

SECOND EDITION

CHEMICAL PRINCIPLES

The Quest for Insight

Peter Atkins Loretta Jones

CHEMICAL PRINCIPLES

The Quest for Insight

SECOND EDITION

PETER ATKINS

Oxford University

LORETTA JONES

University of Northern Colorado

Web animation by

ROY TASKER

University of Western Sydney



W. H. FREEMAN AND COMPANY
NEW YORK

<i>Acquisitions Editor:</i>	JESSICA FIORILLO
<i>Publisher:</i>	MICHELLE RUSSEL JULET
<i>Development Editor:</i>	MARJORIE SINGER ANDERSON
<i>Assistant Editor:</i>	ROBERT JORDAN
<i>New Media and Supplements Editor:</i>	CHARLES VAN WAGNER
<i>Marketing Director:</i>	JOHN A. BRITCH
<i>Senior Project Editor:</i>	GEORGIA LEE HADLER
<i>Copy Editor:</i>	JODI SIMPSON
<i>Cover and Text Designer:</i>	CAMBRAIA FONSECA FERNANDES
<i>Illustration Coordinator:</i>	CECILIA VARAS
<i>Illustrations:</i>	PETER ATKINS WITH NETWORK GRAPHICS
<i>Photo Editor:</i>	MEG KUHTA
<i>Production Coordinator:</i>	PAUL W. ROHLOFF
<i>Composition:</i>	BLACK DOT GRAPHICS
<i>Manufacturing:</i>	RR DONNELLEY & SONS COMPANY
<i>Web Animations:</i>	ROY TASKER UNIVERSITY OF WESTERN SYDNEY CADRE DESIGN

All VisChem animation photos provided by Dr. Roy Tasker, VisChem Project, University of Western Sydney.

Library of Congress Cataloging-in Publication Data

Atkins, P.W. (Peter William)
 Chemical principles: the quest for insight/Peter Atkins, Loretta Jones.—2d ed.
 p. cm.
 Includes index.
 ISBN 0-7167-3923-2
 1. Chemistry. I. Jones, Loretta. II. Title.
 QD33.2.A74 2001
 540—dc21

2001023890

© 1999, 2002 by P. W. Atkins and L. L. Jones. All rights reserved.

No part of this book may be reproduced by any mechanical, photographic, or electronic process, or in the form of a photographic recording, nor may it be stored in a retrieval system, transmitted, or otherwise copied for public or private use, without written permission from the publisher.

Printed in the United States of America

Third printing, 2002

CHEMICAL PRINCIPLES

The Quest for Insight

About the cover: The cover image is a part of a computer-generated molecular model of an enzyme regulator (aspartate carbamoyltransferase). Models such as these help scientists understand how biomolecules such as enzymes control the processes of life—in this case, the biosynthesis of pyrimidine. Molecular representations and graphics in general have transformed the way that chemists do research and are an essential part of learning chemistry and developing insight into the nature and properties of matter. (Francis Leroy/Biocosmos/SPL Photo Researchers.)

PREFACE

ATOMS-FIRST ORGANIZATION

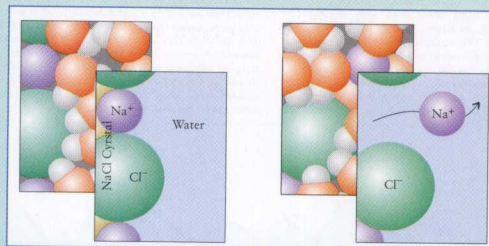
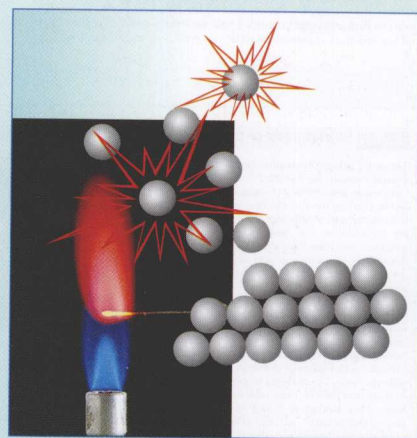
The unique atoms-first sequence of *Chemical Principles* develops student understanding of the concepts of chemistry by starting with the behavior of atoms and molecules and building to more complex properties and interactions:

- **Atoms and molecules** come first (including discussions of quantum mechanics and molecular orbitals), providing the foundation for understanding bulk properties and models of gases, liquids, and solids.
- Next comes an exploration of **thermodynamics and equilibrium** based on conceptual understanding of free energy and entropy. This integrated presentation lays a common foundation for these concepts and provides a basis for the form of the equilibrium constant.
- **Kinetics** then shows the dynamic nature of chemistry and the crucial role of insight and model building in identifying reaction mechanisms.
- A section on **fundamentals**, streamlined and updated in this new edition, precedes Chapter 1 for a flexible overview of the basics.

VISUALIZATION

Conceived and executed by the authors, the art in *Chemical Principles* is designed to help students make the connections between what chemists imagine and what they perceive, between chemical models and laboratory observations. More than 15 percent of the art in the second edition is new.

- **Connections between the microscopic and macroscopic.** Many illustrations are paired with photographs or drawings of chemical systems, starting with the molecular model superimposed on each chapter's opening photograph. The combination of representations, from macroscopic to microscopic, abstract to concrete, and graphical to pictorial, helps students bridge the gap between the imagined and the perceived.
- **Realistic images show molecular dynamics.** Multistep graphics show how molecules and ions move and interact, highlighting the sense of motion so critical to chemical understanding. Most of these sequences are further illustrated by actual animations available on the Web site.



CONTEMPORARY CHEMISTRY

- **Emphasis on thinking like a chemist.** Throughout the book, *Chemical Principles* shows students how chemists propose models based on insight, develop those models with mathematics, and refine them through experimentation. This approach is used to help students

MAJOR TECHNIQUE 2

ULTRAVIOLET AND VISIBLE SPECTROSCOPY

If the colors of vegetation around us arise from the selective absorption and reflection of visible light. If our eyes were sensitive to ultraviolet radiation—the electromagnetic radiation at shorter wavelengths (higher frequencies) than violet light—we would see an even richer tapestry of color, because substances also absorb and reflect selectively in the ultraviolet region. Honeybees do have this ability, and they can “see” radiation in the ultraviolet as well as in the visible range. This selective absorption and transmittance of visible light and ultraviolet radiation is the basis of a technique for identifying compounds and for determining their concentration in samples.

