions, often in the form of hydrogen carbonates. These cations precipitate in furnace boilers and react with soap to form a scum that is hard to remove from laundry. Magnesium and calcium hydrogen carbonates can … r by adding

QUESTIONS

1. Identify (a) the physical processes and (b) the chemical processes used for purifying raw water.

2. Classify by type each of the reactions used in the purification of water. If the reaction is a redox reaction, identify the oxidizing agent and the reducing agent.

3. Slaked lime is used to precipitate heavy metal ions.

chapter, each has its own short bank of questions. Many of the *Case Studies* are entirely new, and each now falls within the body of its chapter, rather than within exercise sets, to signal its relevance to important principles.

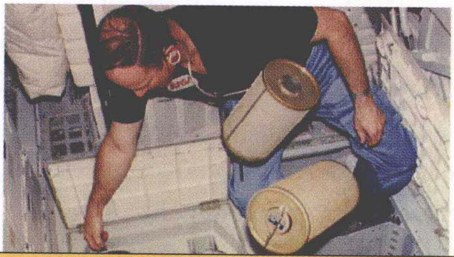
BOXES

NEW *Boxes* contain useful background, including techniques that chemists use today to determine relevant quantities. These *Boxes* are like islands of relief for tormented and shipwrecked students, for at least here they will find no exercises!

BOX 3.1 MAINTAINING AN ARTIFICIAL ATMOSPHERE

On Earth, our atmosphere is kept at a relatively constant composition by natural processes, such as photosynthesis and the movement of air (see Case Study 5). However, a submarine or space ship must use artificial air purifiers. Otherwise, the crew would suffocate in the carbon dioxide, CO_2, they produce. In such sealed environments, waste gases are removed and oxygen regenerated by a variety of acid-base and redox chemical reactions.

Because the space shuttle serves only for short flights, its oxygen can be stored on-board and need not



SKILLS YOU SHOULD HAVE MASTERED

The end-of-chapter summaries now take the form of *Skills You Should Have Mastered*. We have also divided these lists into conceptual, problem-solving, and descriptive skills. That division, NEW to this edition, organizes the information in the chapter, making it much less daunting. Acquiring understanding and information involves a constant to-and-fro between learning and review, and these review aids will make the process more effective by allowing students to monitor their progress easily.

SKILLS YOU SHOULD HAVE MASTERED

Conceptual

1. Explain the significance of a balanced chemical equation.
2. Identify solutions as electrolytes or nonelectrolytes on the basis of the formulas of the solutes.
3. Explain the difference between solutions of strong and weak acids and bases.
4. Define oxidation and reduction in terms of oxidation number and electron transfer.
5. Identify the oxidizing and reducing agents in a reaction.

Problem-Solving

1. Write, balance, and label a chemical equation,

3. Determine the oxidation number of an element in an ion or compound.
4. Use the solubility rules to select appropriate solutions which, when mixed, will produce a desired precipitate.

Descriptive

1. Write three balanced chemical equations for reactions that occur in the carbon cycle and describe their roles in the cycle.
2. Describe chemical properties of acids and bases.
3. Recognize common strong and weak acids and bases from their formulas.
4. Describe how acids react with water to form

BUILDING PROBLEM-SOLVING SKILLS

The interplay between the qualitative and the quantitative is central to the scientific method, but it is the hardest part of the course for many students. We provide a great deal of help.

STRATEGIES

Some 250 worked examples teach problem solving. All books have examples, but we use them in a special way. Not only do they illustrate the material, but—most important—they develop a student's ability to reason chemically. We therefore have retained a popular feature of past editions: *Strategies* that precede the solution to every worked example. The *Strategies* encourage students to collect their thoughts before embarking on a problem, they offer reminders of necessary concepts, and they show how to plan the steps toward a solution. Some *Strategies* suggest how to anticipate the magnitude of an answer before developing it in detail; others help in locating equations and data; still others explain when and how to rearrange an equation to find the unknown. In this edition we have rewritten the *Strategies* to make them more general in application, so that students are prepared to solve new problems on their own.

EXAMPLE 3.5 Devising a means of preparing a gas

Suggest a method for making the gas phosphine, PH_3. Phosphine is an extremely toxic gas that should be made only in a fume hood.

STRATEGY Because phosphine is a gas, we may be able to devise a reaction in which it is produced by the action of an acid on a suitable salt. To identify the salt to use as starting material, we examine the formula of phosphine,

TOOLBOXES

A NEW feature develops the approach of *Strategies* even further. *Toolboxes* set out how to tackle major calculations. Just as a hammer or a screwdriver serves on many occasions, the procedures described in our *Toolboxes* will come into play time and time again, in many different contexts. A student familiar with them will be well prepared for calculations they will encounter throughout their study of chemistry.

TOOLBOX 3.2 How to find oxidation numbers

To assign an oxidation number to an element, we start with two simple rules:

1. The oxidation number of an element uncombined with other elements is zero.
2. The sum of the oxidation numbers of all the atoms in a species is equal to its total charge.

The first of these rules tells us that hydrogen, oxygen, iron, and all other elements have oxidation numbers of 0 in their elemental forms. The second rule implies that the oxidation

by using these two rules in conjunction with the following specific values:

The oxidation number of hydrogen is +1 in combination with nonmetals and −1 in combination with metals.

The oxidation number of oxygen is −2 in most of its compounds.

The oxidation number of all the halogens is −1 unless the halogen is in combination with oxygen or another

SELF-TESTS

The *Self-Tests* are also NEW. Like the in-chapter exercises of previous editions, they let students test their ability to do a calculation similar to the one just presented in a worked example. However, now we supply *Self-Tests* in pairs, more than doubling their number. One has its answer in full view, to give the student instant feedback. The second of the pair has its answer hidden discreetly at the back of the book, as many instructors have requested. These

SELF-TEST 3.10A Find the oxidation numbers of sulfur, phosphorus, and nitrogen in (a) H_2S; (b) PO_4^{3-}; (c) NO_3^-, respectively.

[*Answer:* (a) −2; (b) +5; (c) +5]

SELF-TEST 3.10B Find the oxidation numbers of sulfur, nitrogen, and chlorine in (a) SO_3^{2-}; (b) NO_2^-; (c) $HClO_3$.

Self-Tests follow all worked examples and also appear at strategic places in *Toolboxes*. In addition, they occur on their own throughout the text, when it is important to reinforce understanding.

EXERCISES

Instructors will find plenty of material for assignment. There are now a huge number of *Exercises* at the ends of chapters: some 2000, in addition to several hundred *Self-Tests*. As in former editions, we first classify many by topic, leaving others as Supplementary Exercises, for a more balanced survey of each chapter. NEW to this edition are additional Challenging Exercises that require just a little more thought; they are also suitable for collaborative solution in the classroom. All exercises classified by topic are paired. Answers to odd-numbered *Exercises* appear at the back of the book, and all solutions are given in the *Solutions Manual* (the odd-numbered exercises) or the *Instructor's Resource Manual* (the even-numbered exercises). Every answer has been independently solved three times to ensure its accuracy.

CHALLENGING EXERCISES

3.77 Identify all the principal species that exist in aqueous solutions of (a) $HClO_2$; (b) NH_3; (c) CH_3COOH.

3.78 Identify all the principal species that exist in aqueous solutions of (a) CH_3NH_2; (b) HI; (c) $HClO_4$.

3.79 Write a balanced equation for the complete combustion (reaction with oxygen) of octane, C_8H_{18}, the

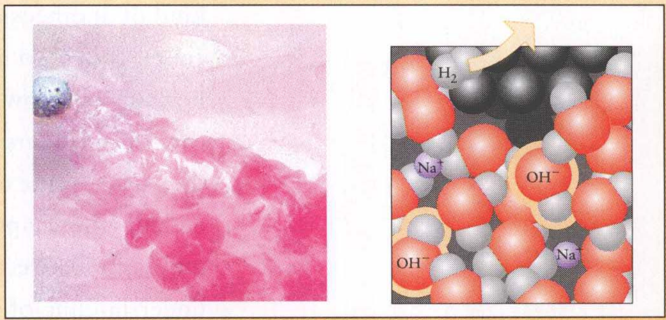
ORGANIZATION OF THIS EDITION

We have taken care that instructors can cover topics in more than one sequence, as they see fit. Yet we have made several innovations that we consider pedagogically important.