The Technique

When electromagnetic radiation falls on a molecule, the electrons in the molecule can be excited to a higher energy state. If the frequency of the radiation is ν (nu), it can raise the molecule to a state that differs in energy from the first state by an amount ΔE , where

$$\Delta E = h\nu \quad (1)$$

h is the Planck frequency constant, which was introduced in Section 1.6; h is the Planck constant, or ultraviolet wavelengths of 300 nm and less corresponding to a frequency of about 10^{15} Hz or

hence be absorbed. Therefore, the study of visible and ultraviolet absorption gives us information about the electronic energy levels of molecules.

Visible and ultraviolet (UV) absorption spectra are measured in an absorption spectrometer. The source gives out intense visible light or ultraviolet radiation. The wavelengths can be selected with a glass prism for visible light and with a quartz prism or a diffraction grating for ultraviolet radiation (which is absorbed by glass). A typical absorption spectrum, that of chlorophyll, is shown in Fig. 1. Note that chlorophyll absorbs red and blue light, leaving the green light present in white light to be reflected. That is why most vegetation looks green. The spectrum can help us to assess the absorption quantitatively and to make a precise analysis of the energy-capturing power of the molecule.

2 Chromophores

The presence of certain absorption bands in visible and ultraviolet spectra can often be traced to the presence of characteristic groups of atoms in the molecules. These groups of atoms are called *chromophores*, from the Greek words for “color bringer.”

One important chromophore is a carbon-carbon double bond. In terms of the language of molecular orbital theory, the electronic transition that occurs when energy is absorbed is the excitation of an electron

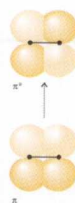


FIGURE 2 In a π -to- π^* transition, an electron in a bonding π -orbital is excited into an empty antibonding π^* -orbital.

The transition can be brought into the visible region—by decreasing the separation between bonding and antibonding orbitals—if the molecule has a chain of alternating single and double bonds. Such “conjugated” double bonding occurs in the compound carotene

for the color of carrots, mangoes, and persimmons. Related compounds account for the colors of shrimp and flamingoes. This transition is also responsible for the primary act of vision, as explained in Section 3.8.

Another important chromophore is the carbonyl group, $\text{C}=\text{O}$, which absorbs at about 280 nm. The transition responsible for the absorption is the excitation of a lone-pair electron on the oxygen atom (a “nonbonding” electron, denoted n) into the empty antibonding π^* -orbital of the $\text{C}=\text{O}$ double bond (Fig. 3). This transition is therefore called an n -to- π^* (n to pi star) transition.

A d -metal ion may also be responsible for color, as is apparent from the varied colors of many d -metal complexes (see Chapter 16). Two types of transitions may be involved. In one, which is called a d -to- d transition, an electron is excited from a d -orbital of one energy to a d -orbital of higher energy. Because the energy differences between d -orbitals are quite small, visible light brings enough energy to cause this excitation, so colors are absorbed from white light and the sample takes on colors complementary to those observed (Fig. 4). A second type of transition is called a charge-transfer transition, in which electrons migrate from the atoms attached to the central metal atom into the latter’s d -orbitals, or vice versa. This transfer of charge can result in very intense absorption; it is

THE IMPACT ON MATERIALS

Metals are the mainstays of technology, and it is hardly surprising that so much effort has gone into the development and understanding of their properties. We deal with their electrical properties in Section 3.14. Here we explore some of their other physical properties.

5.14 The Properties of Metals

In a metallic solid, cations lie in a regular array and are surrounded by a sea of electrons. This structure results in unique properties. The characteristic luster of metals is due to the mobility of their electrons (Section 3.14). An incident light wave is an oscillating electromagnetic field. When it strikes the surface, the electric field of the radiation pushes the mobile electrons backward and forward. These oscillating electrons radiate light, and we see it as a luster—essentially a reflection of the incident light

understand key concepts and also to expand students’ ideas of how to apply these concepts to modern research.

- Major Techniques interchapters introduce students to important experimental methods, connecting the classroom, the laboratory, and the world.
- New and updated Impact on Materials and Impact on Biology sections explore the burgeoning fields of materials chemistry and biological chemistry while reinforcing chemical principles. These sections introduce students to new fields and innovations.
- Frontiers of Chemistry boxed essays explore modern chemical research and communicate the excitement of working at the cutting edge of chemistry. Each Frontiers of Chemistry box asks students, “How Might You Contribute?”—challenging them to lead the way in solving global problems by using their understanding of chemistry.

BOX 3.1

FRONTIERS OF CHEMISTRY: DRUGS BY DESIGN AND DISCOVERY

The search for new drugs relies on the skills of synthetic organic chemists. Because there are so many millions of compounds, it would take too long to start with the elements, combine them in different ways, then test them. Instead, chemists usually start either by *drug discovery*, the identification and possibly the modification of promising medicines that already exist, or by *rational drug design*, the identification of characteristics of a target bacterium or parasite and the design of new compounds to react with it.

In drug discovery, a chemist usually begins by investigating compounds that have already shown medicinal value. A fruitful path is to find a *natural product*, a substance found in nature, that has been shown to have healing characteristics. Nature is the best of all synthetic chemists, with billions of chemicals that fulfill as many different needs. The challenge is to find compounds that have curative powers. These substances are found in different ways: random or “blind” collection of samples that are then tested or collection of specific samples identified by native healers as medically effective.

Observation of the properties of plants and animals can help to guide a random search. For example, if certain types of fruits remain fresh while others rot or become moldy, we might expect them to contain antifungal agents. One example of this type of collection is the gathering of tunicates and sponges in the Caribbean. The chemists harvest the samples by diving from research vessels (see Fig. F.1). The samples are tested for antiviral and antitumor activity in a chemical laboratory on the ship. The antiviral drug didemnin-C and



A field biologist examines a plant in a South American rainforest. The plant produces chemicals that will be investigated for their medicinal value.

the anticancer drug bryostatin 1 were discovered in marine organisms.

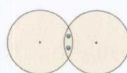
The guided route involves the testing of fewer samples because the chemist works with a native healer, the ancient role guiding the modern chemistry. Often an ethnobotanist, a specialist in plants used for native healing, joins the team. This approach saves time for the scientists and can provide an economic benefit for the healers and their nations as well. Drugs that have been discovered in this way include a variety of anticancer and antimicrobial drugs, blood-clotting agents, antibiotics, and medicines for the heart and digestive system.

PROBLEM SOLVING

Students at all levels benefit from the support of strong pedagogy. These proven strategies that build student confidence in their mastery of the concepts have been improved and enhanced.

- “Bottom line” statements summarize the key ideas in each section.

Atoms of all metallic elements are held in the solid or liquid state by “metallic bonds,” which are discussed in Section 5.9.



and the polyatomic species P_4 and S_8 . Elements near the border between metals and nonmetals can form solids with an extended network of atoms, such as crystalline silicon and the graphite or diamond forms of carbon. Covalent bonding is also important in the formation of compounds. There are also countless examples of diatomic, polyatomic, and extended network compounds between different nonmetallic elements, including the millions of organic compounds.

Lewis thought of the shared pair of electrons as lying between the two atoms and interacting with both their nuclei (6). The two atoms are bound together as a result of the coulombic attraction between the two electrons and the nuclei. Neither atom has to release an electron totally, so neither atom has to be supplied with its full ionization energy.

Nonmetallic elements form covalent bonds to one another by sharing pairs of electrons.

EXAMPLE 4.1 Using Boyle's law

Assume that when you press in the piston of a bicycle pump, the volume inside the pump is decreased from about 100 cm³ to 20 cm³ before the compressed air flows into the tire. Suppose that the compression is isothermal; estimate the final pressure of the compressed air in the pump, given an initial pressure of 1.00 atm.

STRATEGY In calculations of this kind, it is a good idea to summarize in a table the data supplied and the information required. We expect the final pressure, P_2 , to be higher than the initial pressure, P_1 , because the volume occupied by the air has been decreased. Because the product of pressure and volume is a constant, we can use Eq. 4 to write

$$P_2 V_2 = P_1 V_1 \quad \text{or} \quad \frac{P_2}{P_1} = \frac{V_1}{V_2}$$

where V_1 is the initial volume and V_2 is the final volume. We then rearrange this expression into one for P_2 in terms of P_1 and the ratio of volumes, and substitute the data.

SOLUTION The information given and required is summarized in the following table:

	Pressure, P	Volume, V	Temperature, T	Amount, n
1. Initial	1.00 atm	100 cm ³	same	same
2. Final	?	20 cm ³	same	same

- **Worked Examples** include **Strategy** sections that show students how to organize information and solve problems.

- The new edition also introduces the “How can we use this information . . . ?” feature. These brief demonstrations of mathematical formulae and concepts immediately follow and reinforce new material.

How can we use this information . . . to determine the temperature of the surface of a star?

Wien's law can be used to determine the surface temperature of stars, which can be treated as hot black bodies. For example, the maximum intensity of solar radiation occurs at 490 nm, so the surface temperature of the Sun must be about

$$T = \frac{C_2}{5\lambda_{\text{max}}} = \frac{1.44 \times 10^{-2} \text{ K}\cdot\text{m}}{5 \times 4.90 \times 10^{-7} \text{ m}} = 5.88 \times 10^3 \text{ K}$$

or about 6000 K.

Self-Test 1.2A In 1965, it was discovered that the universe is pervaded by electromagnetic radiation with a maximum at 1.05 mm (in the microwave region). What is the temperature of “empty” space? [Answer: 2.74 K]

Self-Test 1.2B A red giant is a dying star. The average wavelength maximum at 700 nm shows that a red giant cools as it dies. What is the surface temperature of a red giant?

- **Toolboxes** show students how to tackle major types of calculations. They are designed as learning aids and handy summaries of key material. In the new edition, each Toolbox now begins with explicit statements of that Toolbox's **conceptual basis** and **procedure**. Each Toolbox is immediately followed by a related example or sample calculation.

Self-Test 1.15A Arrange each pair of ions, (a) Mg²⁺ and Al³⁺, and (b) O²⁻ and S²⁻, in order of increasing ionic radius.

[Answer: (a) $r(\text{Al}^{3+}) < r(\text{Mg}^{2+})$; (b) $r(\text{O}^{2-}) < r(\text{S}^{2-})$]

Self-Test 1.15B Arrange each pair of ions, (a) Ca²⁺ and K⁺, and (b) S²⁻ and Cl⁻, in order of increasing ionic radius.

- **Self-Tests.** All worked examples and “How can we use this information . . . ?” features end with paired self-tests, one answered immediately, the other with a mini-solution in the back of the book.

- **Exercises.** Kenton Whitmire of Rice University has enriched the exercises with additional questions at all levels of difficulty, including questions that require students to use the media on the Web site for this book.

78 CHAPTER 2 CHEMICAL BONDS

TOOLBOX 2.1 How to write the Lewis structure of a polyatomic species**Conceptual Basis**

We look for ways of using all the valence electrons to complete the octets (or duplets).

Procedure

We take the following steps, which are illustrated for HCN in Fig. 2.8:

Step 1 Count the number of valence electrons on each atom. Divide the total number of valence electrons in the molecule by 2 to obtain the number of electron pairs.

Step 2 Predict the most likely arrangements of atoms by using common patterns and the clues indicated in the text, then write the chemical symbols of the atoms to show their layout in the molecule.

Step 3 Place one electron pair between each pair of bonded atoms.

Step 4 Complete the octet (or duplet, in the case

of H) of each atom by placing any remaining electron pairs around the atoms. If there are not enough electron pairs, form multiple bonds.

Step 5 Represent each bonded electron pair by a line.

To check on the validity of a Lewis structure, verify that each atom has an octet or a duplet.

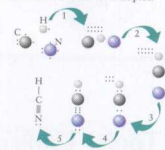


FIGURE 2.8 The five steps used to write the Lewis structure of HCN, as described in this Toolbox.

EXAMPLE 2.3 Writing the Lewis structure of a molecule or an ion

Write the Lewis structures of (a) water, H₂O; (b) methanol, H₃CO; and (c) the chlorite ion, ClO₂⁻.

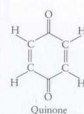
STRATEGY We can write the Lewis structures of molecules and ions by following the steps in Toolbox 2.1 and remembering to adjust the number of electrons for ions. Therefore, we add one electron for the negative charge of ClO₂⁻. Find the central atom by inspecting formulas. In methanol, the central atom must be C, because it has a central position and the H atoms can each form only one bond.