Chapter 1 is not the usual chapter on units. We feel strongly that students ought to be taken to the heart of chemistry on their first encounter with the subject. Therefore, we open the book with an introduction to elements and atoms. Chapter 1 also provides an early introduction to the periodic table, a unifying theme of the book. With this arrangement, students get an immediate introduction to chemistry.

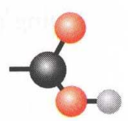
We now discuss units in **Chapter 2**, where we begin the quantitative treatment of data. This order reflects our theme of moving from qualitative understanding to quantitative skills. We include the mole here as simply another unit. Well, it *is* just another unit, and one of exceptional importance to chemists. We think a kid-gloves treatment of moles as something special (and, by implication, subtle and difficult) is misplaced. Given a natural, no-fuss introduction and lots of guidance and practice (which we provide), students should at last find moles easy to understand and deploy.

Another important innovation is **Chapter 11**, an early introduction to organic chemistry. Organic chemistry is so important for our understanding of the world that we consider it regrettable to tuck it away at the end of a text, where it is rarely reached. Although instructors may still defer this chapter if they wish, we believe that it provides superb examples for reviewing the formation and breaking of chemical bonds and an excellent means of reinforcing the ideas of the preceding chapters. It also makes a convenient teaching unit along with the chapter on liquid and solid materials; for that reason, it has an innovative target: synthetic and natural polymers. We introduce very few reactions, just enough to give the flavor of organic chemistry and to show how polymers are made. Students who leave the course after the first semester, and who most likely will never have a formal course in organic chemistry, will have had some exposure to this essential part of a chemical education.



Many of the other chapters will be found in familiar locations, but we have extensively revamped their content with an eye on level, presentation, and readability. We introduce that great organizational principle of chemistry, the periodic table, in **Chapter 1**, for it is so essential to the rationalization—not to mention the remembering—of chemical information, that we believe it should become an intrinsic part of a student's equipment as early as possible. We justify the structure of the periodic table later, providing a focus to **Chapter 7**, the discussion of atomic structure.

Chapter 3 develops an understanding of chemical reaction types early in the course; to maintain this focus, we have deferred balancing redox equations by the half-reaction method to **Chapter 17**. The description of the remaining class of reactions we consider, Lewis acid-base reactions, fits very naturally into the bonding chapter (**Chapter 8**), helping students more easily relate these reactions to the importance of the electron pair in chemistry.



5 Carboxyl group, COOH

Chapter 16 is the second of two bites at thermochemistry and thermodynamics. The first law of thermodynamics is a straightforward account of the production or absorption of heat. The second law accounts for all the equilibria that are encountered in the middle of the course, and we consider that it is correct to place it as a kind of apotheosis of that more quantitative and demanding part of the course. The two laws are presented together in Chapter 16. However, because we know that some instructors prefer to present the first law early in the course we have written the early parts of Chapter 16 so they could quite easily be used in conjunction with the introduction of enthalpy in Chapter 6, where they would certainly illuminate the difference between internal energy and enthalpy. We believe that an understanding of entropy helps to explain many chemical processes. With that in mind, we use the tendency toward disorder in a number of early chapters. In this way, students can build up an intuitive understanding of the concept before having to cope with it quantitatively and before mastering the term *entropy* explicitly.

We have deferred chemical kinetics to **Chapter 18**. Although it too may be taught when the instructor wishes, we chose to set it apart from **Chapters 12–17**, which are essentially the domain of equilibrium and thermodynamics. In short, we think it right to know *where* one is going before worrying about how fast one can get there. Yet, because we concur with the view that a qualitative knowledge of kinetics illuminates dynamic equilibria, we have not hesitated to invoke qualitative rate arguments when discussing equilibria.