SOLUTION

	(a) H ₂ O	(b) H ₃ CO	(c) ClO ₂ ⁻
1 Number of valence electrons	8	12	20
Number of electron pairs	4	6	10
2 Layout of structure	H O H	H C O H	O Cl O

2.101 Quinone, C₆H₄O₂, is an organic molecule that can be reduced to give a dianion: [C₆H₄O₂]²⁻.

(a) Draw the Lewis structure of the reduced product. (b) On the basis of formal charges derived from the Lewis structure, predict which atoms in the molecule are most negatively charged. (c) If two protons are added to the reduced product, where are they most likely to bond?



Quinone

2.102 In air, the NO radical can react with the NO₂ radical. What is the most likely product of the reaction? Answer this question by drawing Lewis structures of the reactants and products.

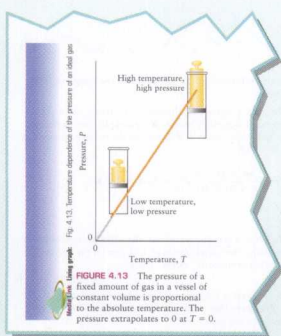
different types of hydrogen atoms will be found in the following molecules: (a) C₂H₂; (b) C₂H₄; (c) C₂H₆Cl₂; (d) cis-C₂H₂Cl₂; (e) trans-C₂H₂Cl₂. (f) In the molecule C₂H₃Cl, the hydrogen atoms could all be different; yet by a variety of experimental techniques, only two types of hydrogen atoms are found. Propose an explanation.

2.106 Predict which bond will absorb light of shorter wavelength and explain why: C—H or C—Cl'. Refer to Major Technique 1 on infrared spectroscopy, which follows these exercises.

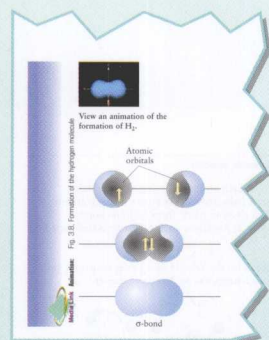
2.107 Infrared spectra show absorption due to C—H bond stretching at 3.38 μm for a methyl (—CH₃) group and at 3.1 μm for an alkyne (—C≡C—H) group. Which C—H bond is stiffer (has the larger force constant k), assuming that the vibrating atoms have the same effective mass? Refer to Major Technique 1 on infrared spectroscopy, which follows these exercises.

2.108 Vibrational spectra are often so complicated that assignment of a particular absorption to a given bond is difficult. One way to confirm that an assignment is

NEW! INTEGRATED WITH MEDIA LINKS TO . . .



- **Living Graphs.** Selected graphs in the text are available on the Web site. Students can manipulate parameters and explore the consequences.

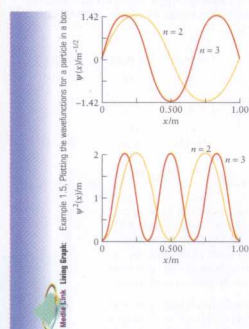


- **Lab Videos.** Video clips of many of the reactions described in the book are provided on the book's Web site.



- **Animations.** Selected art in the text is supported by media. Students can view motion, three dimensional images, atomic and molecular interactions and learn to visualize like chemists—at a microscopic level.

- **Tools.** Tools on the book's Web site allow the study of chemical calculations, graphing, and the exploration of periodic properties from different points of view.



MEDIA EXAMPLE 1.5 Plotting the wavefunctions for a particle in a box

(a) Using the Living Graphs on the Web site for this box, plot the wavefunction for $n = 2$ and $L = 1$ m. (b) Plot the wavefunction for $n = 3$ and $L = 1$ m. (c) What general conclusion about the relation between n and the number of nodes can you draw? (d) Convert the $n = 2$ plot to a probability density plot. (e) Convert the $n = 3$ plot to a probability density plot. (f) Repeat part (e) for $n = 3$.

STRATEGY The wavefunctions for a particle in a box are shown in Fig. 4.28. (a) To graph the wavefunction for $n = 2$ and $L = 1$ m, set the range for the entire 1 m, check the $f(x)$ box, and hit New Plot. (b) The wavefunction for $n = 3$ and $L = 1$ m is shown in the plot at that point. (c) Create a new plot as before. (d) Look for the patterns in node number and n . (e) Repeat part (e) for $n = 3$.

SOLUTION The plots are shown on the left. (b) The plot for $n = 2$ and $L = 1$ m has two nodes at $x = 0.33$ m and $x = 0.67$ m. (d) The number of nodes is equal to $n - 1$. (e)

- **In-Chapter Examples.** Designed to encourage students to use the media, these examples show students how to use the tools and art provided on the book's Web site.

4.73 Calculate the root mean square speeds of (a) methane; (b) ethane; and (c) propane molecules, all at -20°C .

4.74 Calculate the root mean square speed of (a) fluorine gas; (b) chlorine gas; and (c) bromine gas molecules, all at 350°C .

4.75 Consider the Maxwell distribution of speeds found in Fig. 4.28. (a) From the graph, find the location that represents the most probable speed of the molecules. (b) What happens to the percentage of molecules having the most probable speed as the temperature increases?

4.76 (a) Using the Living Graphs program on the Web site for this text, create and print a plot of the Maxwell distribution of molecular speeds for the noble gases He, Ne, Ar, Xe, and Kr from $s = 0$ to 2000 m s^{-1} . (b) Describe the trends observed in the graph in part (a). (c) Again using the Living Graphs program, create graphs for He and Kr at 100 K and at 300 K . (d) Describe the trends observed in part (c).

(b) Under these conditions, which term has the larger effect on the real pressure of CO_2 , the intermolecular attractions or the molar volume? (c) If we consider to be ideal those gases for which the observed pressure differs by no more than 5% from the ideal value, at what pressure does CO_2 become a "real" gas?

4.82 Calculate the pressure exerted by 1.00 mol of (a) an ideal gas; (b) ammonia; (c) oxygen gas, for the range $V = 0.05\text{ L}$ to 1.0 L at 298 K. Use a spreadsheet or the graphical plotter on the Web site for this book. Compare the plots and explain the origin of any differences you find.

4.83 Plot pressure against volume for 1 mol of (a) an ideal gas; (b) ammonia; (c) oxygen gas, for the range $V = 0.05\text{ L}$ to 1.0 L at 298 K. Use a spreadsheet or the graphical plotter on the Web site for this book. Compare the plots and explain the origin of any differences you find.

4.84 Plot pressure against volume for 1 mol of (a) an ideal gas; (b) carbon dioxide; (c) ammonia; (d) benzene for the range $V = 0.1\text{ L}$ to 1.0 L at 298 K. Use the van der Waals

- **End-of-Chapter Exercises.** Selected exercises direct students to use media to solve problems.

SUPPLEMENTS FOR *CHEMICAL PRINCIPLES*, SECOND EDITION

Media

Web-based media support for *Chemical Principles* offers students a range of tools for problem solving and chemical exploration.

Chemical Principles Web site at
www.whfreeman.com/chemicalprinciples

- Animations that allow students to visualize reactions on a molecular level
- “Living Graphs,” which allow the user to control the parameters
- Graphing tools
- Question and Answer—self-scoring quizzes for every chapter and for the Fundamentals provide instant feedback and help students review their knowledge of chemistry.
- Web links that keep students up to date in the world of chemistry
- A calculator adapted for solving equilibrium calculations
- An interactive periodic table of the elements

In addition, all the illustrations and tables from the textbook are available for the instructor in a downloadable format.

Bridging to the Lab (BTL)

Loretta Jones, University of Northern Colorado, and Roy Tasker, University of Western Sydney

The Bridging to the Lab modules are computer-based laboratory simulations with engaging activities that emphasize experimental design and visualization of structures and processes at the molecular level. Every module has a built-in accountability feature that records section completion for use in setting grades.

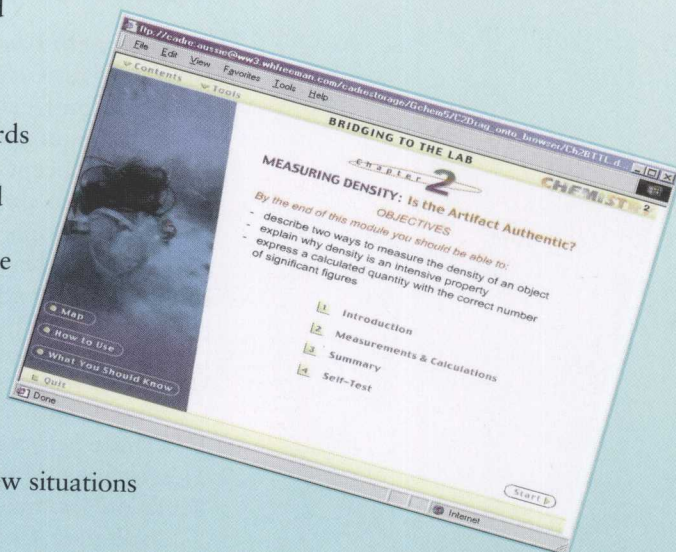
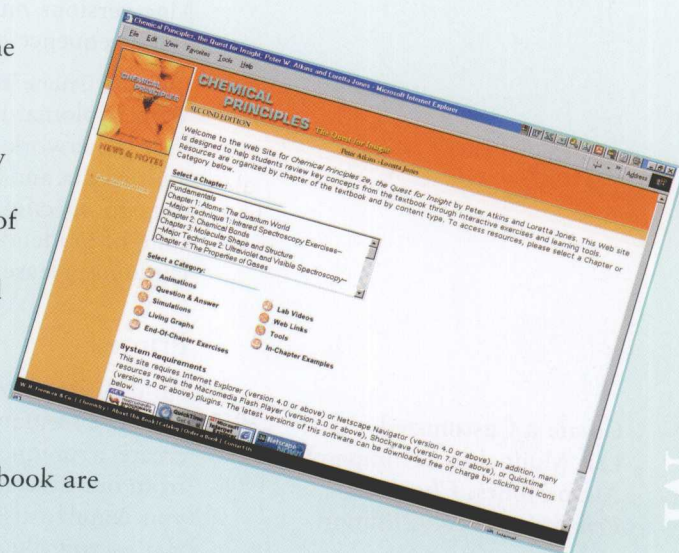
Used either as prelaboratory preparation for related laboratory activities or to expose students to additional laboratory activities not available in their program, these modules motivate students to learn by proposing real-life problems in a virtual environment. Students make decisions on experimental design, observe reactions, record data, interpret these data, perform calculations, and draw conclusions from their results. Following a summary of the experiment, students test their understanding by applying what they have learned to new situations or by analyzing the effect of experimental errors.

Assessment

Online Quizzing, powered by Question Mark

An excellent on-line quizzing bank from which instructors can easily quiz students using prewritten, multiple-choice questions for each text chapter (not from the Test Bank). Students receive instant feedback and can retake quizzes multiple times. Instructors can go into a protected Web site

Access via the
Chemical Principles
 Web site



to view results by quiz, student, or question, or can get weekly results via e-mail. Excellent for practice testing or homework or both.

Test Bank CD-ROM (Windows and Mac versions on one disk)

Robert Balahura of the University of Calgary, 0-7167-4434-1;
printed: 0-7167-4433-3

The Test Bank offers more than 1400 multiple-choice, fill-in-the-blank, and essay questions. The easy-to-use CD version includes Windows and Mac versions on a single disk, in a format that lets instructors add, edit, and resequence questions to suit their needs.

Diploma Online Testing, from the Brownstone Research Group

With Diploma, instructors can easily create and administer secure exams over a network and over the Internet, with questions that incorporate multimedia and interactive exercises. The program allows them to restrict tests to specific computers or time blocks, and includes an impressive suite of gradebook and result-analysis features. For more information on Diploma, please visit their Web site: www.brownstone.net

Printed

For the Laboratory

W. H. Freeman and Company is pleased to offer you the ability to create a unique lab manual for your course in just minutes. Drawing from our diverse library of experiments, you can pick and choose the labs you want to use, and even add your own materials. Organize the material as you like, customize the cover, view your newly created book on-line in PDF format, and then order it on-line with the click of a button. W. H. Freeman's state-of-the-art custom publishing system is easy to use and an excellent alternative to traditional lab manuals. Try it today at <http://custompub.whfreeman.com>

Working with Chemistry Lab Manual, Donald J. Wink and Sharon Fetzer Gislason, University of Chicago, Illinois, and Julie Ellefson Kuehn, William Rainey Harper College, 0-7167-3549-0

With this inquiry-based program, students build skills by using important chemical concepts and techniques to design a solution to a scenario drawn from a professional environment. The scenarios are drawn from the lives of people who work with chemistry every day, ranging from field ecologists to chemical engineers, to health professionals. Instructors: you can download and class-test sample labs from *Working with Chemistry* at the Freeman Web site, www.whfreeman.com/chemistry/wwc

Chemistry in the Laboratory, Fifth Edition, James M. Postma, California State University, Chico, and Julian L. Roberts, Jr., and J. Leland Hollenberg, University of Redlands, 0-7167-3547-4

This clearly written, class-tested manual has long given students essential hands-on training with key experiments. Exceptionally compatible with Atkins/Jones, *Chemical Principles*, the manual is known for its clear instructions and illustrations. All experiments are available as lab separates.