As in earlier editions, the book concludes with a sequence of chapters on descriptive chemistry, but **Chapters 19–21** have been extensively revised, rewritten, and rearranged. Here we show how "descriptions" in fact make use of the principles that students are learning. Of course, there is a great deal of descriptive material in earlier chapters, for we always illustrate the principles with real phenomena. These later chapters, as instructors will recognize, provide a different cross section through the subject, where the properties are used as a vehicle for rationalization by principles rather than the other way round. We have had to be very selective in these chapters, as any instructor will appreciate, and our aim is to show that the elements have varied, intriguing personalities. After all, that is what chemistry is all about.

SUPPLEMENTS

Throughout the compilation of this edition, we have been in constant contact with our team of supplements authors, to ensure that the entire package is consistent and mutually enhancing.

CD-ROM

This multimedia learning tool, developed by W. H. Freeman and Company in conjunction with Sumanas, Inc., complements and enriches the textbook. All the features of the CD function within the context of the book's coverage. The entire textbook—with hyperlinked text and the illustrations in an electronic format—serves as the starting point for the CD. All structures in the book's margins are depicted as three-dimensional animations. These and the many other molecular-level simulations and video demonstrations bring the concepts of the book to life. Practice tools, such as interactive quizzes in every chapter, help students review for exams. The CD's customized calculator and dynamic periodic table/data base reduce the tedium of solving problems. Webnotes™ provide direct links to chemistry sites on the World Wide Web. Presentation software for instructors allows them to prepare a series of illustrations, animations, and videos for lecture.

STUDENT'S STUDY GUIDE

This reassuring volume by David Becker, Oakland University and Oakland Community College, reinforces concepts, provides additional practice exercises with answers, and highlights "Pitfalls," common student mistakes, so they can be better avoided.

STUDENT'S SOLUTIONS MANUAL

This manual by Charles Trapp, University of Louisville, contains complete solutions to the odd-numbered end-of-chapter exercises. Additional commentary on problem-solving techniques is included.

CHEMISTRY IN THE LABORATORY

This well-respected manual by Julian Roberts and Leland Hollenberg, University of Redlands, and James M. Postma, California State University at Chico, is now in its fourth edition. It contains 44 lab-tested experiments and a new emphasis on safety and waste disposal. Many new reduced-scale experiments that do not require a full wet lab have been included. All experiments are available as lab separates.

STUDENT COMPANION

The new *Student Companion: New Tools and Techniques for Chemistry*, by Lynn Geiger, Belia Straushein, and Loretta Jones, University of Northern Colorado, is a unique student supplement that offers blueprints for using innovative approaches and emerging technologies to invigorate the teaching and study of general chemistry. Student worksheets and other materials in the *Companion* will aid instructors in incorporating the new techniques of collaborative learning and guided readings in their classrooms. Worksheets for assignments that involve students in the power of the Web and the features of our CD-Rom are also provided.

INSTRUCTOR'S RESOURCE MANUAL

This useful manual by Lowell Parker, Stevens Institute of Technology, contains sample syllabi, lecture outlines, teaching hints and transparency masters. Solutions to the textbook's even-numbered exercises by Charles Trapp, University of Louisville, are included, as is a guide for using the *Student Companion*.

TEST BANK

The test bank by Robert Balahura, University of Guelph, contains two sets of 75 multiple-choice questions and 10 short-answer questions per chapter—double the number of previous editions. The test bank is available in both printed and electronic form, and the test bank software is also new to this edition.

GENERAL CHEMISTRY VIDEODISC

Approximately 100 vivid experiments are again available to the instructor for lecture presentations.

OVERHEAD TRANSPARENCIES

More than 200 transparencies with large-type labels illustrate the key figures and tables.

CHEMISTRY WEB SITE

Students and instructors should visit our site (http://www.whfreeman.com/chemistry3e) for a variety of useful features including study questions, WebNote links to other useful sites, updates, and video lab demonstrations specially formatted for viewing on the Web.

ACKNOWLEDGMENTS

No project as big as this can make progress, let alone come to fruition, without the assistance of large numbers of people. We are both deeply indebted to all those who shared their time with us: we know that we have benefitted greatly from the suggestions that they have made to us. We try to build on the great store of wisdom and experience that the chemical education community collectively represents—and to push forward the frontiers. We would particularly like to thank the following people for their input:

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