HSG Molecular Structure Model Set, Maruzen Company, Ltd.

Molecular modeling helps students understand physical and chemical properties by providing a way to visualize the three-dimensional arrangement of atoms. This model set uses polyhedra to represent atoms, and plastic connectors to represent bonds (scaled to correct bond lengths). Plastic

plates representing orbital lobes are included for indicating lone pairs of electrons, radicals, and multiple bonds—a feature unique to this set.

Chemistry Laboratory Student Notebook, Second Edition,
0-7167-3900-3

114 pages of graph paper in a convenient $8\frac{1}{2} \times 11$, three-hole punched format, carbon included. The new edition adds tables and graphs that make the Notebook a handy reference as well.

For the Instructor

Instructor's Resource Manual, Kenton H. Whitmire, Rice University, and Charles Trapp, University of Louisville, 0-7167-4432-5

This useful manual contains worked-out solutions and answers to the even-numbered exercises in the textbook.

For Students

Student's Study Guide, John Krenos and Joseph Potenza, Rutgers University, 0-7167-4436-8

Designed to help students avoid common mistakes and understand the material better, this *Study Guide* is an authoritative and thorough introduction to chemistry for students anticipating careers in science or engineering disciplines. The parallel between topical coverage, the symbols, concepts, and style of the *Study Guide* and the textbook enable the student to move easily back and forth between the two.

Student's Solutions Manual, Kenton H. Whitmire, Rice University, and Charles Trapp, University of Louisville, 0-7167-4435-X

This manual contains worked-out solutions and answers to the odd-numbered exercises in the textbook. It also explains important problem-solving techniques.

Individual chapters of the *Student's Study Guide* and the *Student's Solutions Manual* can be purchased and downloaded instantly, one chapter at a time, whenever they are needed through the Freeman On-line Store at whfreeman.com/chemicalprinciples.

ACKNOWLEDGMENTS

The preparation of the second edition of this textbook was an enjoyable yet exacting task that was helped by the generous advice of many who had used the first edition and by the support of many of our colleagues. It is not possible to list everyone who influenced and inspired us, but we wish to recognize those who have made a major impact on our ideas and those who have contributed their expertise to this edition. We would like above all to thank those who so conscientiously reported on the first edition and who read drafts of this edition. Their insights are now part of the text:

Thomas Albrecht-Schmidt, *Auburn University*
David Baker, *Delta College*
Mario Baur, *University of California, Los Angeles*
Paul Braterman, *University of North Texas*
Paul Charlesworth, *Michigan Tech University*
William Cleaver, *University of Vermont*
James Davis, *Harvard University*
Ronald Drucker, *City College of San Francisco*
Robert Eierman, *University of Wisconsin*
Lawrence Fong, *City College of San Francisco*
Regina Frey, *Washington University*
Dennis Gallo, *Augustana College*
David Harris, *University of California, Santa Barbara*

Michael Henchman, *Brandeis University*
Robert Kolodny, *Armstrong Atlantic State University*
Mariusz Kozik, *Canisius College*
Julie Ellefson Kuehn, *William Rainey Harper College*
Donald Parkhurst, *The Walker School*
George Schatz, *Northwestern University*
Michael Sommer, *Harvard University*
Tim Su, *City College of San Francisco*
Larry Thompson, *University of Minnesota*
James Whitten, *University of Massachusetts, Lowell*
Martin Zysmilich, *Massachusetts Institute of Technology*

The contributions of the reviewers of the first edition remain embedded in the text, so we also wish to renew our thanks to:

Matthew P. Augustine, *University of California, Davis*

Ken Brooks, *New Mexico State University*

Robert K. Bohn, *University of Connecticut*

Julia R. Burdge, *University of Akron*

William R. Brennan, *University of Pennsylvania*

David Dalton, *Temple University*

J. M. D'Auria, *Simon Fraser University*

James E. Davis, *Harvard University*

Jimmie Doll, *Brown University*

Jetty Duffy-Matzner, *State University of New York, Cortland*

Donald D. Fitts, *University of Pennsylvania*

David Harris, *University of California,*

Santa Barbara

Geoffrey Herring, *University of British Columbia*

Paul Hunter, *Michigan State University*

Petra van Koppen, *University of California, Santa Barbara*

Alison McCurdy, *Harvey Mudd College*

Noel Owen, *Brigham Young University*

Montgomery Pettitt, *University of Houston*

Philip J. Reid, *University of Washington*

Barbara Sawrey, *University of California, San Diego*

Carl Seliskar, *University of Cincinnati*

Herb Silber, *San Jose State University*

Lee G. Sobotka, *Washington University*

Dino Tinti, *University of California, Davis*

Sidney Toby, *Rutgers University*

Ken Whitmire, *Rice University*

The contributions of Ken Whitmire, Rice University, to this book have been substantial. He had full responsibility for the end-of-chapter exercises, generating new exercises, rewriting many of the existing ones, and writing the *Student's Solutions Manual* and *Instructor's Resource Manual*. In the process he gave more than was required and used his expertise in inorganic chemistry to critique the text as well. Some others contributed in substantial ways. We would particularly like to thank Regina Frey, Washington University, and Jamie Nossal, Rice University, for painstakingly checking the accuracy of the worked examples and Self-Tests and providing the Self-Test mini-solutions. We would also like to thank Jetty Duffy-Matzner, Augustana College, and the late Ken Brooks, New Mexico State University, for reading and thoroughly checking final sections of the text. Exercise solutions were double-checked by Maximilienne Bishop and David Price, Rice University. The supplement authors, particularly John Krenos, Joseph Potenza, and Ken Whitmire, have offered us much useful and sage advice. As before, our students have been our most important critics; they helped us to see the world of chemistry through their eyes and made many important suggestions.

We are grateful to our publishers, who understood our vision and helped bring it to fruition. The enthusiasm and skill with which they applied their considerable talents to this project have earned our gratitude. In particular, we would like to acknowledge Jessica Fiorillo, chemistry editor, who kept our spirits high and was perpetually enthusiastic and helpful; Michelle Russel Julet, publisher, who lent her insight and perspective to the project; Marjorie Singer Anderson, our perceptive development editor, who replaced murk with clarity and won our admiration; Jodi Simpson, our copy editor, who pinpointed and corrected flaws with accuracy and precision; Georgia Lee Hadler, senior project editor, who molded raw manuscript into final form; Meg Kuhta, who has an eye for exactly the right photographs; and Charlie van Wagner, who oversaw the development and production of the substantial array of supplements and media.

Special thanks go to Roy Tasker at the University of Western Sydney for the use of his VisChem animations and intellectual contribution to other animations on the Web site.

FUNDAMENTALS

Welcome to chemistry! You are about to embark on an extraordinary voyage, during which you will acquire new insights into the world around you. You will stand in the center of science. Looking in one direction, toward physics, you will see how the principles of chemistry are based on the behavior of atoms and molecules. Looking in another direction, toward biology, you will see how chemists contribute to an understanding of that most awesome property of matter, life. You will be able to look at an everyday object, see in your mind's eye its composition in terms of atoms, and understand its properties. Chemistry gives us the tools to become magicians with matter and to make forms of matter that have never existed before and perhaps do not exist anywhere else in the universe.

INTRODUCTION AND ORIENTATION

Chemistry is the science of matter and the changes it can undergo. The world of chemistry therefore embraces everything material around us—the stones we stand on, the food we eat, the flesh we are made of, and the silicon we build into computers. There is nothing material beyond the reach of chemistry, be it living or dead, vegetable or mineral, on Earth or in a distant star.

Chemistry and Society

We have only to look around us to appreciate the impact of chemistry on technology and society. In the earliest days of civilization, when the Stone Age gave way to the Bronze Age and then to the Iron Age, people did not realize that they were doing chemistry. But they were. They were changing the material they found as stones—we would now call them *minerals*—into metals (Fig. 1). The possession of metals gave them a new



FIGURE 1 Copper is easily extracted from its ores and was one of the first metals worked. The Bronze Age began following the discovery that adding some tin to copper made the metal harder and stronger. These four bronze swords date from 1250–850 BCE, the Late Bronze Age, and are from a collection in the Naturhistorisches Museum, Vienna, Austria. From bottom to top, they are a short sword, an antenna-type sword, a tongue-shaped sword, and a Liptau-type sword.



FIGURE 2 Cold weather triggers a reduction of the amount of the green chlorophyll in leaves, allowing the colors of various other pigments to show.

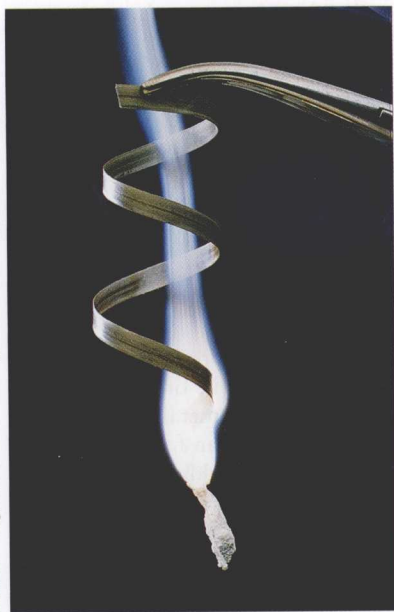


FIGURE 3 When magnesium burns in air, it gives off a lot of heat and light. The gray-white powdery product looks like smoke.

power over their environment, and treacherous nature became less brutal. The trappings of civilization emerged as skills in transforming materials grew: glass, jewels, coins, ceramics, and, inevitably, weapons became more varied and effective. Art, agriculture, and warfare became more sophisticated. None of this would have happened without chemistry.

The development of steel accelerated the profound impact of chemistry on society. Better steel led to the Industrial Revolution, when muscles gave way to steam and giant enterprises could be contemplated. With improved transport and greater output from factories came more extensive trade, and the world became simultaneously a smaller but busier place. None of this would have happened without chemistry.

With the twentieth century came enormous progress in the development of the chemical industry. Chemistry transformed agriculture. Synthetic fertilizers provided the means of feeding the enormous, growing population of the world. Chemistry transformed communication and transportation. It provided advanced materials, such as polymers for fabrics, ultrapure silicon for computers, and glass for optical fibers; it developed more efficient and renewable fuels. It gave us the tough, light alloys that are needed for modern aircraft and space travel. Chemistry transformed medicine, substantially extended life expectancy, and provided the foundations of genetic engineering. None of this would have happened without chemistry.

We have to admit, though, that the price of all these benefits has been high. The rapid growth of industry and agriculture, for instance, has stressed the Earth and damaged our inheritance. Now, at the dawn of the twenty-first century, there is a rising concern about the preservation of our extraordinary planet. It will be up to you and your contemporaries to draw on chemistry—in whatever career you choose—to build on what has already been achieved. Perhaps you will help to start a new phase of civilization based on new materials, just as semiconductors transformed society during the twentieth century. Perhaps you will help to do so in a way that reduces the harshness of the impact of progress on our environment. To do that, you will need chemistry.

Chemistry: A Science at Two Levels

Chemistry operates on two levels. At one level, chemistry is about matter and its transformations. At this level, we can actually see the changes, as when a fuel burns, a leaf changes color in the fall (Fig. 2), or magnesium burns brightly in air (Fig. 3). This level is the **macroscopic level**, the level dealing with the properties of large, visible objects. However, there is an underworld of change, a world that we cannot see directly. At this deeper **microscopic level**, chemistry interprets these phenomena in terms of the rearrangements of atoms (Fig. 4).

The **symbolic language** of chemistry, the expression of chemical phenomena in terms of chemical symbols and mathematical equations, ties the two levels together. Chemical equations describe observations at the macroscopic level in a way that can be interpreted in terms of events at the microscopic level. It has been said that a chemist thinks at the microscopic level, conducts experiments at the macroscopic level, and represents both symbolically. Success in chemistry depends on our ability to move



FIGURE 4 When a chemical reaction takes place, atoms exchange partners. As a result, two forms of matter (left inset) are changed into another form of matter (right inset). Atoms are neither created nor destroyed in chemical reactions.

between these levels and relate them symbolically. To foster communication between scientists, international standards have been developed. For example, measurements from around the world are reported in *Système International* units (SI units); these units are described in Appendix 1B.

How Science Is Done

Science pursues ideas in an ill-defined but effective way called the **scientific method**. The scientific method takes many forms. There is no strict rule of procedure that leads you from a good idea to a Nobel prize, or even a publishable discovery. Some scientists are meticulously careful, others are highly creative. The best scientists are probably both creative and careful. Although there are various scientific methods in use, a typical approach consists of a series of steps (Fig. 5). The first step is to collect **data** by making observations and measurements. These measurements are usually made on small **samples** of matter, representative pieces of the material we want to study.

Scientists are always on the lookout for patterns. When a pattern is observed in the data, it can be stated as a scientific **law**, a succinct summary of a wide range of observations. For example, one of the earliest laws of chemistry was the “law of constant composition,” which states that *a compound has the same composition regardless of the source of the sample*. Thus, a sample of water has twice as many hydrogen atoms as oxygen atoms, regardless of where the sample is collected.

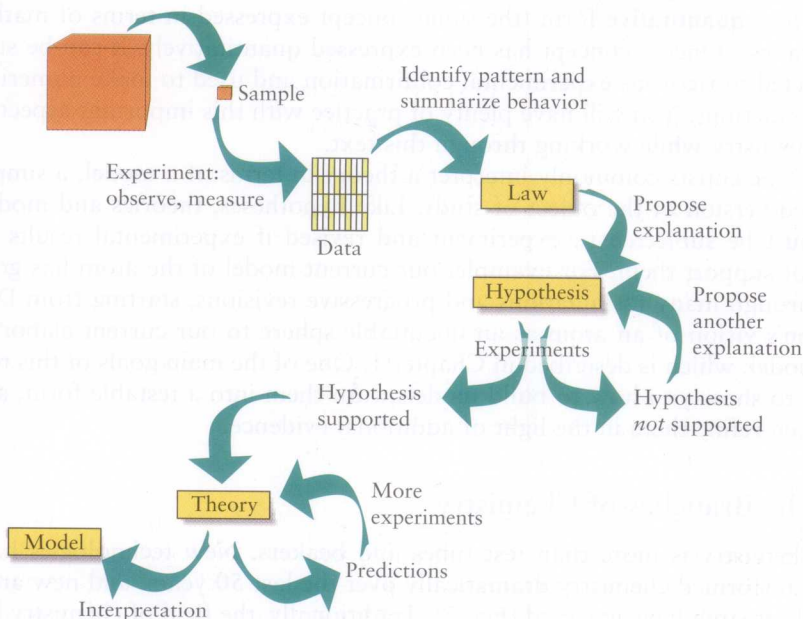
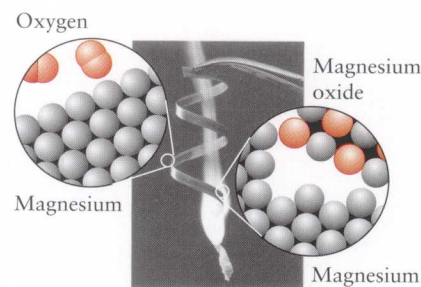


FIGURE 5 A summary of the principal activities that constitute the scientific method. At each stage, the crucial activity is experiment and its comparison with prevailing views.

The postulates of Dalton's atomic hypothesis are described in Section B.

In 1996, the Nobel prize in chemistry was awarded to R. F. Curl, R. E. Smalley, and H. W. Kroto for their discovery of C_{60} molecules.



View an animated structure of a buckminsterfullerene molecule.

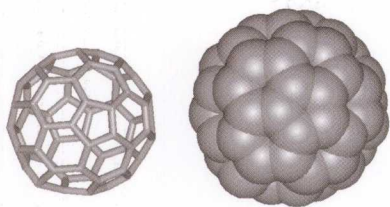


FIGURE 6 Buckminsterfullerene, C_{60} , consists of 60 carbon atoms arranged in five- and six-membered rings. The structure on the left is a line structure that shows only the bonds between the atoms. That on the right shows how the atoms occupy space.

Media Link Animation: Fig. 6, Bucky ball

Not all observations are summarized by laws. There are many properties of matter (such as superconductivity, the ability of a few cold solids to conduct electricity without any resistance) that are currently at the forefront of research but are not described by grand “laws” that embrace hundreds of different compounds. Formulating a law is just one way, not the only way, of summarizing data.

Once they have detected patterns, scientists develop **hypotheses**, possible explanations of the laws—or the observations—in terms of more fundamental concepts. Observation requires careful attention to detail, but the development of a hypothesis requires insight, imagination, and creativity. In 1807, John Dalton interpreted experimental results to propose the hypothesis that matter consists of atoms. Although Dalton could not see individual atoms, he was able to imagine them and formulate his *atomic hypothesis*. Dalton's hypothesis was a monumental insight that helped others understand the world in a new way. The process of scientific discovery never stops. In 1985, chemists found molecules composed of 60 carbon atoms in soot produced when graphite was struck by a laser beam; their hypothesis that these molecules were shaped like soccer balls generated great excitement (Fig. 6). The hypothesis—since confirmed—that buckminsterfullerene has a certain structure is not on the grand scale of Dalton's discovery, but it might nevertheless have a profound impact on the future of chemistry. With luck and application, you may acquire that kind of insight as you read through this text, and one day you may make your own extraordinary hypotheses.

After formulating a hypothesis, scientists design further **experiments**, carefully controlled tests, to verify their hypothesis. Experiments often require ingenuity and sometimes good luck. If the results of repeated experiments support the hypothesis, scientists may go on to formulate a **theory**, a formal explanation of a law. Quite often, and particularly in the physical sciences, of which chemistry is a part, the theory is expressed mathematically. An enormously powerful procedure in science is the conversion of a **qualitative** concept (a concept expressed in words or pictures) into a **quantitative** form (the same concept expressed in terms of mathematics). Once a concept has been expressed quantitatively, it can be subjected to rigorous experimental confirmation and used to make numerical predictions. You will have plenty of practice with this important aspect of chemistry while working through this text.

Scientists commonly interpret a theory in terms of a **model**, a simplified version of the object of study. Like hypotheses, theories and models must be subjected to experiment and revised if experimental results do not support them. For example, our current model of the atom has gone through many formulations and progressive revisions, starting from Dalton's vision of an atom as an uncuttable sphere to our current elaborate model, which is described in Chapter 1. One of the main goals of this text is to show you how to build models, turn them into a testable form, and then refine them in the light of additional evidence.

The Branches of Chemistry

Chemistry is more than test tubes and beakers. New technologies have transformed chemistry dramatically over the last 50 years, and new areas of research have emerged (Fig. 7). Traditionally, the field of chemistry has been organized into three main branches: