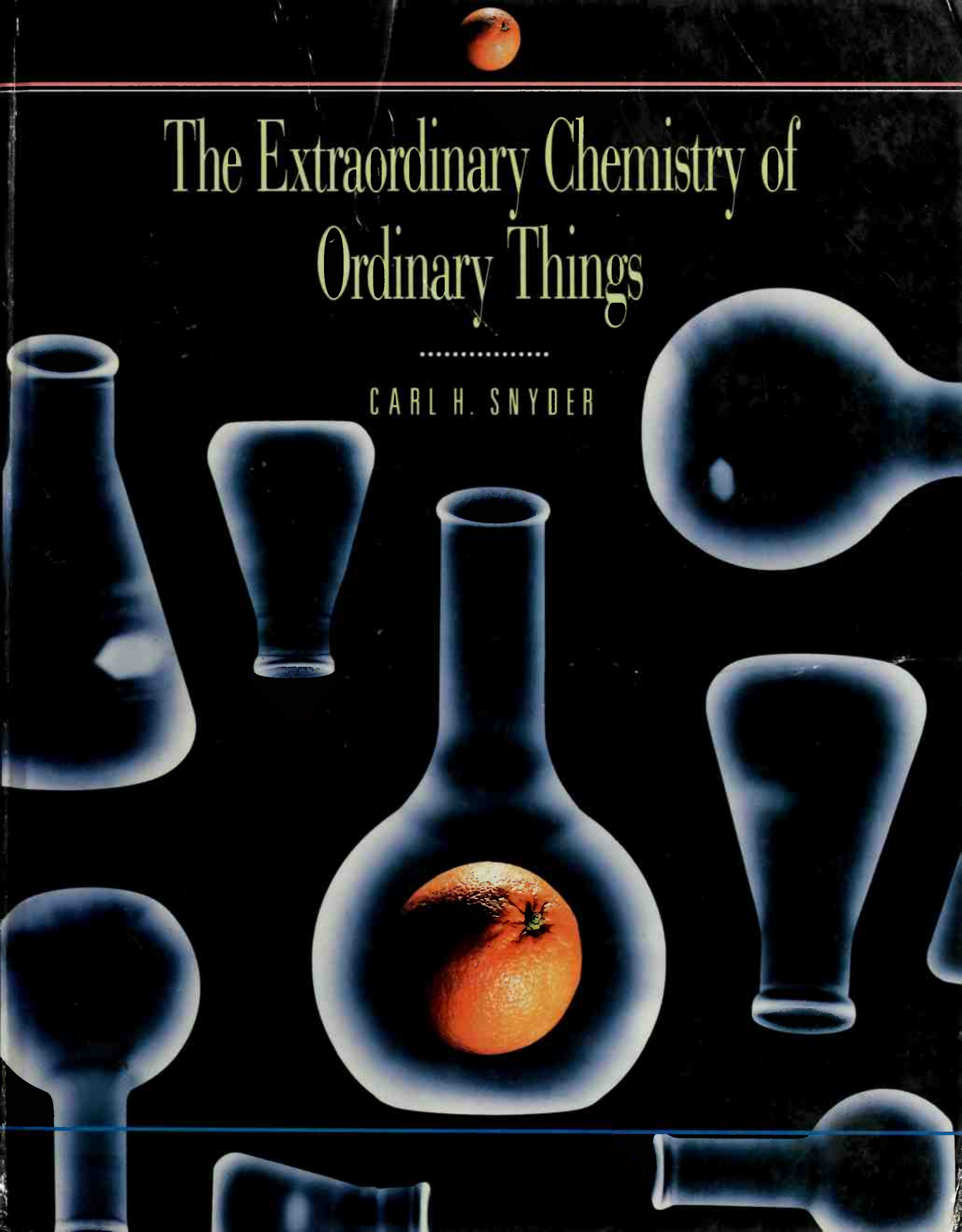
The Extraordinary Chemistry of Ordinary Things

CARL H. SNYDER



PERIODIC TABLE OF THE ELEMENTS[a]

Atomic number

1 H 1.00794

Atomic mass

Periods	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII		
1	1 H 1.00794									
2	3 Li 6.941	4 Be 9.01218								
3	11 Na 22.98977	12 Mg 24.3050								
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.95591	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.93320	28 Ni 58.69
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc 98.9072	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42
6	55 Cs 132.90543	56 Ba 137.327	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08
7	87 Fr 223.0197	88 Ra 226.0254	89 †Ac 227.0278	104 Unq 261.11	105 Unp 262.114	106 Unh 263.118	107 Uns 262.12		109 Une	

IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases 0
							2 He 4.00260
		5 B 10.811	6 C 12.011	7 N 14.00674	8 O 15.9994	9 F 18.99840	10 Ne 20.1797
		13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92159	34 Se 78.96	35 Br 79.904	36 Kr 83.80
47 Ag 107.8682	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.90447	54 Xe 131.29
79 Au 196.96654	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98037	84 Po 208.9824	85 At 209.9871	86 Rn 222.0176

*	58 Ce 140.115	59 Pr 140.90765	60 Nd 144.24	61 Pm 144.9127	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
†	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu 244.0642	95 Am 243.0614	96 Cm 247.0703	97 Bk 247.0703	98 Cf 242.0587	99 Es 252.083	100 Fm 257.0951	101 Md 258.10	102 No 259.1009	103 Lr 260.105

[a] Atomic masses are the 1985 values given in the Table of Atomic Masses and Atomic Numbers (opposite) but rounded, where appropriate to the fifth decimal place.

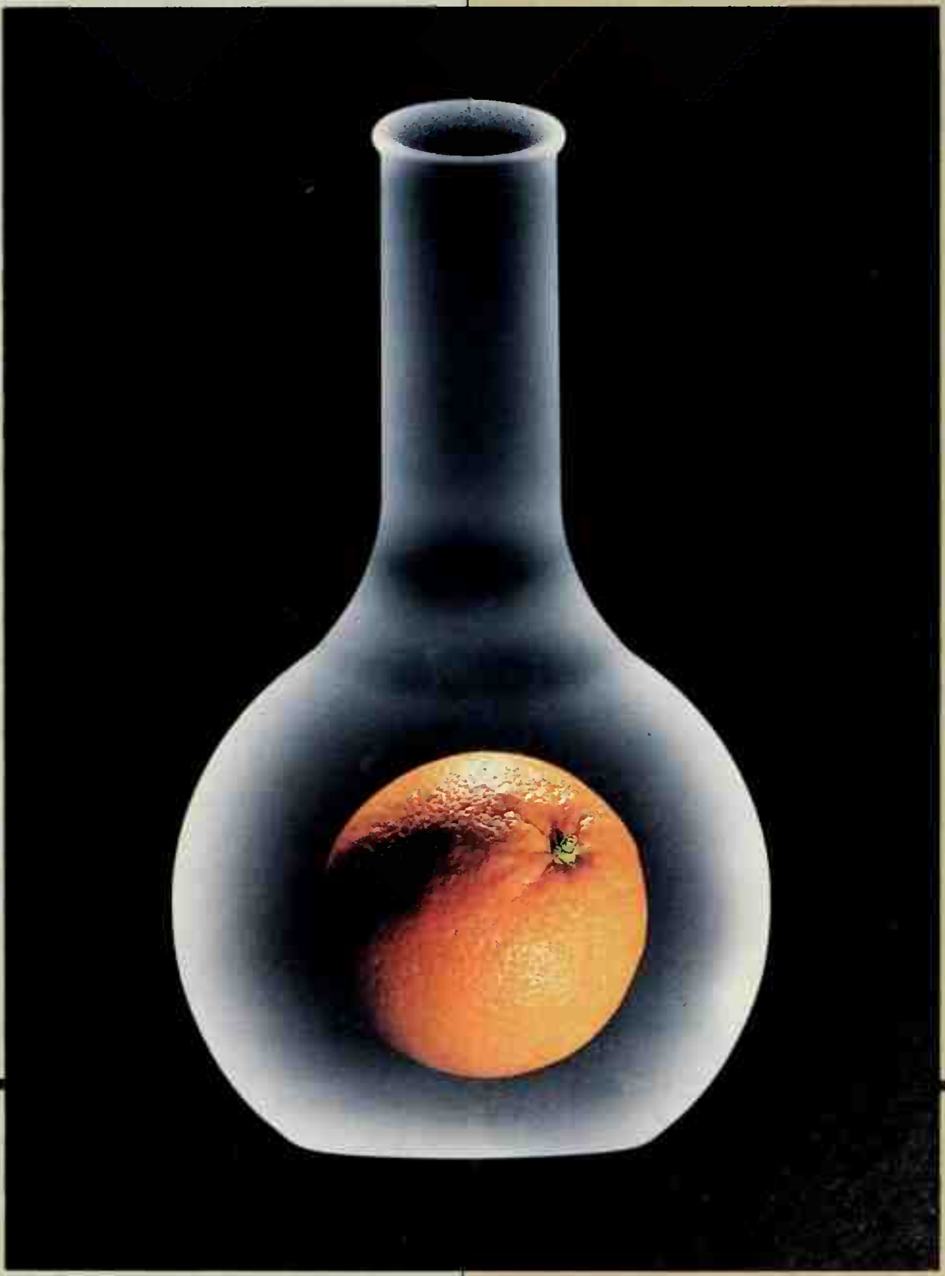
The Extraordinary Chemistry of Ordinary Things

WARNING

Descriptions of experiments that appear in this book are intended only to illustrate chemical principles. They are not intended to cause or encourage misuse of commercial or any other products. Household bleach, ammonia, tincture of iodine, and other products described in this work are and can be hazardous, corrosive, and poisonous, and must be used only as directed by the manufacturer. Be aware that anything can be hazardous if it is used improperly and that all materials must be disposed of according to law.

The Extraordinary Chemistry of Ordinary Things

CARL H. SNYDER
University of Miami



John Wiley & Sons, Inc.
New York
Chichester
Brisbane
Toronto
Singapore

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About the Cover

One hundred and sixty years ago, photography was invented when an object, left on top of a paper specifically treated to be sensitive to light, left its image on the paper. Over 100 years later, the Surrealists used a similar technique, called *photogramming*, to startle the world.

For the cover photo, we created our own photogram by placing several glass flasks on a piece of black and white photo paper and using an enlarger light to cast shadows of them on the paper. The shadows left behind their image. After the print was processed and dried, it was copied onto color film in a double exposure, carefully arranged so that the orange, from a second exposure, appeared to be inside one of the flasks.

Library of Congress Cataloging in Publication Data:

Snyder, Carl H.
The extraordinary chemistry of ordinary things / Carl H. Snyder.

p. cm.
Includes index.
ISBN 0-471-62971-5
1. Chemistry. I. Title.
QD33.S69 1992
540—dc20 91-34931
CIP

Printed and bound by Von Hoffmann Press, Inc.

10 9 8 7 6 5 4 3

To David N. Lewis

For good books, good conversation, good company.

Preface

This book was written for a course in which nonmajors learn chemistry in the context of the things that can or do affect them in their everyday lives.

Its origin lies in a course originally titled "Consumer Chemistry." In the early 1970s, at a time of severe inflation, it occurred to me that such a course combining chemistry with consumerism and directed at nonscience students was badly needed. I developed this as a one-credit, one-semester course in which I taught chemistry through its applications to consumer products and used consumer products to illustrate chemical principles. Each reinforced the other in examinations of gasoline and petroleum, detergents, foods and food additives, plastics, and the like.

With time, the course expanded beyond consumerism and the more common of our consumer products, but without ever losing sight of either. Although radioactive substances, for example, aren't commonly classified as consumer products, we do encounter them as consumers of medical care. Although ozone isn't itself a consumer product, our use of the gasoline engine and of chlorofluorocarbons affects both the undesirable generation of ozone (in the air we breathe) and the undesirable destruction of ozone (in the stratospheric ozone layer). In evolving, the course content came to include not only such topics as nuclear chemistry and the chemistry of gases, including ozone, but other facets of chemistry as well, facets that aren't easily defined in terms of consumer goods.

It evolved into a course about the chemistry of the substances of our everyday world, from the banal to the contentious, from table salt to perception-altering drugs, from drinking water to nuclear power. It evolved to include questions of safety, of the meaning and measurement of pollution, and particularly of the ambiguity of terms like "good" and "bad" as they are applied to chemicals. It evolved to bring the students themselves into the realm of chemistry, not only to demonstrate that we ourselves are constructed physically of chemicals but also to show that we can and must have the power of choice in how we use the chemicals of our universe. Appropriate choices require wisdom, and wisdom is founded on knowledge.

The course changed in other ways as well. It grew in steps from a one-credit, one-semester offering into a two-semester sequence of two three-credit courses, acceptable toward the science requirement for graduation. With these changes I have tried always to remain true to my original goal: teaching chemistry through illustrations taken from the common substances, objects, and processes of the world around us. Each hand—chemistry as one, and the things and substances of our everyday world as the other—shakes the other.

OBJECTIVES

The objectives of this approach are to teach chemistry:

- In the context of the ordinary things of our everyday lives, and some that aren't quite so ordinary but that nonetheless can and do affect our lives.
- In the context of the larger realm of science, drawing on chemical principles and examples to illustrate the workings of science as a whole and the scientific method.
- In the context of the need for science literacy to enable all, scientist and nonscientist alike, to make reasoned judgments on societal issues that are founded on the processes and fruits of science in general and chemistry in particular.
- In the context of chemistry as an experimental science.

CHEMISTRY, AN EXPERIMENTAL SCIENCE

The fourth of these objectives deserves further comment. I, and perhaps others as well, have long taught chemistry as we know it to be, with an understanding shaped by many years, even decades of study. We see chemistry as a coherent, rational whole and we transmit this model of the chemical universe to our students. Yet I have found, and I suspect many others agree, that transmitting this model alone is insufficient and unsatisfying, to both the teacher and the student. It's important to teach not only the coherent model of the universe that the science of chemistry presents to us, but to demonstrate why we are forced to accept it.

I use the word "forced" because the model of the world that chemistry presents to us is one that we are absolutely and unconditionally required to mold and to accept. We are forced to this particular model by our contact with physical reality, by our tests of physical reality, by the questions we frame as we test this real universe experimentally, and by the answers we receive from our experimental tests. Chemistry is, above and beyond all else, an experimental science.

We are forced to mold the universe into one particular intellectual construct because of our commitment to the scientific method and its experimental approach to knowledge. To teach chemistry, I am convinced, requires teaching the broad outlines of the scientific method, explicitly or implicitly. We have no choice, for example, but to acknowledge that atoms, subatomic particles, and chemical bonds do actually exist. But *why* are we forced to this view of the world? This is what students must come to understand if they are to learn chemistry in its richest context: why we are forced to see the physical universe as we do.

We accept the reality of atoms and all the other structures and concepts of chemistry because we have no other rational choice. Our experimental tests of our universe, through the scientific method, lead us to them and only to them. Let us then give our students hard, physical, real, demonstrable evidence that what we are about to tell them is, indeed, true chemistry, real chemistry. Let us show them in lectures and in textbooks that what we tell them is true not because we say it is, but because they see it is.

DEMONSTRATIONS

To emphasize the experimental basis of chemistry, all but two chapters begin with a demonstration or an action of some sort that the students themselves can perform with simple equipment and common substances. The first chapter, for example, begins with an illustration of the electrical conductivity of salt water and the nonconductivity of sugar water that employs table sugar, table salt, and a simple flashlight. The materials of the demonstration are about as common and ordinary as any we can find. Yet we see, at the first moment of contact with this realm of chemistry, that there's something demonstrably different about these two substances other than mere taste, something different that *forces* us to the concept of ions. Ions are real not because we say they are, but because students see that they are.

All the other demonstrations, vignettes, and historical sketches that start off chapters lead us to observations and conclusions about the chemistry of (mostly) ordinary things that we run across again, as textbook chemistry, somewhere in the chapter. These can be used as lecture demonstrations, but they are more than that. All of these demonstrations can be repeated by students, using common household goods. (Some chapters, like the two on nuclear chemistry, are better off without descriptions of hands-on experiments.)

SEQUENCE OF CHAPTERS

The sequence of chapters allows the text to be used for either a one- or a two-semester course. Of the 22 chapters, the first 11 cover most topics considered to be fundamental to the science of chemistry. The first three are introductory, dealing with atoms, ions, molecules, elements, compounds and the periodic table. The next several chapters carry the student from the nucleus, through the valence shell, to the covalent bond. Chapters 9, 10, and 11 round out the introductory material with the mole concept and solutions, acids and bases, and an introduction to the three phases of matter. With applications intimately tied to concepts throughout, there is no sacrifice of applications if the book is used in a one-semester course. Furthermore, any of the chapters in the set 13–22 can be included in a one-semester course with little or no modification. Organic chemistry appears in both the first set with a discussion of hydrocarbons, petroleum, and gasoline (Chapters 7 and 8), and the second set with an examination of the components of food and additives.

ORGANIZATION OF CHAPTERS

Every chapter but the two on nuclear chemistry starts with a demonstration or activity of some sort that leads to the substance of the chapter. In the spirit of the experimental approach, the results of the demonstration are explained in the context of the principles of chemistry developed within the chapter.

Virtually every section is followed by a question designed to induce the student to reflect on or review the material just covered. Exercises at the end of each chapter are divided into three categories: 1) review, written for a straightforward re-examination of the factual material of the chapter; 2) mathematical, for those who wish to emphasize the mathematical aspects of chemistry; and 3) thought-provoking. Exercises in this last category sometimes have no "right" answer but are intended to stimulate thought about the interconnection of chemistry, society, and individual values.

Many of the chapters, especially the earlier ones, contain worked examples to ease the student's way through the more difficult concepts.

Other characteristics of the presentation include the introduction of definitions, concepts, symbols, and the like largely on a need-to-know basis. It seems to me to make more sense to explain and describe the world about us as we encounter it, rather than to start by defining and categorizing ideas well before we need to use them. It's also clear that I like etymologies. I've found that students learn technical terms more easily if they know where they came from. I have other preferences that I'm unaware of, and I'm sure they show up in the book here and there, beneficially I hope. The major themes of the text are spelled out in Chapter 1 and need not be repeated here.

SUPPLEMENTS

An innovative package of supplements to accompany *The Extraordinary Chemistry of Ordinary Things* is available to assist both the instructor and the student.

1. **Study Guide,** by David Dever of Macon College. This Guide is an invaluable tool for the student, containing unusual, illustrative scenarios as well as the more traditional study guide features such as chapter overviews and solutions to in-text questions. Dr. Dever has also included worked-out solutions to the problems in the text's "A Little Arithmetic" sections, along with additional exercises of the same nature and level of difficulty.
2. **Laboratory Manual,** by Thomas Chasteen of Sam Houston State University and Bruce Richardson of Highline Community College. Twenty-five laboratory exercises are included in this manual, all written in a clear, concise, and unintimidating fashion. The themes emphasized in the Laboratory Manual closely parallel those of the text, incorporating experiments with both consumer and environmental applications.
3. **Instructor's Manual,** by Sharmaine Cady of East Stroudsburg University. In addition to lecture outlines, chapter overviews, and additional class demonstrations for each chapter in the text, the Manual also contains background information and suggestions for using the *The Extraordinary Chemistry of Ordinary Things* videotape.
4. **Test Bank.** Written by the text author, the Test Bank contains over 1000 multiple-choice questions.
5. **Computerized Test Bank.** IBM, Apple II, and Macintosh versions of the entire Test Bank are available with full editing features to help you customize texts.

6. **Full-Color Overhead Transparencies.** Over 100 full-color illustrations are provided in a form suitable for projection in the classroom.
7. **Videotape.** Over 15 experiments are demonstrated by the author on this videotape. A few selected chapter-opening experiments are brought to life; other demonstrations illustrate other pertinent chapter material. In addition, the author and two chemists from the Dade County Department of Environmental Resource Management discuss air and water quality control, pollution tracking, and other vital environmental issues.

THE MAGIC OF CHEMISTRY

Some of the chapters start with what appear to be demonstrations of magic. Household bleach, for example, mysteriously makes colors appear rather than disappear, exhaled breath mysteriously causes colors to change, we mysteriously "squeeze" air out of a glass bottle, and so on. As each of these chapters unfolds, the "magic" is explained as the operation of a chemical principle and the "magic" is seen to be no more than the rational operation of the laws of the universe. The "magic" is transformed into "chemistry" as the student comes to understand how the chemical universe about us works. In this way I illustrate to students one of the most important contributions that science in general and chemistry in particular have made to the development of our civilization: the conversion of superstition into understanding, of fearsome magic into useful science, all through the acquisition of knowledge. After all, *the difference between "magic" and "science" is knowledge.*

ACKNOWLEDGMENTS

I wrote down all the material on the pages that follow, mostly because of my former department chairman, Harry P. Schultz. After my initial suggestion that we introduce a course for nonscientists, Harry gave me unreserved support, encouragement, and recognition. Harry also asked, repeatedly, "Why don't you put all this down on paper?" He asked once too often, and so here it is. With his enthusiastic support for the course, and, I must add, for our students as well, and his repeated urgings that I put it all on paper, this book owes its existence more to Harry Schultz than to any other person. Without Harry neither the course nor the book would exist.

From a more personal point of view, I thank my wife Jean for her patience, unfailing good humor, and astute suggestions and comments that eased the effort of a work like this. In addition, she also did much of the research into nonchemical documents that round out this work, and she proofread the entire first draft of the manuscript with better effect that any word processor's spell checker. Invariably she was there when needed.

I'm particularly grateful to all those at John Wiley & Sons who brought this book into physical being, and especially to Barbara Heaney for her quick and early perception of what this book is about—what I set about to do—and for her combination of professionalism and personal grace in her capacity as Developmental Editor.

I am also grateful for the assistance and encouragement generously given by others at John Wiley & Sons, especially Savoula Amanatidis, Production; John Balbalis, Illustration; Randi Goldsmith, Video; Joan Kalkut, Supple-

ments; Karin Kincheloe, Design; Stella Kupferberg, Photos; Kaye Pace, Editorial; Nedah Rose, Editorial; Marjorie Shustak, Copy Editing.

Finally, I want to thank the reviewers for their contributions. Their suggestions and guidance, consistently both positive and useful, were invaluable. For their help in bringing this to fruition, I want to thank:

Arthur Breyer
Beaver College
Thomas Briggle
University of Miami
Kenneth Busch
Georgia Institute of Technology
R.P. Ciula
California State University–Fresno
Melvyn Dutton
California State University–Bakersfield
Seth Elsheimer
University of Central Florida
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Florida International University
Edward Wong
University of New Hampshire

Carl H. Snyder

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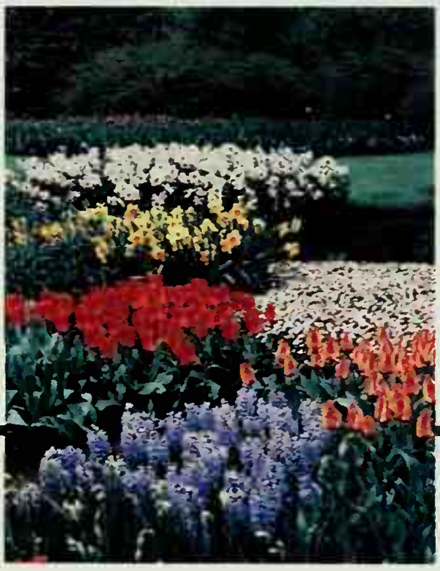

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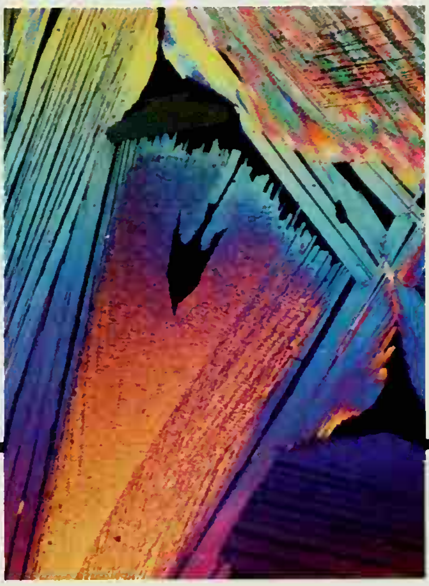

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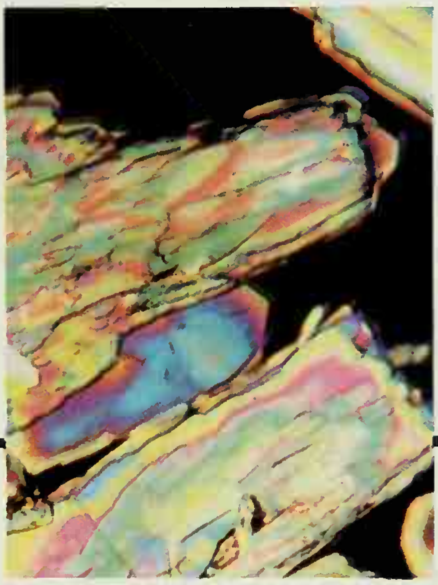

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FEATURED IN THIS BOOK

Demonstrations

To emphasize the experimental basis of chemistry, all but two chapters begin with a demonstration that students can perform with simple equipment and common household goods.

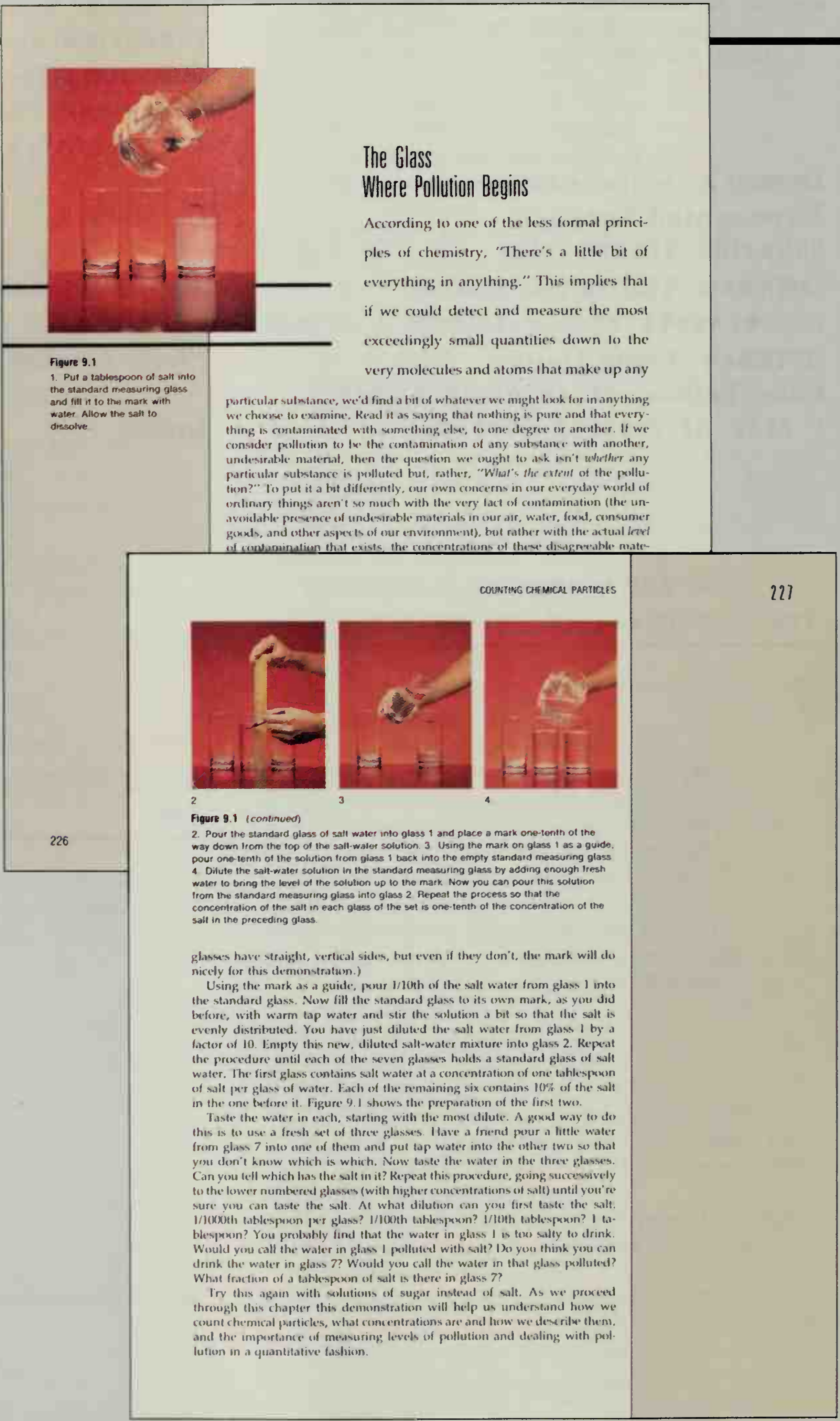

Figure 9.1

1. Put a tablespoon of salt into the standard measuring glass and fill it to the mark with water. Allow the salt to dissolve.

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The Glass Where Pollution Begins

According to one of the less formal principles of chemistry, "There's a little bit of everything in anything." This implies that if we could detect and measure the most exceedingly small quantities down to the very molecules and atoms that make up any particular substance, we'd find a bit of whatever we might look for in anything we choose to examine. Read it as saying that nothing is pure and that everything is contaminated with something else, to one degree or another. If we consider pollution to be the contamination of any substance with another, undesirable material, then the question we ought to ask isn't *whether* any particular substance is polluted but, rather, "*What's the extent* of the pollution?" To put it a bit differently, our own concerns in our everyday world of ordinary things aren't so much with the very fact of contamination (the unavoidable presence of undesirable materials in our air, water, food, consumer goods, and other aspects of our environment), but rather with the actual *level* of contamination that exists, the concentrations of these disagreeable mate-

COUNTING CHEMICAL PARTICLES

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2 3 4

Figure 9.1 *(continued)*

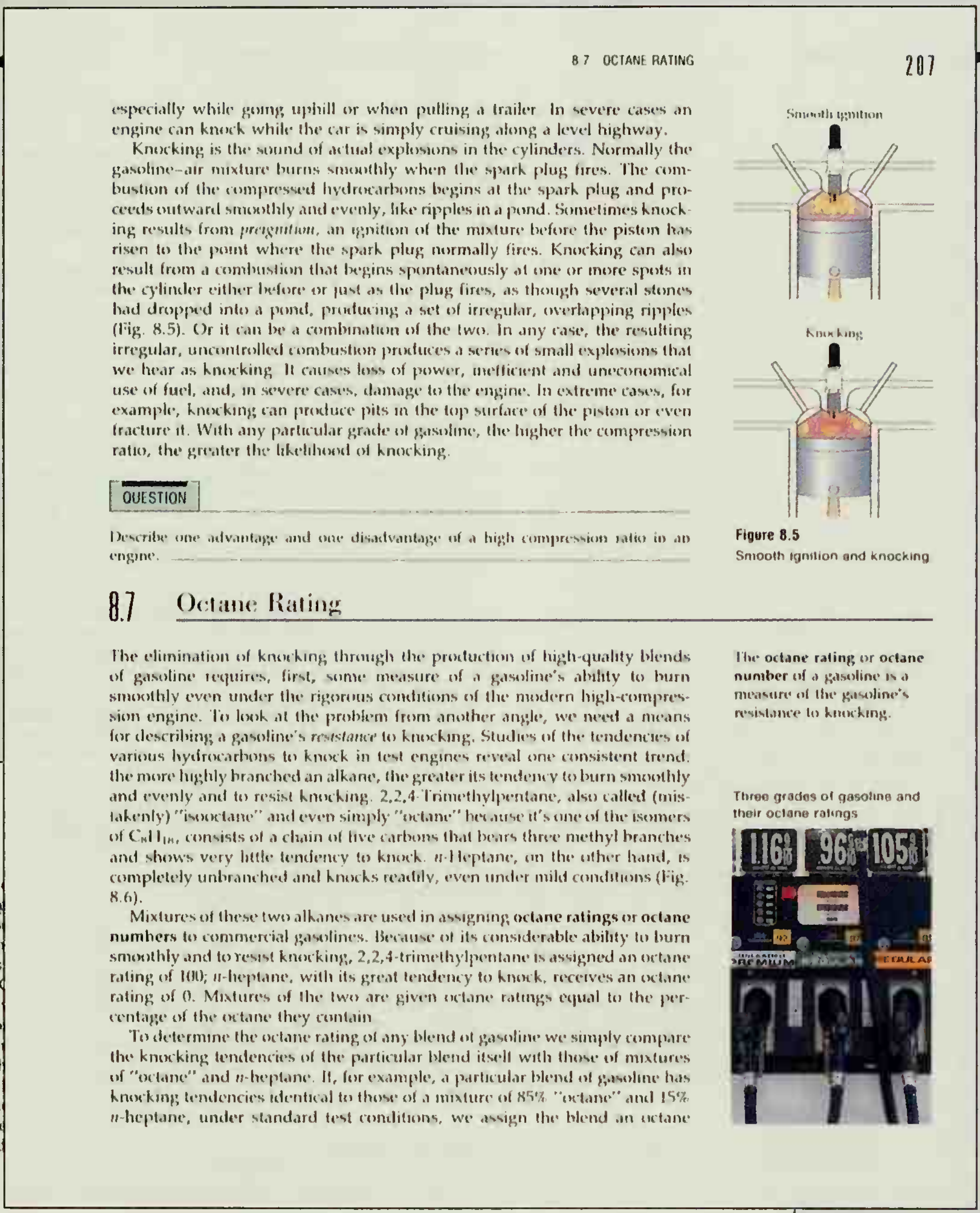
2. Pour the standard glass of salt water into glass 1 and place a mark one-tenth of the way down from the top of the salt-water solution. 3. Using the mark on glass 1 as a guide, pour one-tenth of the solution from glass 1 back into the empty standard measuring glass. 4. Dilute the salt-water solution in the standard measuring glass by adding enough fresh water to bring the level of the solution up to the mark. Now you can pour this solution from the standard measuring glass into glass 2. Repeat the process so that the concentration of the salt in each glass of the set is one-tenth of the concentration of the salt in the preceding glass.

glasses have straight, vertical sides, but even if they don't, the mark will do nicely for this demonstration.)

Using the mark as a guide, pour 1/10th of the salt water from glass 1 into the standard glass. Now fill the standard glass to its own mark, as you did before, with warm tap water and stir the solution a bit so that the salt is evenly distributed. You have just diluted the salt water from glass 1 by a factor of 10. Empty this new, diluted salt-water mixture into glass 2. Repeat the procedure until each of the seven glasses holds a standard glass of salt water. The first glass contains salt water at a concentration of one tablespoon of salt per glass of water. Each of the remaining six contains 10% of the salt in the one before it. Figure 9.1 shows the preparation of the first two.

Taste the water in each, starting with the most dilute. A good way to do this is to use a fresh set of three glasses. Have a friend pour a little water from glass 7 into one of them and put tap water into the other two so that you don't know which is which. Now taste the water in the three glasses. Can you tell which has the salt in it? Repeat this procedure, going successively to the lower numbered glasses (with higher concentrations of salt) until you're sure you can taste the salt. At what dilution can you first taste the salt. 1/1000th tablespoon per glass? 1/100th tablespoon? 1/10th tablespoon? 1 tablespoon? You probably find that the water in glass 1 is too salty to drink. Would you call the water in glass 1 polluted with salt? Do you think you can drink the water in glass 7? Would you call the water in that glass polluted? What fraction of a tablespoon of salt is there in glass 7?

Try this again with solutions of sugar instead of salt. As we proceed through this chapter this demonstration will help us understand how we count chemical particles, what concentrations are and how we describe them, and the importance of measuring levels of pollution and dealing with pollution in a quantitative fashion.



8.7 OCTANE RATING 207

especially while going uphill or when pulling a trailer. In severe cases an engine can knock while the car is simply cruising along a level highway.

Knocking is the sound of actual explosions in the cylinders. Normally the gasoline–air mixture burns smoothly when the spark plug fires. The combustion of the compressed hydrocarbons begins at the spark plug and proceeds outward smoothly and evenly, like ripples in a pond. Sometimes knocking results from *preignition*, an ignition of the mixture before the piston has risen to the point where the spark plug normally fires. Knocking can also result from a combustion that begins spontaneously at one or more spots in the cylinder either before or just as the plug fires, as though several stones had dropped into a pond, producing a set of irregular, overlapping ripples (Fig. 8.5). Or it can be a combination of the two. In any case, the resulting irregular, uncontrolled combustion produces a series of small explosions that we hear as knocking. It causes loss of power, inefficient and uneconomical use of fuel, and, in severe cases, damage to the engine. In extreme cases, for example, knocking can produce pits in the top surface of the piston or even fracture it. With any particular grade of gasoline, the higher the compression ratio, the greater the likelihood of knocking.

Smooth ignition

Knocking

Figure 8.5
Smooth ignition and knocking

QUESTION

Describe one advantage and one disadvantage of a high compression ratio in an engine.

8.7 Octane Rating

The elimination of knocking through the production of high-quality blends of gasoline requires, first, some measure of a gasoline's ability to burn smoothly even under the rigorous conditions of the modern high-compression engine. To look at the problem from another angle, we need a means for describing a gasoline's *resistance* to knocking. Studies of the tendencies of various hydrocarbons to knock in test engines reveal one consistent trend: the more highly branched an alkane, the greater its tendency to burn smoothly and evenly and to resist knocking. 2,2,4-Trimethylpentane, also called (mistakenly) "isooctane" and even simply "octane" because it's one of the isomers of C_8H_{18}, consists of a chain of five carbons that bears three methyl branches and shows very little tendency to knock. *n*-Heptane, on the other hand, is completely unbranched and knocks readily, even under mild conditions (Fig. 8.6).

Mixtures of these two alkanes are used in assigning **octane ratings** or **octane numbers** to commercial gasolines. Because of its considerable ability to burn smoothly and to resist knocking, 2,2,4-trimethylpentane is assigned an octane rating of 100; *n*-heptane, with its great tendency to knock, receives an octane rating of 0. Mixtures of the two are given octane ratings equal to the percentage of the octane they contain.

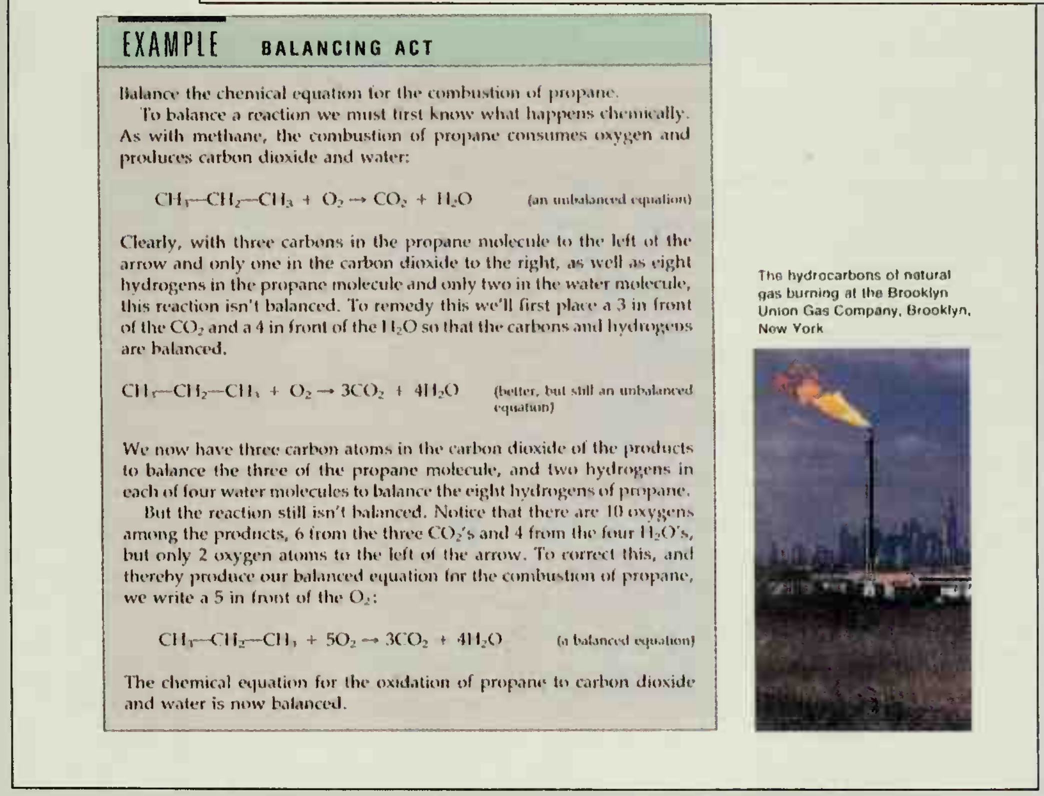
To determine the octane rating of any blend of gasoline we simply compare the knocking tendencies of the particular blend itself with those of mixtures of "octane" and *n*-heptane. If, for example, a particular blend of gasoline has knocking tendencies identical to those of a mixture of 85% "octane" and 15% *n*-heptane, under standard test conditions, we assign the blend an octane

The **octane rating** or **octane number** of a gasoline is a measure of the gasoline's resistance to knocking.

Three grades of gasoline and their octane ratings

Questions

Virtually every section is followed by a Question designed to induce students to reflect on or review the material just covered. Questions can be of three types: straightforward review, mathematical, or thought-provoking.



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EXAMPLE **BALANCING ACT**

Balance the chemical equation for the combustion of propane.

To balance a reaction we must first know what happens chemically. As with methane, the combustion of propane consumes oxygen and produces carbon dioxide and water:

$$CH_3{-}CH_2{-}CH_3 + O_2 \rightarrow CO_2 + H_2O \quad \text{(an unbalanced equation)}$$

Clearly, with three carbons in the propane molecule to the left of the arrow and only one in the carbon dioxide to the right, as well as eight hydrogens in the propane molecule and only two in the water molecule, this reaction isn't balanced. To remedy this we'll first place a 3 in front of the CO_2 and a 4 in front of the H_2O so that the carbons and hydrogens are balanced.

$$CH_3{-}CH_2{-}CH_3 + O_2 \rightarrow 3CO_2 + 4H_2O \quad \text{(better, but still an unbalanced equation)}$$

We now have three carbon atoms in the carbon dioxide of the products to balance the three of the propane molecule, and two hydrogens in each of four water molecules to balance the eight hydrogens of propane.

But the reaction still isn't balanced. Notice that there are 10 oxygens among the products, 6 from the three CO_2's and 4 from the four H_2O's, but only 2 oxygen atoms to the left of the arrow. To correct this, and thereby produce our balanced equation for the combustion of propane, we write a 5 in front of the O_2:

$$CH_3{-}CH_2{-}CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \text{(a balanced equation)}$$

The chemical equation for the oxidation of propane to carbon dioxide and water is now balanced.

The hydrocarbons of natural gas burning at the Brooklyn Union Gas Company, Brooklyn, New York

Worked Examples

Worked Examples are provided to help students work through difficult concepts or some of the quantitative aspects of chemistry. Frequently broken down into step-by-step stages, these examples serve as models for some of the end-of-chapter Exercises.

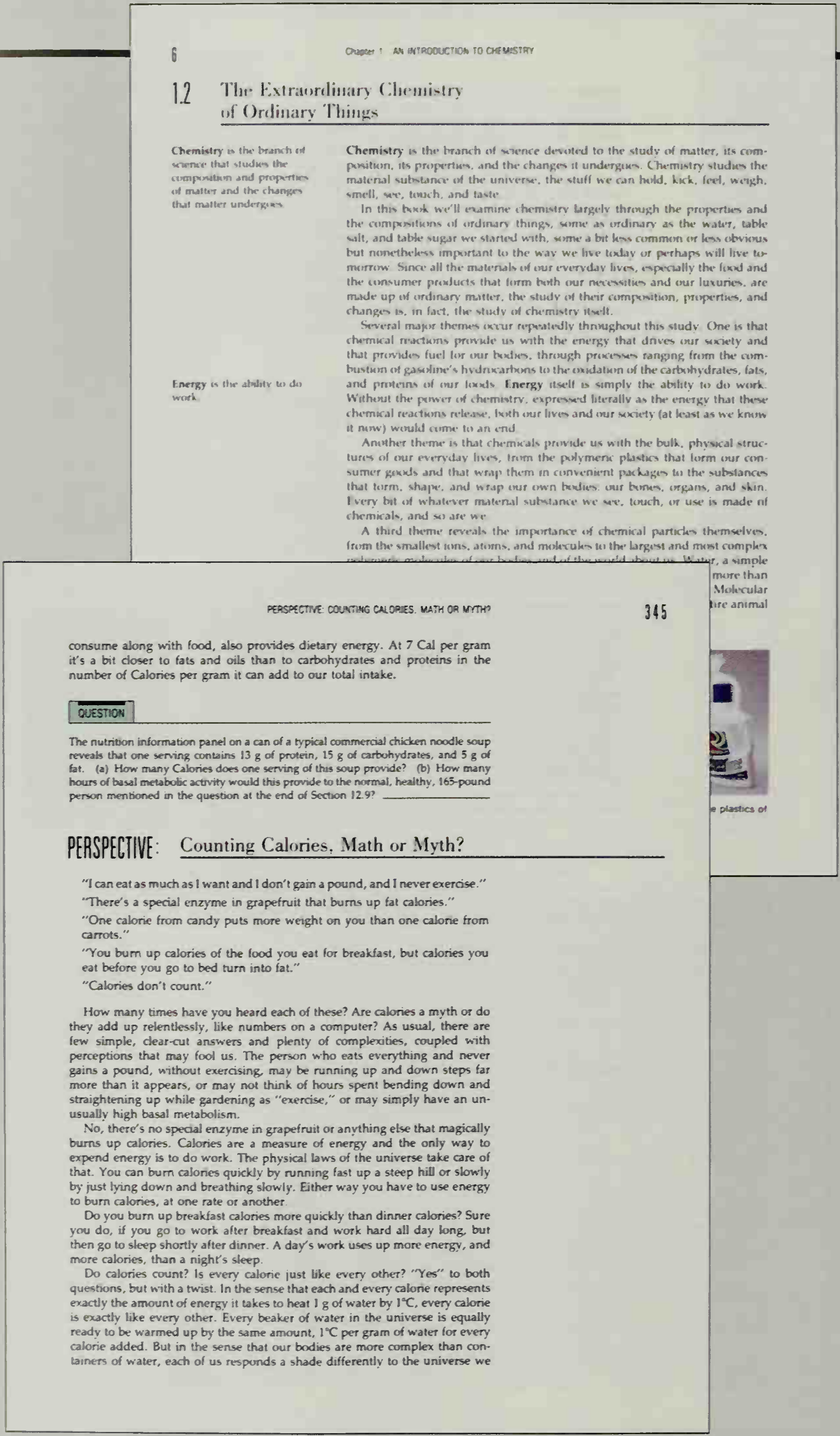
FEATURED IN THIS BOOK

Running Glossary

Key terms are defined both in text and in the margin, helping students identify the most important concepts.

Perspectives

Every chapter closes with a Perspective that places the content of that chapter within the book's themes: presenting informed choices to students, analyzing risks and benefits, discussing the experimental basis of science, and/or revealing the chemistry all around us.



6 Chapter 1 AN INTRODUCTION TO CHEMISTRY

1.2 The Extraordinary Chemistry of Ordinary Things

Chemistry is the branch of science that studies the composition and properties of matter and the changes that matter undergoes.

Chemistry is the branch of science devoted to the study of matter, its composition, its properties, and the changes it undergoes. Chemistry studies the material substance of the universe, the stuff we can hold, kick, feel, weigh, smell, see, touch, and taste.

In this book we'll examine chemistry largely through the properties and the compositions of ordinary things, some as ordinary as the water, table salt, and table sugar we started with, some a bit less common or less obvious but nonetheless important to the way we live today or perhaps will live tomorrow. Since all the materials of our everyday lives, especially the food and the consumer products that form both our necessities and our luxuries, are made up of ordinary matter, the study of their composition, properties, and changes is, in fact, the study of chemistry itself.

Energy is the ability to do work.

Several major themes occur repeatedly throughout this study. One is that chemical reactions provide us with the energy that drives our society and that provides fuel for our bodies, through processes ranging from the combustion of gasoline's hydrocarbons to the oxidation of the carbohydrates, fats, and proteins of our foods. **Energy** itself is simply the ability to do work. Without the power of chemistry, expressed literally as the energy that these chemical reactions release, both our lives and our society (at least as we know it now) would come to an end.

Another theme is that chemicals provide us with the bulk, physical structures of our everyday lives, from the polymeric plastics that form our consumer goods and that wrap them in convenient packages to the substances that form, shape, and wrap our own bodies: our bones, organs, and skin. Every bit of whatever material substance we see, touch, or use is made of chemicals, and so are we.

A third theme reveals the importance of chemical particles themselves, from the smallest ions, atoms, and molecules to the largest and most complex

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more than

Molecular

ure animal

e plastics of

PERSPECTIVE: COUNTING CALORIES, MATH OR MYTH? 345

consume along with food, also provides dietary energy. At 7 Cal per gram it's a bit closer to fats and oils than to carbohydrates and proteins in the number of Calories per gram it can add to our total intake.

QUESTION

The nutrition information panel on a can of a typical commercial chicken noodle soup reveals that one serving contains 13 g of protein, 15 g of carbohydrates, and 5 g of fat. (a) How many Calories does one serving of this soup provide? (b) How many hours of basal metabolic activity would this provide to the normal, healthy, 165-pound person mentioned in the question at the end of Section 12.9? ______

PERSPECTIVE: Counting Calories, Math or Myth?

"I can eat as much as I want and I don't gain a pound, and I never exercise."

"There's a special enzyme in grapefruit that burns up fat calories."

"One calorie from candy puts more weight on you than one calorie from carrots."

"You burn up calories of the food you eat for breakfast, but calories you eat before you go to bed turn into fat."

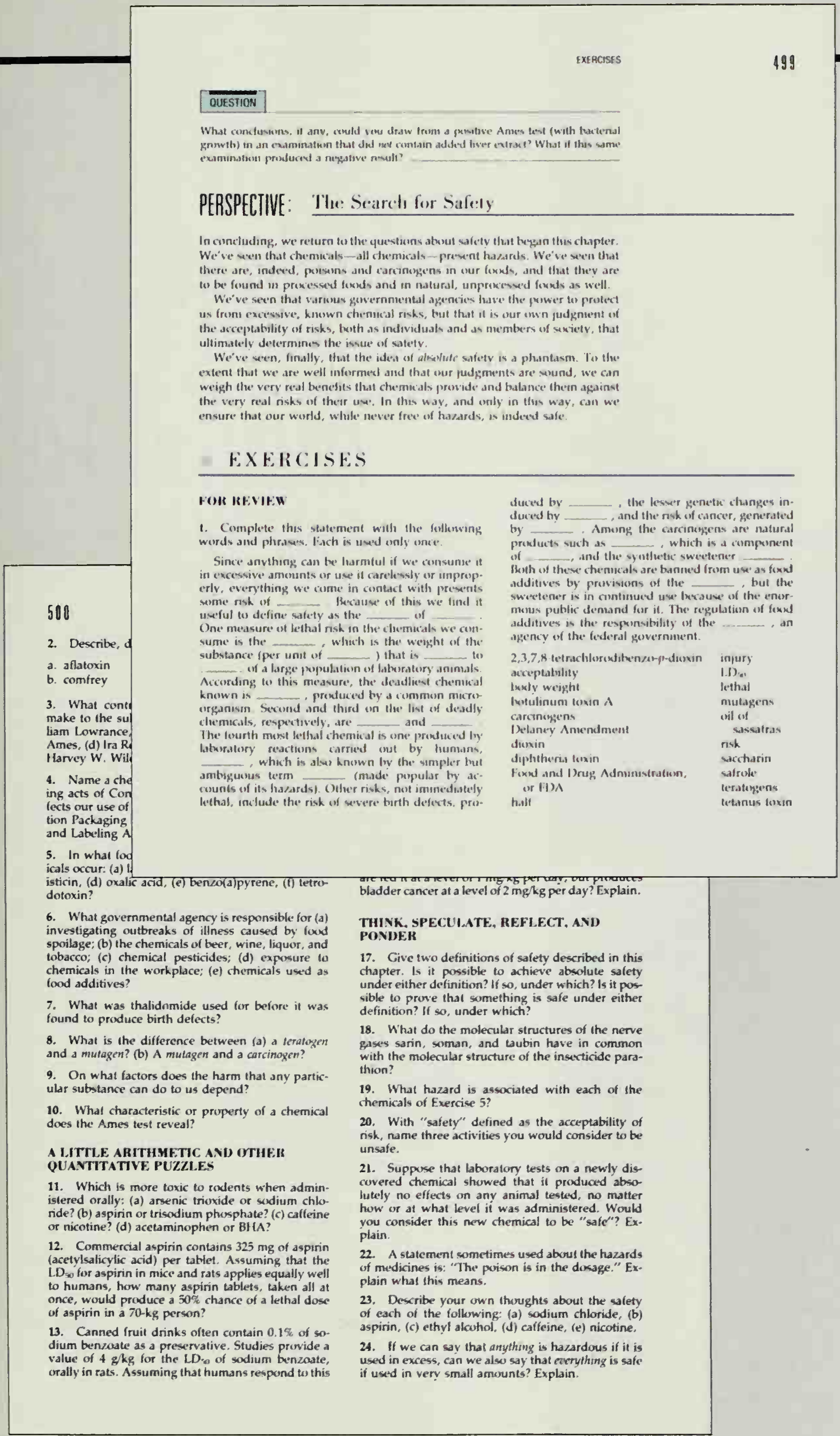
"Calories don't count."

How many times have you heard each of these? Are calories a myth or do they add up relentlessly, like numbers on a computer? As usual, there are few simple, clear-cut answers and plenty of complexities, coupled with perceptions that may fool us. The person who eats everything and never gains a pound, without exercising, may be running up and down steps far more than it appears, or may not think of hours spent bending down and straightening up while gardening as "exercise," or may simply have an unusually high basal metabolism.

No, there's no special enzyme in grapefruit or anything else that magically burns up calories. Calories are a measure of energy and the only way to expend energy is to do work. The physical laws of the universe take care of that. You can burn calories quickly by running fast up a steep hill or slowly by just lying down and breathing slowly. Either way you have to use energy to burn calories, at one rate or another.

Do you burn up breakfast calories more quickly than dinner calories? Sure you do, if you go to work after breakfast and work hard all day long, but then go to sleep shortly after dinner. A day's work uses up more energy, and more calories, than a night's sleep.

Do calories count? Is every calorie just like every other? "Yes" to both questions, but with a twist. In the sense that each and every calorie represents exactly the amount of energy it takes to heat 1 g of water by 1°C, every calorie is exactly like every other. Every beaker of water in the universe is equally ready to be warmed up by the same amount, 1°C per gram of water for every calorie added. But in the sense that our bodies are more complex than containers of water, each of us responds a shade differently to the universe we



EXERCISES 499

QUESTION

What conclusions, if any, could you draw from a positive Ames test (with bacterial growth) in an examination that did *not* contain added liver extract? What if this same examination produced a negative result? ________________

PERSPECTIVE: The Search for Safety

In concluding, we return to the questions about safety that began this chapter. We've seen that chemicals—all chemicals—present hazards. We've seen that there are, indeed, poisons and carcinogens in our foods, and that they are to be found in processed foods and in natural, unprocessed foods as well.

We've seen that various governmental agencies have the power to protect us from excessive, known chemical risks, but that it is our own judgment of the acceptability of risks, both as individuals and as members of society, that ultimately determines the issue of safety.

We've seen, finally, that the idea of *absolute* safety is a phantasm. To the extent that we are well informed and that our judgments are sound, we can weigh the very real benefits that chemicals provide and balance them against the very real risks of their use. In this way, and only in this way, can we ensure that our world, while never free of hazards, is indeed safe.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used only once.

Since anything can be harmful if we consume it in excessive amounts or use it carelessly or improperly, everything we come in contact with presents some risk of ______. Because of this we find it useful to define safety as the ______ of ______. One measure of lethal risk in the chemicals we consume is the ______, which is the weight of the substance (per unit of ______) that is ______ to ______ of a large population of laboratory animals. According to this measure, the deadliest chemical known is ______, produced by a common microorganism. Second and third on the list of deadly chemicals, respectively, are ______ and ______. The fourth most lethal chemical is one produced by laboratory reactions carried out by humans, ______, which is also known by the simpler but ambiguous term ______ (made popular by accounts of its hazards). Other risks, not immediately lethal, include the risk of severe birth defects, produced by ______, the lesser genetic changes induced by ______, and the risk of cancer, generated by ______. Among the carcinogens are natural products such as ______, which is a component of ______, and the synthetic sweetener ______. Both of these chemicals are banned from use as food additives by provisions of the ______, but the sweetener is in continued use because of the enormous public demand for it. The regulation of food additives is the responsibility of the ______, an agency of the federal government.

2,3,7,8-tetrachlorodibenzo-*p*-dioxin
acceptability
body weight
botulinum toxin A
carcinogens
Delaney Amendment
dioxin
diphtheria toxin
Food and Drug Administration, or FDA
half
injury
LD$_{50}$
lethal
mutagens
oil of sassafras
risk
saccharin
safrole
teratogens
tetanus toxin

500

2. Describe, d

a. aflatoxin
b. comfrey

3. What cont
make to the su
liam Lowrance,
Ames, (d) Ira R
Harvey W. Wil

4. Name a che
ing acts of Con
fects our use of
tion Packaging
and Labeling A

5. In what foo
icals occur: (a) l
isticin, (d) oxalic acid, (e) benzo(a)pyrene, (f) tetrodotoxin?

6. What governmental agency is responsible for (a) investigating outbreaks of illness caused by food spoilage; (b) the chemicals of beer, wine, liquor, and tobacco; (c) chemical pesticides; (d) exposure to chemicals in the workplace; (e) chemicals used as food additives?

7. What was thalidomide used for before it was found to produce birth defects?

8. What is the difference between (a) a *teratogen* and a *mutagen*? (b) A *mutagen* and a *carcinogen*?

9. On what factors does the harm that any particular substance can do to us depend?

10. What characteristic or property of a chemical does the Ames test reveal?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

11. Which is more toxic to rodents when administered orally: (a) arsenic trioxide or sodium chloride? (b) aspirin or trisodium phosphate? (c) caffeine or nicotine? (d) acetaminophen or BHA?

12. Commercial aspirin contains 325 mg of aspirin (acetylsalicylic acid) per tablet. Assuming that the LD$_{50}$ for aspirin in mice and rats applies equally well to humans, how many aspirin tablets, taken all at once, would produce a 50% chance of a lethal dose of aspirin in a 70-kg person?

13. Canned fruit drinks often contain 0.1% of sodium benzoate as a preservative. Studies provide a value of 4 g/kg for the LD$_{50}$ of sodium benzoate, orally in rats. Assuming that humans respond to this

bladder cancer at a level of 2 mg/kg per day? Explain.

THINK, SPECULATE, REFLECT, AND PONDER

17. Give two definitions of safety described in this chapter. Is it possible to achieve absolute safety under either definition? If so, under which? Is it possible to prove that something is safe under either definition? If so, under which?

18. What do the molecular structures of the nerve gases sarin, soman, and taubin have in common with the molecular structure of the insecticide parathion?

19. What hazard is associated with each of the chemicals of Exercise 5?

20. With "safety" defined as the acceptability of risk, name three activities you would consider to be unsafe.

21. Suppose that laboratory tests on a newly discovered chemical showed that it produced absolutely no effects on any animal tested, no matter how or at what level it was administered. Would you consider this new chemical to be "safe"? Explain.

22. A statement sometimes used about the hazards of medicines is: "The poison is in the dosage." Explain what this means.

23. Describe your own thoughts about the safety of each of the following: (a) sodium chloride, (b) aspirin, (c) ethyl alcohol, (d) caffeine, (e) nicotine.

24. If we can say that *anything* is hazardous if it is used in excess, can we also say that *everything* is safe if used in very small amounts? Explain.

Exercises

The end-of-chapter Exercises are broken into three sections.

For Review, with its fill-in-the-blank, matching, and straightforward review questions, provides students with the opportunity of building their own chapter summary, thus checking and reinforcing their comprehension of the chapter's content.

A Little Arithmetic and Other Quantitative Puzzles drills students on the more quantitative aspects of the chapter.

Think, Speculate, Reflect, and Ponder problems, which sometimes have no "right" answer, are intended to stimulate thought about the interconnections among chemistry, society, and individual values.

An Introduction to Chemistry

1

TURNING ON THE LIGHT

Science—to know and to understand the universe.

Table sugar (sucrose) and table salt (sodium chloride).

Enlightenment from a Flashlight

Our study of chemistry begins with two of our most common consumer products, chemicals that most of us use virtually every day: table salt and table sugar. Table salt, known chemically as *sodium chloride*, and table sugar, *sucrose* to the chemist, are both white, crystalline solids. It's almost impossible for most of us to tell them apart except by taste.

There's another important way they differ, though, and that is through their electrical behavior in water. The difference in how each of these consumer products conducts—or doesn't conduct—electricity when it's dissolved in water tells us a great deal about their composition.

We can observe the difference with a simple flashlight, some salt, sugar, a bit of warm water, and a sponge or absorbent towel. (This demonstration works best with fresh batteries and a new flashlight, with clean electrical contacts.) In a small glass dissolve a tablespoon of sodium chloride (table salt) in about a quarter of a cup of warm water. Do the same with a tablespoon of sucrose (table sugar) in another small glass. Now wet a sponge or a piece of an absorbent towel with some warm water. Turn the flashlight on and unscrew the back of the flashlight.

Naturally, the flashlight goes off when you remove the back. The spring that you see on the back part of the flashlight does two jobs. It pushes the batteries firmly up against the bulb and it serves as part of the flashlight's **electrical circuit**, which is simply the path the electrons follow within the flashlight. Electrons leave the base of the batteries, travel to the bulb over metal parts within the flashlight, move through the bulb's filament (causing it to heat up and emit light), and then back to the batteries (Fig. 1.1). The flow of electrons along this path constitutes an **electric current.**

An electric current is a flow of electrons. An **electric circuit** is the path the electrons follow.

The spring we've just removed is part of this circuit. It acts as the path that carries the electrons from the bottom of the nearest battery to the inside wall of the flashlight. When we unscrew the back of the flashlight we interrupt the path and so the light goes out. We're now going to try to make the light go back on by replacing the metal spring with something else.

First we'll try plain tap water. With the bulb pointed upward (to keep water from running down into the flashlight), press the wet sponge or towel firmly

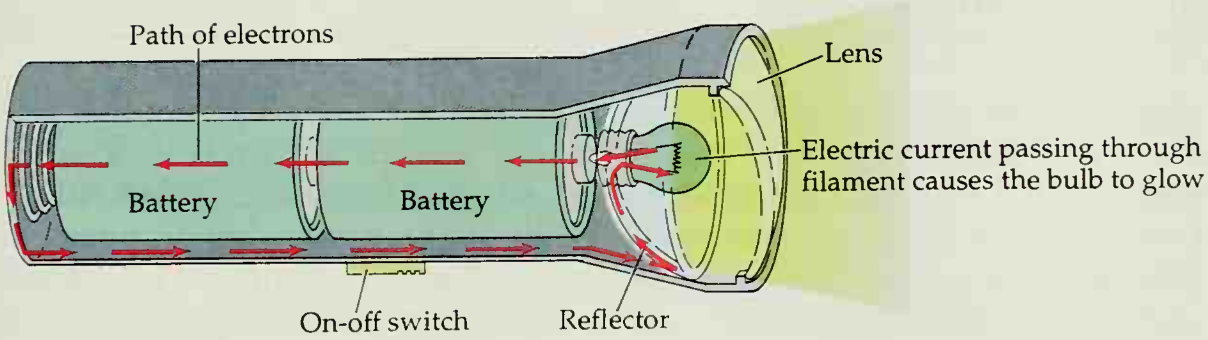


Figure 1.1
The electrical circuit of a flashlight.

against the back of the exposed battery. Push hard against both the back of the battery and the inside wall of the flashlight so that you make good contact with both. Watch the bulb as you make contact. You'll see that the flashlight bulb remains dark since water itself is a poor conductor of electricity. With tap water, not enough electrons flow across the wet sponge or towel to heat the filament to glowing. Remove the batteries, clean and dry them and the inside of the flashlight, and reinsert the batteries.

Now squeeze the tap water out of the sponge and wet it with the warm sugar-water solution. Repeat the process of pushing the sponge or towel into the back of the flashlight so that it forms a tight bridge between the back of the battery and the inside wall of the flashlight. There's still no sign of a glow. We're forced to conclude that sugar water is no better at conducting an electric current than plain tap water. Once again, remove and dry the batteries, dry the flashlight, and reinsert the batteries.

Repeat the entire process with the salt water. If you watch the bulb, in dim light, you'll see it glow faintly for a few moments just as you first press the sponge or towel against the back of the battery and the inside wall of the flashlight. This must mean that while sugar doesn't add to water's ability to conduct a current, salt does. Figure 1.2 sums up these observations.

With the low voltage of the flashlight battery, this demonstration of the difference in electrical behavior between salt and sugar is simple and safe enough for you to carry out (and does no damage to the flashlight or batteries as long as they are cleaned and dried thoroughly at the end). Yet the batteries' low voltage pushes electrons through the salt water too weakly to cause more than a dim glow in the bulb.

Figure 1.2
The electrical conductivity of tap water, sugar water, and salt water.

1.1 Light Bulbs, Salt, and Sugar

A much more dramatic (*and much more dangerous*) demonstration would use pure water rather than tap water, a common household light bulb, and 120 volts of house current, along with table salt and table sugar. **WARNING: Don't actually try to do this next version of the demonstration yourself!** Attempting it would involve a potentially lethal combination of bare wires and house current—120 volts—which must not be handled by anyone who isn't professionally skilled in working with electricity.

We know that if we plug a light bulb into an electric outlet, the bulb lights up (Fig. 1.3). The same principles are at work here as in the flashlight. If someone skilled in working with the high voltages of house current were to change the circuit by cutting one of the wires and then bending the free ends into a beaker of pure water, the bulb would be dark. As we saw with the flashlight, pure water is a poor conductor of electricity. With water in the circuit, too little current could pass through the bulb's filament to make it glow. Replacing the pure water by a solution of sucrose (table sugar) in water would make no difference whatever. The light bulb would remain dark and so we would conclude, as we did with the flashlight, that a solution of sucrose in water is no better a conductor of electricity than is pure water itself. With the bent wires dipping into a solution of sodium chloride (table salt), though, the bulb would now glow brightly.

An **electrolyte** is a substance that conducts electricity when it is dissolved in water or when it is melted.

The remarkable difference between sucrose and sodium chloride, visible with the flashlight batteries and dramatically apparent with 120 volts of house current, is that sodium chloride conducts electricity when it's dissolved in water, but sucrose doesn't. Substances that conduct electricity when dissolved in water—or when melted if they don't dissolve—are called **electrolytes.** Those that don't are *nonelectrolytes*. Sodium chloride, then, is an electrolyte while sucrose is a nonelectrolyte. This difference in electrical conductivity between salt and sucrose arises from differences in the chemical compositions

Figure 1.3

An electric light bulb. Pure water is a very poor conductor of electricity, as is a solution of sucrose (table sugar) in water. A solution of sodium chloride (table salt) in water is a good conductor of electricity.

of these two everyday substances. More exactly, it comes from differences in the kinds of forces that hold matter together in the two.

To understand what these forces are, and how they differ in sucrose and in sodium chloride, we'll examine the *atoms, ions, molecules,* and *chemical bonds* that make up the world around us (and that make up us as well) and that hold it all together. For the moment it's enough to know that

- Atoms, which were once thought to be the ultimate, indivisible particles that make up all matter, are among the fundamental particles of the science of chemistry.
- Molecules are groups of two or more atoms held together by the forces of chemical bonds.
- Ions are atoms or groups of atoms that carry a positive or negative electrical charge.

In the first few chapters of this book we'll examine these particles in more detail, we'll define them more precisely, and we'll learn how they are held together in the substances about us. We'll find, among other things, that atoms are extraordinarily small particles. Strung along in a straight line like beads on a necklace, for example, it would take 500,000,000 atoms of gold to stretch across the length of a dollar bill (Fig. 1.4).

After we have laid this foundation, we'll move on, in later chapters, to some of the ordinary (and sometimes not so very ordinary) things that these particles form and make work. Before we do, though, we'll examine briefly just what chemistry is and how we are going to explore it in the chapters that lie ahead. Then we'll return to our investigation of sugar, salt, water, and the light bulb to learn why table salt makes the bulb light up, but sugar doesn't.

QUESTION

What do you think would be the result of placing the wires into a solution made up of a *mixture* of equal parts of sucrose and sodium chloride? (You'll find a question of this sort at the end of most of the sections in this book. Each one is written to help you review the material and the ideas contained in the section it concludes.)

Figure 1.4
Gold atoms and a dollar bill.

1.2 The Extraordinary Chemistry of Ordinary Things

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Chemistry is the branch of science devoted to the study of matter, its composition, its properties, and the changes it undergoes. Chemistry studies the material substance of the universe, the stuff we can hold, kick, feel, weigh, smell, see, touch, and taste.

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Another theme is that chemicals provide us with the bulk, physical structures of our everyday lives, from the polymeric plastics that form our consumer goods and that wrap them in convenient packages to the substances that form, shape, and wrap our own bodies: our bones, organs, and skin. Every bit of whatever material substance we see, touch, or use is made of chemicals, and so are we.

A third theme reveals the importance of chemical particles themselves, from the smallest ions, atoms, and molecules to the largest and most complex polymeric molecules of our bodies and of the world about us. Water, a simple molecule consisting of one oxygen and two hydrogen atoms, forms more than half the weight of our bodies; no living thing can exist without it. Molecular oxygen, a union of two small oxygen atoms, provides life to the entire animal


Shopping for the chemicals of our everyday lives.


The chemicals of gasoline provide energy for transportation.


Polymeric chemicals form the plastics of wrappers and containers.

kingdom. Atmospheric ozone, a molecular structure built of three oxygen atoms, shields and protects living things from deadly doses of ultraviolet solar radiation. Atmospheric chlorine atoms, among the simplest and smallest of chemical particles, threaten to erode and perhaps destroy that very ozone shield. At the other end of this spectrum are the large and intricately designed protein molecules that govern the operations of our bodies.

Our final theme is that chemicals are good or bad, beneficial or harmful, only in the ways we use them. Chemicals can cause illness and death, and yet as judiciously chosen food additives they can also protect us against microorganisms that cause illness and death. The sturdy and durable synthetic polymers that have long and useful lives in consumer products can become persistent, degradation-resistant components of our trash. And the by-products of the chemical reactions that provide energy and materials to today's world can themselves become pollutants that foul our air, land, and water. Our wise use of chemicals depends both on our own good judgment and on our clear understanding of what these chemicals of our world are and what they can do for us and to us.

In a real and broader sense the study of chemistry is the study of our society itself. To examine either without an understanding of the other is to leave a void of ignorance about the modern world.

QUESTION

Which of the following are suitable investigations for the science of chemistry? (a) Finding the best method for converting old newspapers into writing paper; (b) learning which air pollutants produce the most corrosive forms of acid rain; (c) determining the intensity of sunlight falling on an asteroid located between Earth and Mars; (d) learning how to prepare plastic garbage bags that degrade to harmless products after they are discarded; (e) designing a low-calorie fat substitute for fried foods; (f) learning whether weightlessness has any effect on our perception of the distance of nearby objects; (h) determining which of our foods are electrolytes and which are not; (i) analyzing the rocks and soil of the surface of the moon to determine their composition; (j) measuring the force of gravity at the moon's surface.

1.3 Ions: Electricity in Motion and at Rest

Now, with our understanding of what chemistry is and how we are going to examine it, we can return to our investigation of table salt and table sugar and learn how our observations of their properties help us understand them and the world about us.

We've seen that the light bulb of Figure 1.3 glows as electricity passes through its filament. An electric current moves through the wires of the circuit in the form of electrons, which are extremely small particles that carry a negative electrical charge.

Since the bulb remains dark when a beaker of pure water is put into the circuit, we can conclude that water itself doesn't conduct electricity very well. Actually, we rarely find pure water in the world around us. Most water we encounter contains dissolved salts, much like the table salt of Figure 1.3, and therefore most of the water we find in our everyday lives does conduct electricity. Dissolved salts are partly responsible for the common observation that (impure) water often conducts electricity, and sometimes very well indeed.

Sucrose doesn't change water's ability to conduct electricity, but sodium chloride does. A solution of sodium chloride in water (or molten sodium chloride, at a very high temperature) is very effective at conducting an electric current. Clearly, adding the sodium chloride introduces something into the water that allows electricity to flow from one wire to the other. Adding sucrose does not.

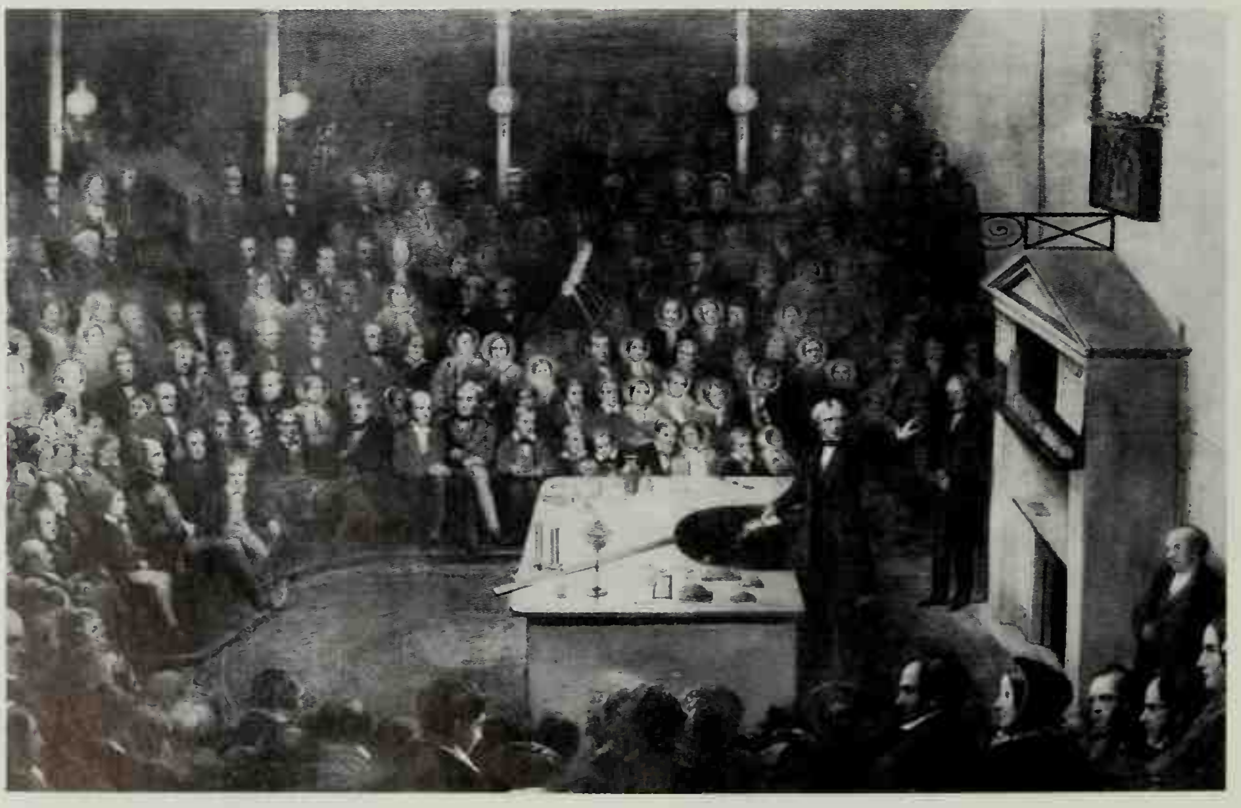
The simplest explanation for all this and other, related observations is that sodium chloride is made up of electrically charged particles that can move about in water and can transport an electric current through water much as electrons transport current through the wires of an electrical circuit. On the other hand, we have to conclude that sucrose is *not* made up of electrically charged particles.

An **ion** is an atom or a group of atoms that carries an electrical charge.

These small particles of sodium chloride and other electrolytes, each bearing a negative or positive electric charge, are called **ions.** As we saw in Section 1.1, an *ion* is *an atom or a group of atoms that carries an electrical charge.* To understand more fully what ions are—and how it is that sodium chloride can carry an electric current although sucrose cannot—we have to understand what atoms are (and, later, what molecules are). We'll have more to say about atoms and ions in Chapter 2.

An **anion** is a negatively charged ion; a **cation** is a positively charged ion.

Ion is a term derived from a Greek word meaning "to go." In 1834 the English physicist Michael Faraday used the word to describe chemical particles that move to one electrical pole or another. He divided ions into two categories: **anions** are the negatively charged chemical particles that move to the positive electrical pole (the anode); **cations** are the positively charged chemical particles that move to the negative electrical pole (the cathode). We still use the same definitions today, but now we recognize that ions can remain



Michael Faraday delivering a lecture to an audience that includes the Prince Consort of Great Britain.

at rest, too. The sodium chloride of our crystalline table salt is made up entirely of ions that remain quietly in the salt shaker.

Sodium chloride, we now know, is composed of sodium cations and chloride anions held together in crystalline table salt by the mutual attraction of opposite electrical charges. The positively charged sodium cations and the negatively charged chloride anions are held close to each other through the action of **ionic bonds,** whose strength comes from this mutual attraction of opposite electrical charges. Together, the two *elements,* sodium and chlorine, form the *compound* sodium chloride.

An **ionic bond** is a chemical bond resulting from the mutual attraction of oppositely charged ions.

QUESTION

Would you expect to find many ions in pure water? Explain your answer. ______

1.4 Elements and Compounds

Elements are the fundamental substances of chemistry, composed of the atoms described in Section 1.1. Today we recognize the existence of 109 different elements, including hydrogen, oxygen, nitrogen, gold, carbon, calcium, zinc, iron, uranium, sodium, chlorine, phosphorus, helium, and sulfur. Neither these nor any other element can be decomposed or converted to a simpler substance by any form of energy we deal with in our everyday lives. Neither heat, light, electricity, sound, magnetism, nor any other common form of energy, no matter how intense, can produce either of these changes in an element. Nor can one element be transformed into another element, a process known as *transmutation,* except under conditions far removed from our com-

The elements gold and silver.

The elements mercury, copper, and carbon.

TABLE 1.1 Representative Elements of the Human Body

Element	Grams in the Body of a 60-kg (132-lb) Person (Approximate)	Bodily Location and Function	Dietary Source
Calcium	1300.	More than 99% of the body's calcium is in the bones and teeth	Milk and milk products including cheese and ice cream
Chlorine	90.	As chloride ion, it is the principal cellular anion; when combined with hydrogen ion, forms the hydrochloric acid of gastric juices	Sodium chloride (table salt)
Cobalt	Trace	Component of vitamin B_{12}	Widely distributed (as a component of vitamin B_{12}) in meat, especially liver, kidney, and heart; also in clams, oysters, milk, and milk products
Copper	Trace	Component of many enzymes	Widely distributed, especially in nuts, shellfish, kidneys, and liver
Iodine	Trace	Thyroid; necessary for normal functioning of the thyroid	Seafood, iodized table salt
Iron	2.	Red blood cells; a component of hemoglobin	Beef, liver, dried fruits, whole-grain and enriched cereal products, and egg yolk
Magnesium	20.	Second most abundant cation in body cells (after potassium); over half the body's magnesium is in the bones	Green, leafy vegetables
Phosphorus	690.	Component of ATP, a cellular energy-releasing agent	Meat, eggs, milk, and milk products
Potassium	200.	Most abundant cation in body cells; regulates water balance in cells	Widely distributed in a large variety of foods
Sodium	60.	Most abundant cation in body fluids outside cells; regulates water balance in the body	Sodium chloride; widely distributed in a large variety of foods
Zinc	Trace	Occurs in bones and many enzymes	Seafood, especially oysters; meat, liver, eggs, milk, and whole-grain products

mon experience, such as at extraordinarily high temperatures, close to those found at the surface of the sun, and in some other unusual ways as well. We'll examine some of these in Chapter 4.

Alone or (more often) in combination with other elements they form our water, air, food, clothing, homes, automobiles, medicines, and our own bodies. Table 1.1 describes some of the elements that make up the human body.

The tank contains oxygen, a gaseous element.

Sodium chloride, hydrogen peroxide, water, and sucrose are some of the more common compounds of our everyday world.

By combining with each other in precise, well-defined ratios, two or more elements can form a pure substance known as a **compound.** The table salt, sugar, and water of our investigation with the light bulb are examples of compounds. Table salt (sodium chloride) is a pure substance formed from a combination of the two elements sodium and chlorine, with both elements present in a specific, well-defined, fixed ratio to each other. Table sugar (sucrose) is a pure substance formed from a combination of the three elements carbon, hydrogen, and oxygen in a distinct ratio; water forms when hydrogen and oxygen combine, again in a fixed proportion. Hydrogen peroxide, a bleaching agent and an antiseptic, also consists of a combination of hydrogen and oxygen in a specific ratio, but one different from the ratio of these two elements that forms water.

A **compound** is a pure substance formed by the chemical combination of two or more different elements in a specific ratio.

Any compound can be decomposed into its individual elements, some by the action of heat or light, some by the effect of an electric current, and some through reaction with still another compound or with an element. Water, for example, decomposes into hydrogen and oxygen when an electric current passes through it. Heating sucrose decomposes it into another compound (water) and the element carbon.

It's worth noting that when elements react with one another their *ratio* determines the nature of the product. If exactly 23.0 g of sodium and 35.5 g of chlorine are allowed to react with each other, they form 58.5 g of pure sodium chloride, with neither sodium nor chlorine left over. As long as this weight ratio, 23.0/35.5, is maintained, only pure sodium chloride results. If either sodium or chlorine is present in excess, though, the product is a mixture of sodium chloride and the element that is in excess. We'll see why this is so in Chapter 9.

For an illustration of the importance of the ratios of reacting substances, consider the following example.

EXAMPLE REACTING IN RATIOS

Suppose we allow 10.0 g of sodium to react with an equal weight of chlorine. What is the composition of the product?

We know that a ratio of 23.0 g of sodium to 35.5 g of chlorine produces pure sodium chloride and that if either sodium or chlorine is present in excess, the product is a mixture of sodium chloride and the element that is present in excess. Since 35.5 g of chlorine reacts with a *smaller* weight of sodium (23.0 g) to produce sodium chloride, it's clear that with equal weights of the two there's an excess of sodium. Our problem, then, is to calculate just how much excess sodium is present. To find this value we multiply the 10.0 g of chlorine we're given by the ratio 23.0 g sodium/35.5 g chlorine.

$$10.0 \text{ g chlorine} \times \frac{23.0 \text{ g sodium}}{35.5 \text{ g chlorine}} = 6.5 \text{ g sodium}$$

This means that to maintain the ratio of 23.0 g sodium to 35.5 g chlorine, 6.5 g of sodium must react with the 10.0 g of chlorine provided in this illustration. The reaction consumes all of the chlorine present (10.0 g) and 6.5 g of the original 10.0 g of sodium to produce 16.5 g of sodium chloride (from the 10.0 g of chlorine and 6.5 g of sodium), with

$$\begin{array}{rl} 10.0 & \text{g sodium} \\ \underline{-6.5} & \text{g sodium} \\ 3.5 & \text{g sodium left over} \end{array}$$

The product, then, is composed of 16.5 g sodium chloride and 3.5 g of sodium. (You might want to consult the appendices at the end of the book for help with this example and others throughout the text.)

QUESTION

(a) Name three elements. (b) Name three different compounds, each of which contains at least one of these elements. ____________________

PERSPECTIVE: Science—Understanding the Universe

Let's pause here to review what we've just done and seen. We've begun our study of chemistry with the observation that pure water is a very poor conductor of electricity, that dissolving *table sugar* in water doesn't improve its conductivity, but that dissolving *table salt* in water does increase its conductivity dramatically. We've used the words *ion, anion,* and *cation* to help us interpret this particular behavior of salt and sugar. We've also used the word *electrolyte* to name the category that table salt occupies, and the word *non-*

electrolyte for the category that contains table sugar. We've learned that common table salt is a *compound*, sodium chloride, composed of the *elements* sodium and chlorine, held together by *ionic bonds*. All of this gives us our first glimpse of the science of chemistry in action.

Science itself is a way of knowing and understanding the universe we live in. (The word **science** comes to us from the Latin *scire*, "to know.") Science often operates by

Science is a way of knowing and understanding the universe.

- Asking questions of the universe by means of experiments and similar tests of the physical world (just as we asked, implicitly, "Does pure water conduct electricity?" when we carried out the investigation of Fig. 1.3).
- Observing the way these questions are answered (as we observed that the light bulb does not glow when its wires are immersed in water).
- Asking additional questions that are generated by the answers to our earlier question (as we asked, again implicitly, "Does adding sucrose or sodium chloride to the water improve its electrical conductivity?").
- Interpreting the answers to our questions—what we have observed—to help us understand how the universe operates and increase our understanding of it (as we inferred from our observations of the light bulb that adding sodium chloride to the water introduces something into the water, something we call "ions," that allows electricity to flow from one wire to the other, but that adding sucrose does not introduce these ions).
- Communicating our observations and interpretations to others so that they can examine what we have done, repeat and confirm our own observations, perhaps suggest alternative explanations for what we have observed, ask questions of their own based on our observations and interpretations, and thereby continue the entire process.

This general procedure provides us with a never-ending supply of questions to be asked and results in a continuously refined interpretation of the universe we live in. Its fruits are the hypotheses and theories we use to explain our world. A *hypothesis* is a shrewd but tentative explanation of a relatively small set of observations; a *theory* is more firmly grounded interpretation, based on a larger set of confirmed observations and generally accepted by a large number of people. It's important to understand, though, that even a universally accepted theory supported by a great number and variety of observations may have to be modified, revised, or even abandoned completely as a result of even a single new observation. In this sense the ultimate value of science is that it allows us to explain what we continue to observe and experience in the world about us, through sets of descriptions (which we may call theories) that are relatively simple, that are consistent with one another, that cover large numbers of observations and experiments, and that are generally accepted by most of us.

Taken as a whole, this method of learning is known as the **scientific method.** The specific steps of the scientific method may vary from time to time and from investigation to investigation, but they always involve asking a question of the universe, determining the answer through an experiment or other test, and then using the results of the experiment to refine our knowledge of the universe, often with the generation of still other questions. The quality of the investigation and of our resulting understanding of the universe

The **scientific method** is the process by which science operates.

depends on the cleverness of the questions we ask, the skill with which we carry out the experiments, and our ability to convert the results of the experiments into an ever more sophisticated understanding of ourselves and all that surrounds us.

As we proceed in this study of the composition and properties of common (and sometimes not so common) substances of the world we live in, and of the changes they undergo, we'll use the results of the scientific method: the questions that have been asked by those who preceded us and the hypotheses, theories, interpretations, pictures, and models of the world that they constructed to explain the answers they received.

QUESTION

What is the principal objective of all scientific investigations? ________________

EXERCISES

The exercises that appear at the ends of chapters fall into three categories. *For Review* contains exercises to help you review the content of the chapter you have just finished. Each *For Review* section starts with one or more fill-in-the-blank paragraphs that provide a brief summary of the major points of the chapter. Then comes a series of questions that review the substance of the chapter, sometimes including material presented in the tables and figures.

The next category, *A Little Arithmetic and Other Quantitative Puzzles,* emphasizes the quantitative basis of chemistry. The problems are often short, requiring only a bit of simple arithmetic to arrive at the answer. Occasionally the route to the answer is a little more involved, requiring some quantitative reasoning. In any case, you never need more than the four steps of arithmetic—addition, subtraction, multiplication, and division—to arrive at the solution.

Think, Speculate, Reflect, and Ponder challenges you to go beyond the content of the chapter, to think about the ideas presented, to speculate on alternative possibilities, to reflect on your own response to the interplay of chemistry and society, to ponder over certain details. While the exercises of the first two sections have specific, unique "right" answers, many of those you'll find here have no such "right" answer, but only the particular response that you give. Others have a wide choice of answers that can be considered to be "right," as well as traditionally "wrong" answers. Occasionally you may find a challenge that has no "right" answer at all, given our current knowledge of chemistry and the problems facing today's society. Still other exercises in this group have a single, unique "right" answer, as in the first two categories, but require a more thorough understanding of the material of the current chapter and perhaps previous chapters as well, coupled with careful thought and some insight as well.

FOR REVIEW

1. Complete this statement with the words and phrases that follow. Each is used once.

Pure _______ is a very poor conductor of electricity. Adding common table salt, known chemically as _______, introduces _______ into the water in the form of sodium _______ and chloride _______. These small chemical particles carry _______ and as they move through the water they transport an electrical current through it. The anions are _______ charged and the cations are _______ charged. Any substance that carries an electric current when it is dissolved in water, or when it is melted, is called an _______. Unlike sodium chloride, common table sugar, or _______, cannot carry an electric current when it is dissolved in water. Table sugar is thus an example of a _______.

~~anions~~
~~cations~~
~~electrical charges~~
~~electrolyte~~
~~ions~~
~~negatively~~
nonelectrolyte
~~positively~~
~~sodium~~ chloride
sucrose
water

2. Complete this statement with the words and phrases that follow. Each is used once.

_______, which is the study of the composition and properties of matter, and of the changes that it undergoes, is a branch of _______, which itself provides us with a way of knowing and understanding the universe we live in. In the operation of the _______ we ask questions of the universe through tests and _______. By observing the results that we get we can formulate additional questions, perform additional experiments, and finally develop a tentative explanation of what we have learned. If this tentative explanation or _______ is confirmed by others and becomes widely accepted it becomes a _______ and helps us understand better the world about us.

chemistry
experiments
hypothesis
science
scientific method
theory

3. Match each item in Group A with one in Group B.

Group A

_____ a. chloride anion
_____ b. compound
_____ c. electrolyte
_____ d. ion
_____ e. ionic bond
_____ f. molecule
_____ g. sodium cation
_____ h. sulfur

Group B

1. assembly of atoms
2. chemical particle that carries either a positive or a negative electrical charge
3. conducts electricity when it is dissolved in water or when it is molten
4. element
5. negatively charged ion
6. positively charged ion
7. pure substance formed by combination of two or more elements in a specific ratio
8. results from the attraction of oppositely charged ions

4. Of the elements listed in Table 1.1,
  a. Which is the most abundant in the human body?
  b. Which is a component of the hemoglobin of red blood cells?
  c. Which occurs primarily in the thyroid gland?
  d. Which forms the most abundant cation of the body fluids found outside the body's cells?
  e. Which do we obtain principally from milk and milk products, such as cheese?

5. In your own words, describe briefly the steps of the scientific method.

6. In a dozen words or less, describe what the science of chemistry examines.

7. What is the difference between a *hypothesis* and a *theory*?

8. Why is *communication* an important part of the scientific method?

9. What evidence indicates that sodium chloride is composed of ions? What evidence indicates that sucrose is not composed of ions?

10. In what way are water and hydrogen peroxide similar in chemical composition? In what way are they different? (See Section 1.3.)

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

11. Suppose you carry out a large number of tests as follows. In each experiment you use 10.0 g of sodium. In the first experiment you allow the 10 g of sodium to react with 0.1 g of chlorine; in the second you allow 10 g of sodium to react with 0.2 g of chlorine; in the third, with 0.3 g of chlorine, and so forth. In each subsequent test you allow 10 g of sodium to react with an additional 0.1 g of chlorine until the series ends with 10 g of sodium and 20.0 g of chlorine. Describe qualitatively how the product(s) of the individual reactions change(s) as the series of experiments progresses from 0.1 g of chlorine to 20.0 g of chlorine.

12. How much chlorine would you have to use if you wanted 10.0 g of sodium to react with it to produce pure sodium chloride, with neither excess sodium nor excess chlorine left over?

THINK, SPECULATE, REFLECT, AND PONDER

13. Describe three activities or investigations, other than those mentioned in the question at the end of Section 1.2, that involve the science of chemistry.

14. Would you expect seawater to be a good conductor of electricity? Explain.

15. Suppose you discovered a new substance and weren't sure whether you should classify it as a new element or a new compound. How would you go about determining whether you discovered a new element or a new compound?

16. The following table summarizes the results we described for the light bulb, water, sodium chloride, and sucrose early in this chapter:

	Condition of the Light Bulb
pure water only	dim or dark
water and sucrose	dim or dark
water and sodium chloride	bright

What would you have concluded for each of the following results:

A	Condition of the Light Bulb
pure water only	dim or dark
water and sucrose	bright
water and sodium chloride	dim or dark

B	Condition of the Light Bulb
pure water only	dim or dark
water and sucrose	bright
water and sodium chloride	bright

C	Condition of the Light Bulb
pure water only	bright
water and sucrose	bright
water and sodium chloride	bright

Why was it necessary to test the electrical conductivity of pure water before adding sodium chloride and sucrose?

17. Several centuries ago, it was generally believed that heavy objects fall faster than lighter objects, that the more an object weighs the faster it falls. According to one legend, the Italian scientist Galileo Galilei, who lived from 1564 to 1642, corrected this error by dropping two spheres of different weight simultaneously from a high point of the Leaning Tower of Pisa and demonstrating that they reach the ground at the same time. Describe what Galileo supposedly did in terms of the scientific method. What question did he ask of the universe? What test did he use to obtain an answer? What did he observe? How did he interpret this observation?

18. The old saying "A watched pot never boils" comes from the observation that a pot of water *seems* to take longer to come to a boil if you are watching it than if you aren't. Describe how you could use the scientific method to learn whether water really does take longer to boil if you are watching it. If water takes just as long to boil whether or not you are watching it, how could you use the scientific method to determine whether water actually does *seem* to take longer if you are, indeed, watching it, and just *how much* longer it seems to take? Describe what questions you would ask, how you would go about finding experimental tests that would give you answers to these questions, and how you would interpret the answers.

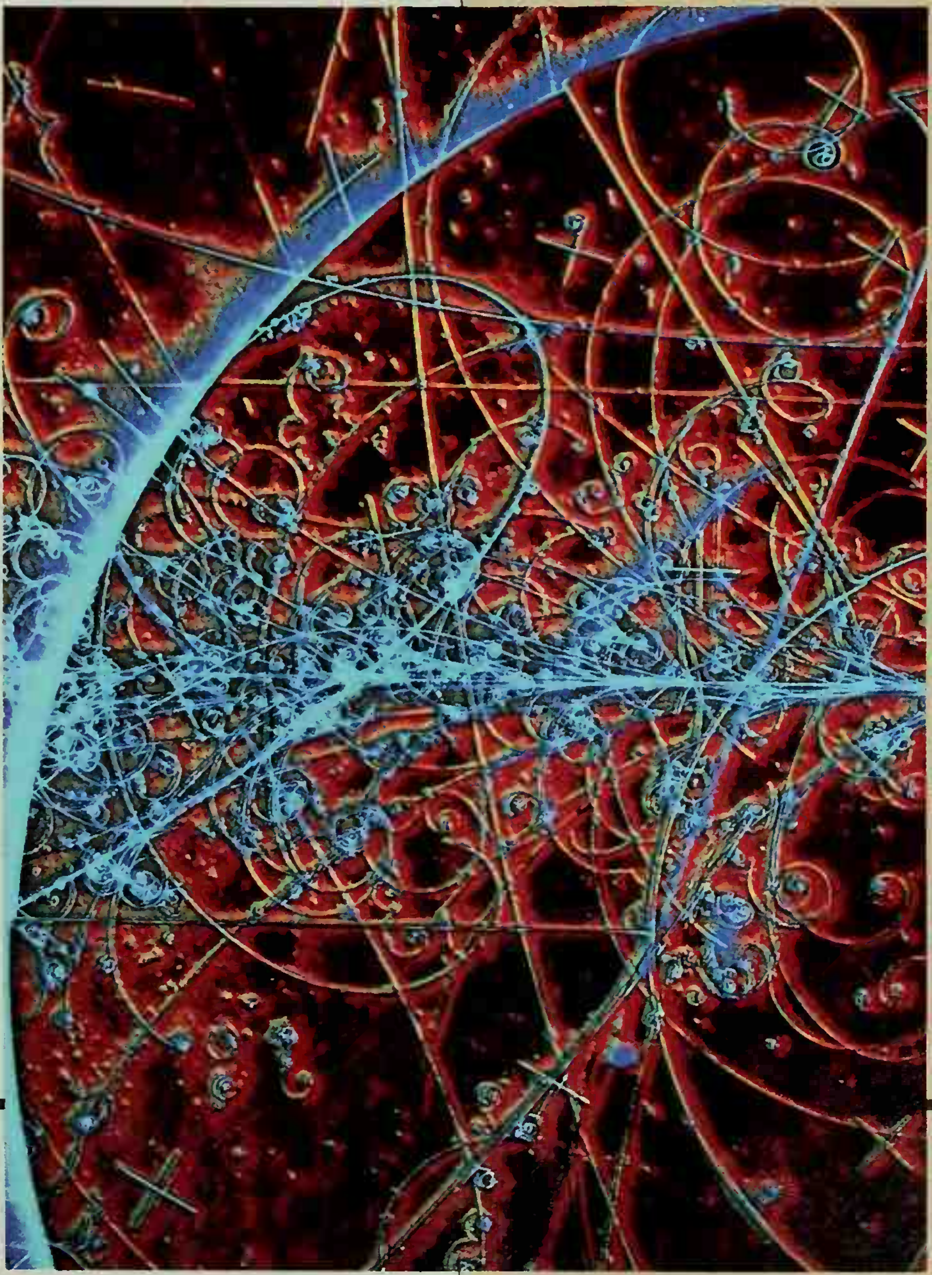
19. Describe another popular belief or perception, similar to the one about the watched pot or falling objects, that you could investigate by application of the scientific method.

20. Water can be considered to be a "good" chemical in the sense that we cannot live without it. Yet it is "bad" when floods destroy property or when someone drowns. Similarly, aspirin is "good" in the sense that it relieves headaches, yet it is "bad" in that children have mistaken it for candy, taken overdoses, and died. (a) Give examples of two other chemicals that are ordinarily beneficial yet can produce undesirable, even deadly effects. (b) Give examples of two chemicals that are ordinarily thought of as hazardous or harmful, yet in the right circumstances can be beneficial.

2

Atoms and Elements

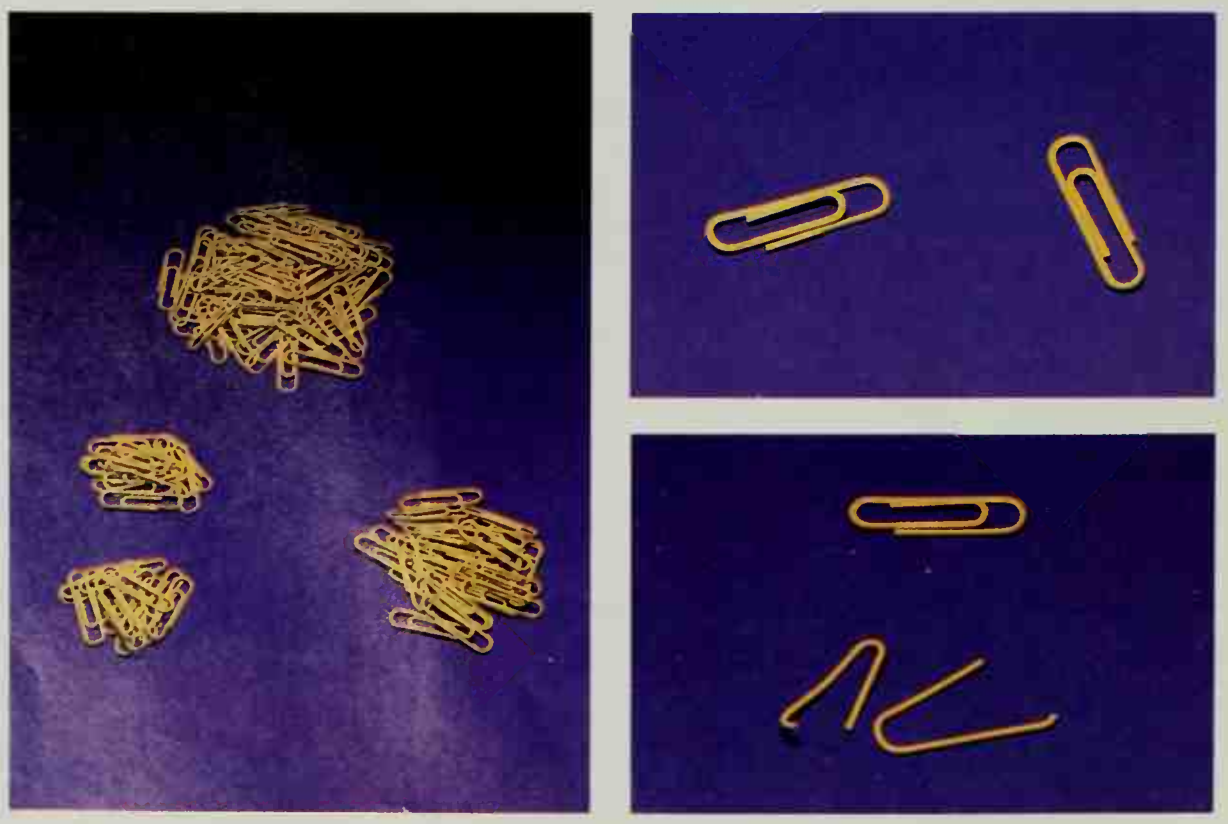
THE BUILDING BLOCKS OF CHEMISTRY



Tracks of subatomic particles.

Atoms and Paper Clips

To gain some insight into the modern view of an atom, try this demonstration. It draws an analogy between a pile of paper clips and a small amount of one of the 109 known elements, a bar of gold for example. Although it's only a simple analogy, one that can't be stretched very far, it does illustrate an important point about atoms. Place a pile of paper clips, perhaps 15 or 20, on a level surface and imagine a bar of pure gold sitting next to them (Fig. 2.1). Now divide the pile of paper clips roughly in half. Subdivide one of the new, smaller piles in half and repeat the process again and again until you are down to a "pile" that consists of a single paper clip. In our analogy, that single paper clip represents an "atom" of paper clips, the smallest part of the original pile of paper clips that



Piles of paper clips, individual paper clips, and fragments of a paper clip. The fragments no longer represent a paper clip.

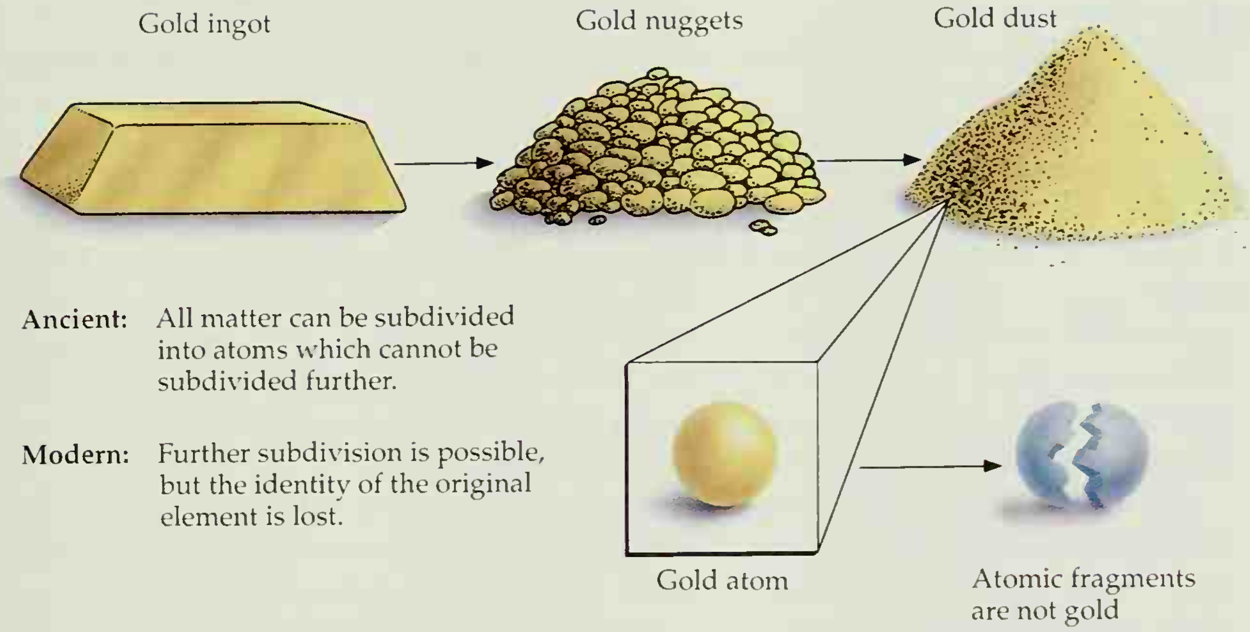


Figure 2.1
In a parallel to the demonstration with the paper clips, repeatedly subdividing a piece of gold produces smaller and smaller groups of atoms. Dividing a single gold atom into two parts produces fragments that no longer represent the element gold.

you can still identify as a paper clip. The result of all this is that you have divided and subdivided the original pile of paper clips into ever smaller piles until you finally came to the smallest part of the original pile that you can still identify as a paper clip. By analogy, that simple paper clip represents an "atom."

Now imagine that you perform the same operation with the bar of gold. Picture yourself dividing the (imaginary) bar in half again and again, as you did with the paper clips, until you finally reach the smallest particle of the bar that you can identify as the element gold. Like the single paper clip you eventually reached, that smallest particle, the smallest one you can still identify as gold, is an atom of gold. This time, though, it's an authentic atom.

We can't carry this analogy very far. The paper clip that remains has all the properties we expect of a paper clip, but even if we could see the atom of gold, which has a diameter about 1/500,000,000th the length of a dollar bill, as we saw in Figure 1.4, we wouldn't expect it to have many of the properties of the shiny, yellow metal we started with. Nonetheless, as we'll see in Section 2.5, you would still be able to characterize this ultimate particle of the bar as a bit of the element gold.

Now for the final part of the analogy. Suppose you cut the paper clip in half or twist it and break it into two pieces, as in Figure 2.1. Each of these pieces might have some sort of use. Perhaps you can even devise sensible names for them. Whatever their value, though, and whatever names you might assign to them, it's impossible to identify either of the fragments as a paper clip. You divided and subdivided the pile of paper clips down to its smallest component that you could still identify as a paper clip and then you divided that smallest piece once more, this time into fragments you can no longer identify as paper clips and that no longer have any of the properties of a paper clip.

Similarly, we can divide a portion of an element into smaller and smaller pieces, until we reach a single atom of that particular element. As with the paper clip, we can split an atom into fragments, but whatever the uses and properties of these fragments, and whatever names we may give them, we cannot identify any of them as the element from which the atom originally came.

2.1 Democritus and a Bar of Gold

The ancient Greeks, who gave us the word *ion* for a moving electrical particle, also gave us the word for the structure that is both the smallest particle of an element and the fundamental particle of chemistry, the *atom*. The word comes from the Greek *atomos*, meaning *indivisible* or an *indivisible particle*. One of the Greek philosophers of antiquity, Democritus, held that infinitely small, indivisible and eternal particles constitute the essence of all matter and give substances their particular properties. Democritus and his followers believed that any particular piece of matter can be divided and subdivided down to its ultimate particles, its *atomos*, and no further.

Both philosophy and science have advanced quite a bit since the time of Democritus. Although we now know that atoms have extremely small but finite sizes and can indeed be divided or split, Democritus was nonetheless right in one limited but very real sense. Today chemists recognize atoms as the smallest particles of 109 known elements that make up our entire universe. We can subdivide any quantity of any element as much as we wish and still have that unique element, until we reach the atoms that compose it. Once we split an atom we can no longer identify the element from which it came. An **atom** is *the smallest particle of an element that we can identify as that element.*

An **atom** is the smallest particle of an element that can be identified as that element.

2.2 The Size and Abundance of Atoms

Atoms themselves seem almost as small as Democritus believed them to be. They are far too small to be seen with even the most powerful optical microscope. A gold atom, for example, is about 3×10^{-8} cm in diameter and has a mass of about 3.3×10^{-22} g. (For an explanation of this form of writing numbers, called *exponential notation* or *scientific notation*, please turn to Appendix A.) In other terms, a gold atom has a diameter of about 0.00000003 cm and weighs about 0.00000000000000000000033 g. Compared with atoms of other elements, the gold atom is about average. Other atoms range in size from those of helium, a little over half the diameter of a gold atom, to atoms even larger than those of cesium, which has almost twice gold's diameter (Fig. 2.2).

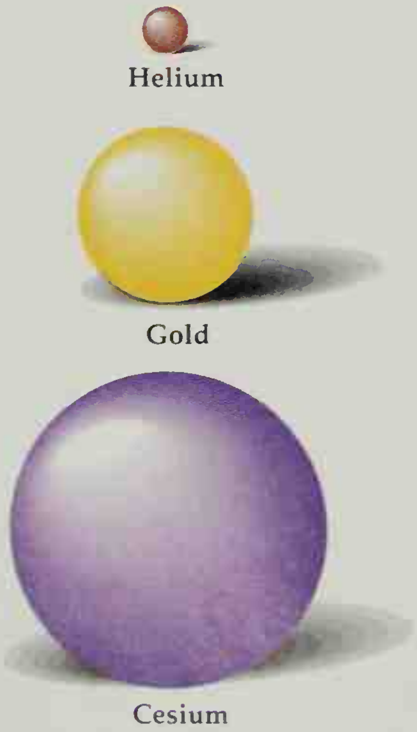
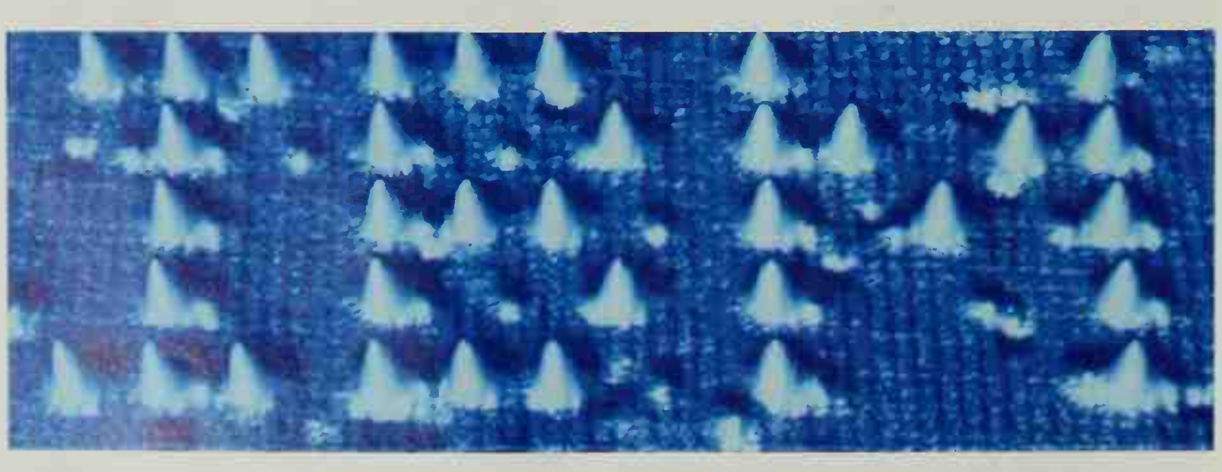


Figure 2.2
Relative sizes of helium, gold, and cesium atoms.



Individual atoms of xenon spell out I.B.M. The images are seen through a scanning tunneling microscope.

EXAMPLE BILL OF GOLD

How much does a sheet of gold atoms weigh that is the size of a dollar bill and just 1 atom deep?

A dollar bill is 15.7 cm long and 6.6 cm wide. If, as we've already seen, it takes about half a billion spherical gold atoms to stretch across the length of a dollar bill, it takes a proportionally smaller number of atoms to run along its width:

$$500{,}000{,}000 \text{ gold atoms} \times \frac{6.6 \text{ cm (the bill's width)}}{15.7 \text{ cm (the bill's length)}}$$

$$= 210{,}000{,}000 \text{ gold atoms along the width}$$

If we assume that the atoms are lined up on the dollar bill in 210,000,000 rows (or 2.1×10^8 rows) of 500,000,000 (or 5.0×10^8) atoms each, then we can calculate that there are

$$2.1 \times 10^8 \text{ rows} \times \frac{5.0 \times 10^8 \text{ atoms of gold}}{\text{row}}$$

$$= 10.5 \times 10^{16} \text{ atoms of gold}$$

present in the rectangle. Since, as we've just seen, each gold atom weighs 3.3×10^{-22} g, the entire rectangle of gold weighs

$$10.5 \times 10^{16} \text{ atoms} \times \frac{3.3 \times 10^{-22} \text{ g}}{\text{atom}} = 35. \times 10^{-6} \text{ g}, \quad \text{or} \quad 0.000035 \text{ g.}$$

As for the abundance of the various elements, in terms of the actual numbers of atoms present, hydrogen is by far the most plentiful element both in the universe (Fig. 2.3) and in our bodies (Fig. 2.4). The four elements hy-

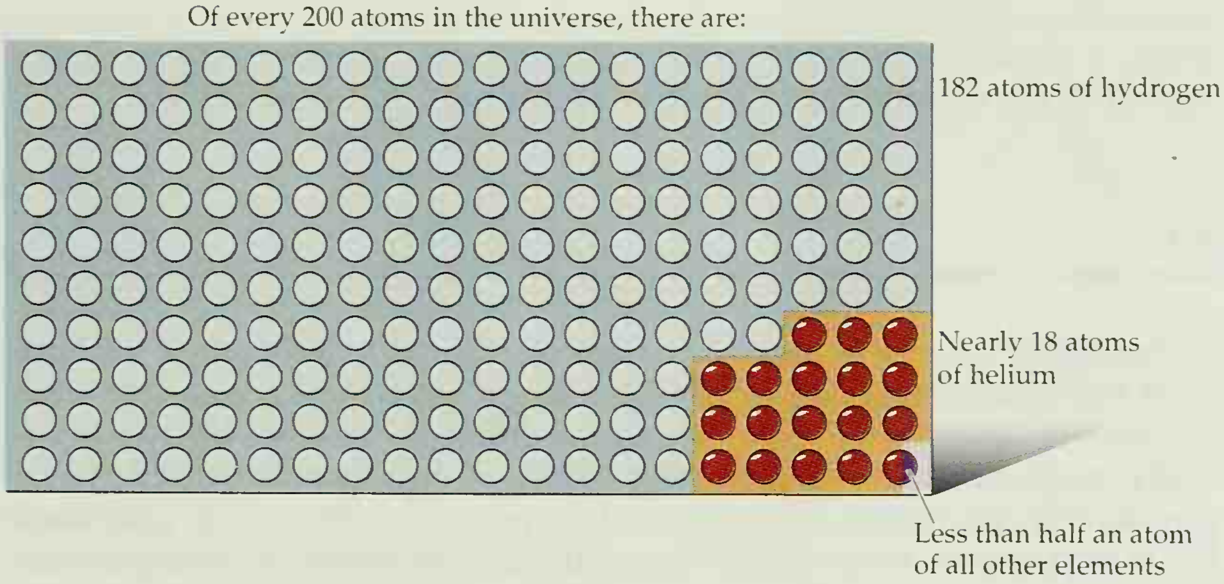


Figure 2.3
Distribution of the elements in the universe.

Figure 2.4
Distribution of the elements in the human body.

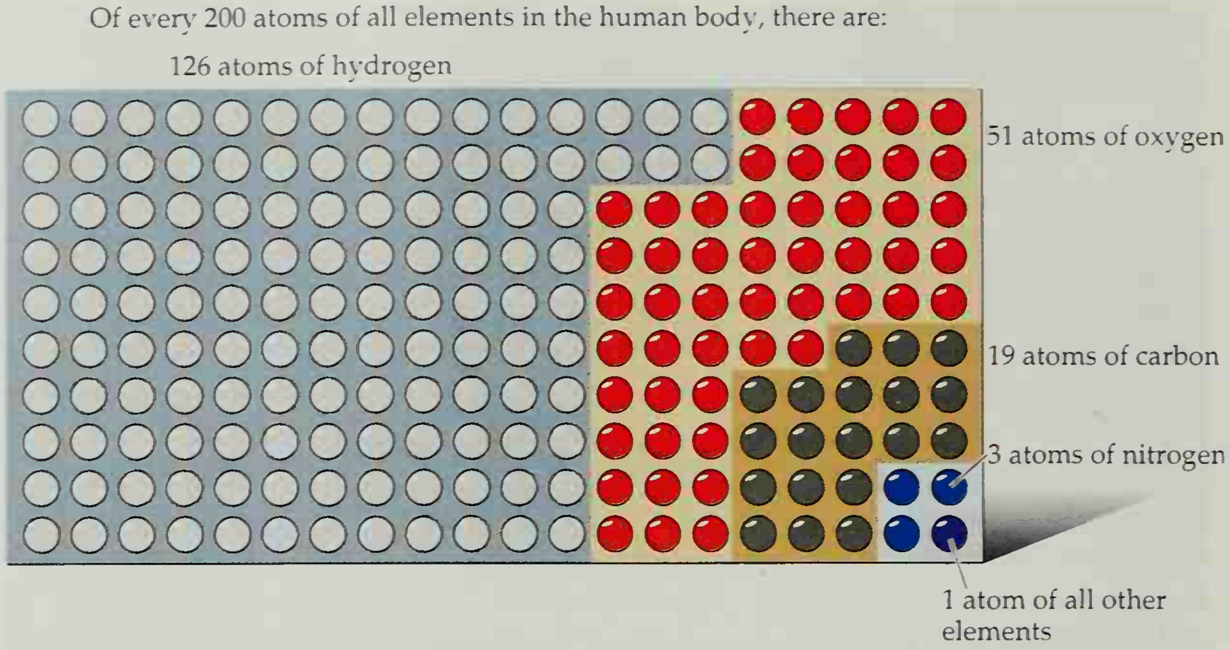
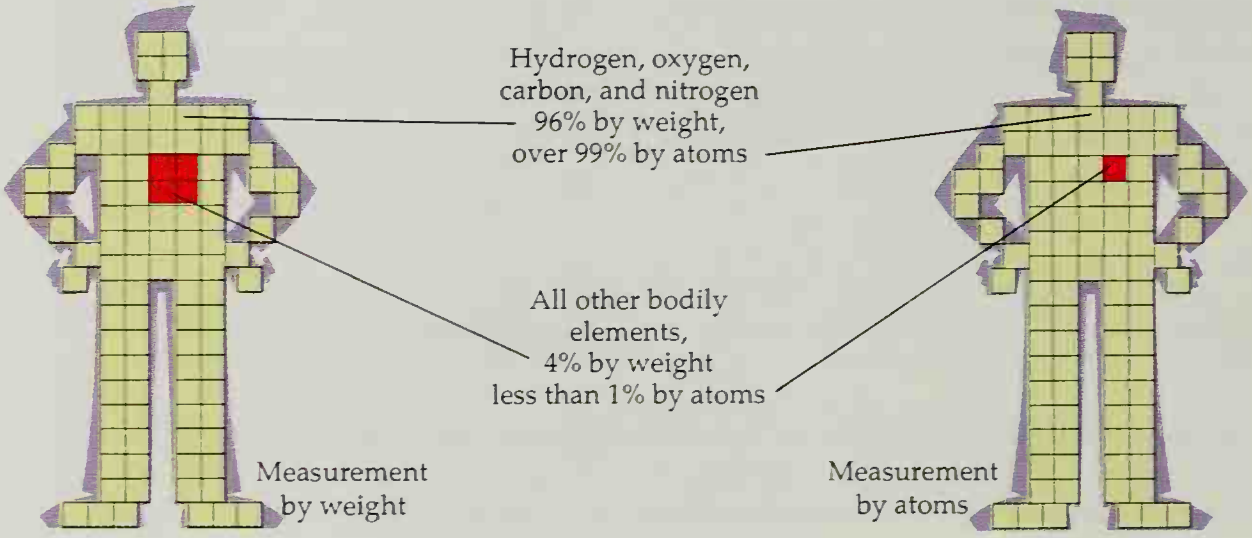


Figure 2.5
Composition of the human body.



drogen, oxygen, carbon, and nitrogen make up 96% of our weight and over 99% of all the atoms of our bodies (Fig. 2.5).

QUESTION

Measure the width and length of the page you are reading and, with a calculation similar to the one we have just carried out, calculate the weight of a sheet of gold 1 atom thick and with the same dimensions as this page. ________________

2.3 Mass and Weight

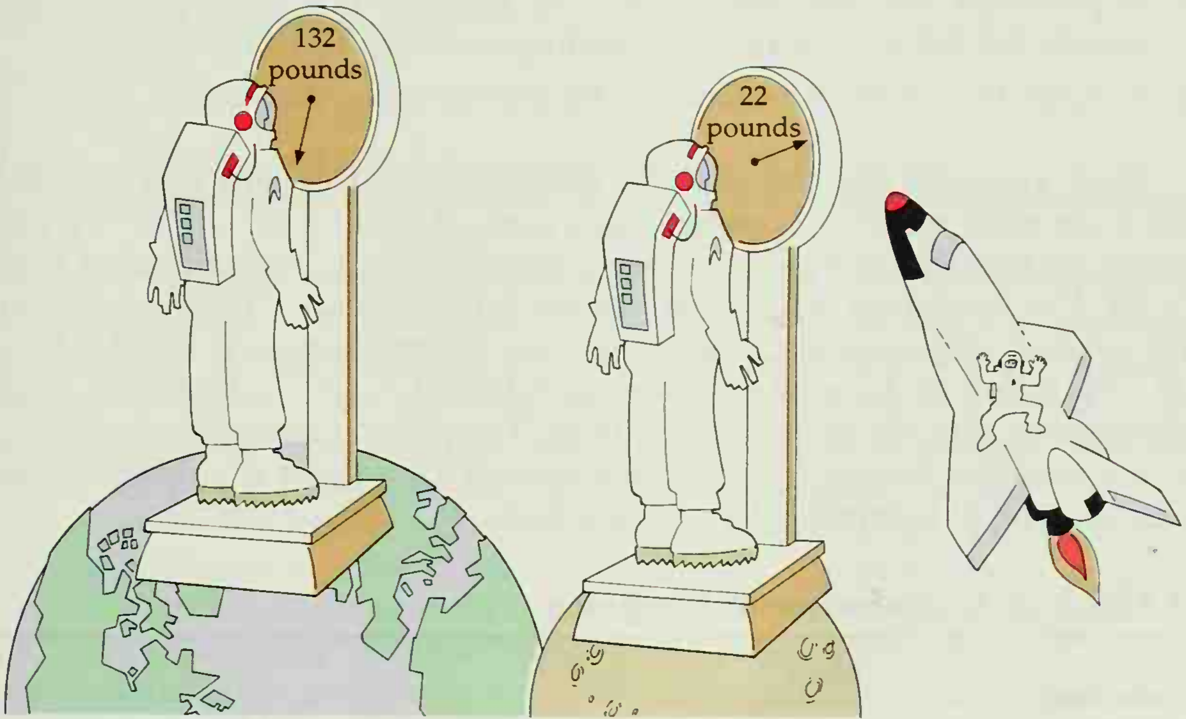
Mass is observed as a body's resistance to acceleration. **Weight** results from the pull of gravity.

In describing the size of atoms and their abundance in our bodies, we have used two terms, **mass** and **weight,** that might seem to be completely interchangeable. They aren't, even though the difference between the two is virtually insignificant in the practical activities of our everyday world. To be precise, though, *mass* is a fundamental property of matter that is unaffected by its location; the mass of a body is defined as its resistance to acceleration

The astronauts have mass but no weight.

no matter where in the universe it may be. *Weight*, on the other hand, results from the force of gravity. A body's weight depends on where it is, on what gravitational force is acting on it. (Appendix B contains a discussion of units of mass and weight in the metric system and in the English system.)

A person who weighs 60 kg (132 lb) on earth would weigh only 10 kg (22 lb) on the moon, where the gravitational force is only one-sixth that of the earth, and nothing at all in an orbiting spaceship (Fig. 2.6). Yet that person's



Earth
Mass = 60 kg (132 lb)
Weight = 60 kg (132 lb)

Moon
Mass = 60 kg (132 lb)
Weight = 10 kg (22 lb)

Spaceship
Mass = 60 kg (132 lb)
Weight = 0

Small mass; small force needed for acceleration

Large mass; large force needed for acceleration

Figure 2.6
Mass and weight.

mass remains the same on the moon and in the spaceship as it is on earth. (*Mass*, a body's resistance to acceleration, is sometimes defined more simply as the *quantity of matter* present.)

At any rate, since all the activities of our daily lives take place on or near the surface of the earth, with insignificant variations in the effects of gravity, we can use the terms *mass* and *weight* interchangeably, even in chemistry. We speak of atomic *weights*, for example, and then define them in terms of *mass*, as we'll see in the next section.

QUESTION

Suppose you were an astronaut floating weightless at one end of an orbiting spaceship. An astronaut at the other end of the ship wants two screwdrivers you have in your hands. One of the tools has a mass of 50 g; the other has a mass of 100 g. (a) What does each of the screwdrivers *weigh* in the orbiting spaceship? (b) Would you have to push one with more force than you would use on the other to get them moving with the same speed toward the other astronaut, or would you be able to use the same force on each? (c) Explain your answers. ______

2.4 Subatomic Particles: Protons, Neutrons, and Electrons

The **nucleus** is the positively charged central core of an atom.

Protons, neutrons, and electrons are the three subatomic particles that determine the properties of an atom. Structurally, all atoms consist of two parts:

1. A positively charged central core, the **nucleus,** that holds protons and (except for the great majority of hydrogen atoms) neutrons as well.
2. Surrounding shells of negatively charged electrons (Fig. 2.7).

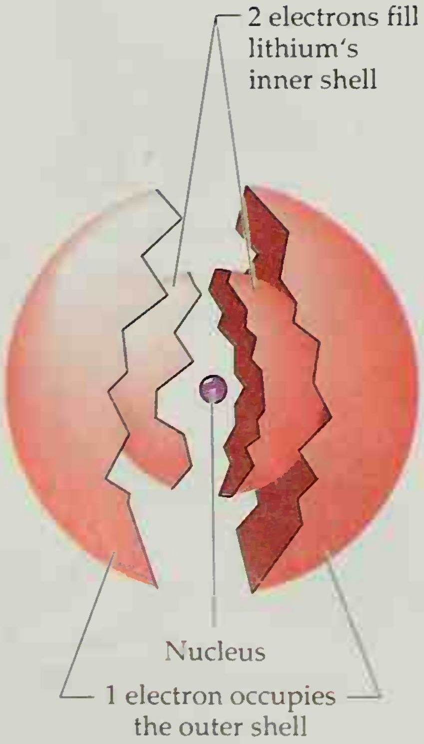


Figure 2.7
The nucleus and electron shells of a lithium atom, a typical small atom.

Small as atoms are, the protons, neutrons, and electrons that compose them are even smaller. A **proton** has a mass of about 1.673×10^{-24} g and carries an electrical charge of 1+, a unit positive charge. With a mass of 1.675×10^{-24} g, a **neutron** is just a bit heavier than a proton. Unlike the proton, the neutron carries no electrical charge. An **electron**'s mass is about 9.11×10^{-28} g, which we'll round off and write as 0.0009×10^{-24} g for a more direct comparison with the proton and neutron. The electron bears a charge of 1−, a unit negative charge. It is often convenient to use p or p^+ to represent a proton, n or n^0 to represent a neutron, and e or e^- for an electron.

TABLE 2.1 Subatomic Particles

Subatomic Particle	Mass		Location in Atom	Charge	Symbol
	grams	amu			
Neutron	1.67×10^{-24}	1	Nucleus	0	n, n^0
Proton	1.67×10^{-24}	1	Nucleus	1+	p, p^+, H^+
Electron	0.0009×10^{-24}	0	Outside the nucleus	1−	e, e^-

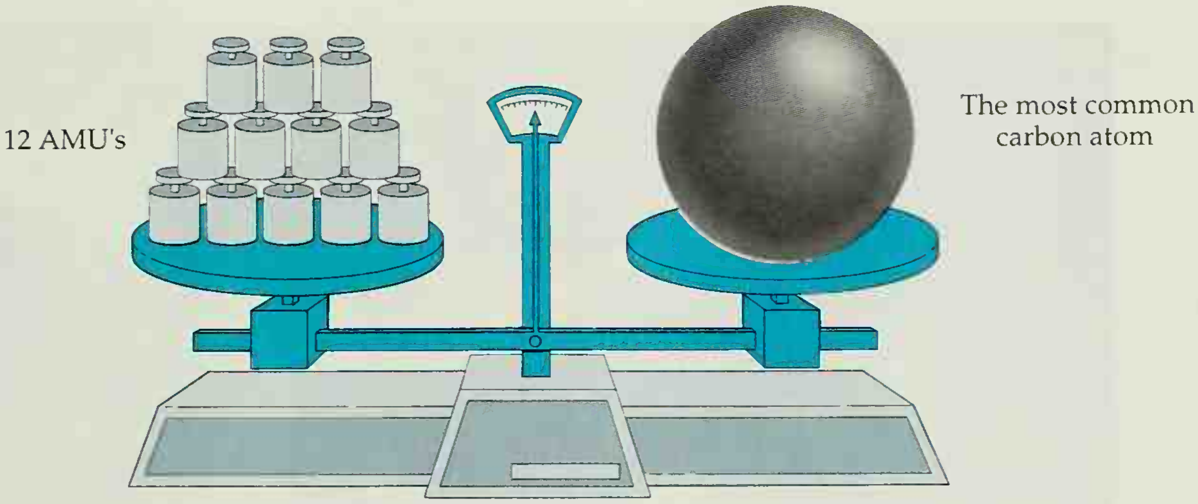


Figure 2.8
The atomic mass unit, amu.

Using these numerical values, expressed in grams, for the weights of subatomic particles and atoms soon becomes cumbersome. It's much more convenient to describe the masses of subatomic particles and of the various atoms by a unit called the **atomic mass unit,** or **amu.** An *atomic mass unit* is defined as exactly one-twelfth the mass of the most common kind of carbon atom (Fig. 2.8). This gives the proton a mass of 1.007 amu and the neutron a mass of 1.009 amu. For most ordinary uses we can round both of these off to 1 amu. The mass of the electron (0.0005 amu) is so small in comparison with the other particles that we can consider it as zero. Table 2.1 summarizes the characteristics of these three subatomic particles.

The **atomic mass unit,** or **amu,** is one-twelfth the mass of the most common kind of carbon atom. A **neutron** is a subatomic particle with a mass of 1 amu and no electrical charge. A **proton** is a subatomic particle with a mass of 1 amu and a charge of 1+. An **electron** is a subatomic particle with negligible mass and a charge of 1−.

QUESTION

(a) The nucleus of a hydrogen atom contains only a single proton. What is the mass of a hydrogen atom in atomic mass units? (b) The nucleus of a fluorine atom contains 9 protons and 10 neutrons. What is the mass of a fluorine atom in amu? ________

2.5 Atoms, the Essence of an Element

Atoms of hydrogen are the simplest of all atoms and provide a good starting point for a study of atomic structure. As we saw in Section 2.2, hydrogen atoms are the most abundant of all atoms in the universe as a whole and also in our own bodies. They make up two-thirds of all atoms in water, but just over 11% of the water's weight. Through a process we'll describe near the end of Chapter 4, hydrogen atoms provide the energy of the sun.

The overwhelming majority of all hydrogen atoms consist of just one proton and one electron. The proton forms the nucleus of the atom, and the electron occupies a spherical shell or envelope surrounding the nucleus (Fig. 2.9). Since the single negative charge of hydrogen's lone electron exactly balances the single positive charge of its single proton, the hydrogen atom itself has no net electrical charge. This illustrates a general rule: *in all atoms of all elements, the number of electrons surrounding the nucleus exactly equals the number of protons within the nucleus.* All atoms of all elements, then, are electrically neutral.

Because the mass of the electron is negligible in comparison with the mass of the proton, and of a neutron as well, virtually the entire mass (99.95%) of

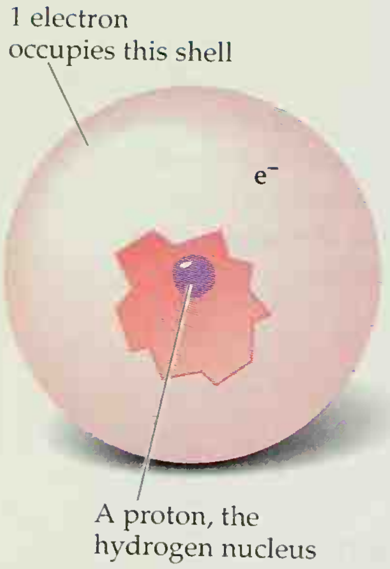
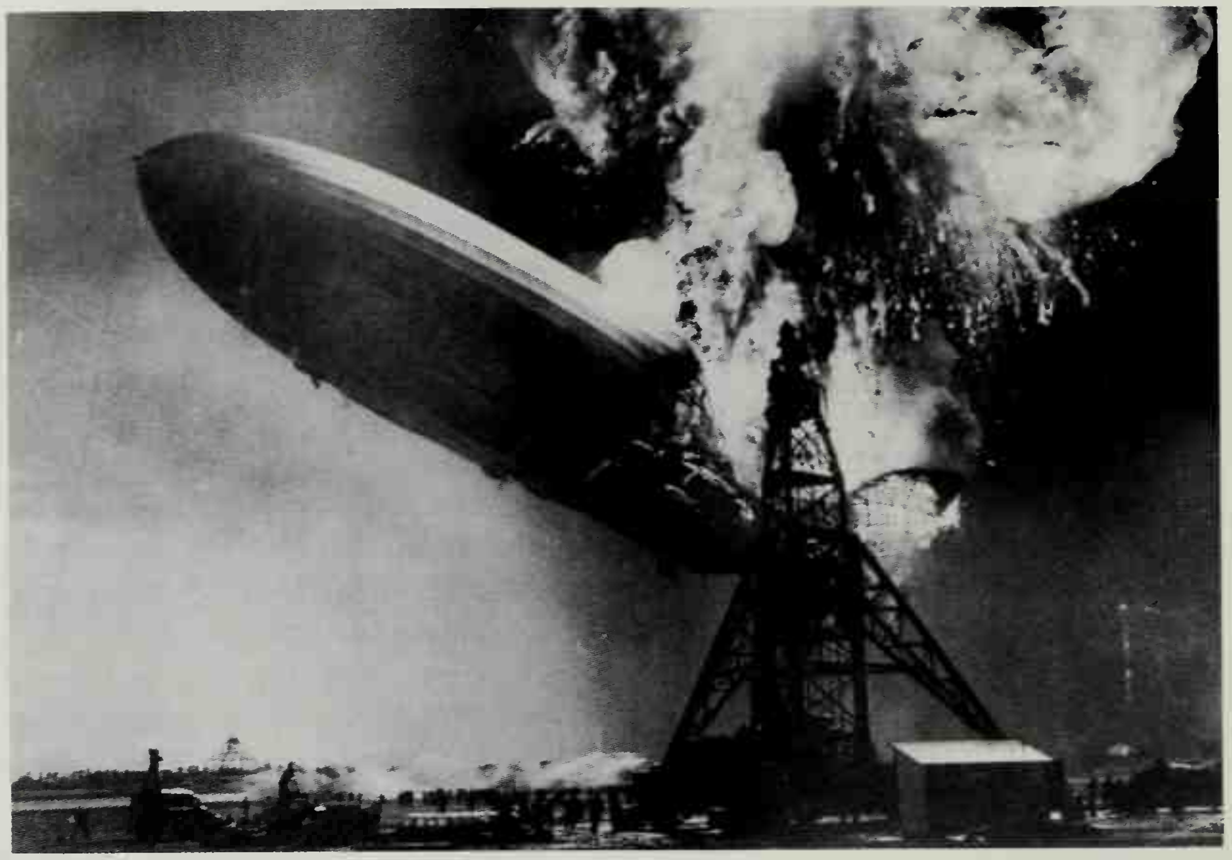


Figure 2.9
The structure of the hydrogen atom.



Filled with the flammable element hydrogen for buoyancy, the German airship *Hindenburg* burned in May 1937. The hydrogen ignited as the airship approached its dock in Lakehurst, New Jersey, after a transatlantic crossing. Thirty-six people were killed as a result.

The **mass number** of an atom is the sum of the protons and neutrons in its nucleus.

an atom lies in its nucleus. Since both protons and neutrons have masses of very nearly 1 amu, we need only count up all the protons and all the neutrons in an atomic nucleus to get a value for the mass of an atom. This sum of an atom's protons and neutrons is known as its **mass number,** represented by the symbol A. For a hydrogen atom with a nucleus consisting of a single proton, the mass number is 1. That is, $A = 1$.

To gain some sense of the difference in mass between the proton and the electron, and of the enormous distance between the two in the hydrogen atom, we can represent its nucleus, the single proton, as an adult of average weight sitting in an empty field. The atom's electron could then appear as a small bird, perhaps a common sparrow, flying around the person at a distance of 2 miles (Fig. 2.10).

The **atomic number** is the sum of all of an atom's protons. An **element** is a substance whose atoms all have the same atomic number.

In addition to mass numbers, one more atomic value is important to us, the **atomic number,** represented by the symbol Z. The atomic number, Z, is simply *the total number of protons in an atomic nucleus.* With one proton in its nucleus, hydrogen's atomic number is 1. For hydrogen, $Z = 1$. Atomic numbers are particularly important in chemistry because *all atoms of the same* **element** *have the same atomic number.* Conversely, *all atoms of any specific atomic number are atoms of the same element.* This gives us a convenient definition of an element as a substance whose atoms all have the same atomic number.

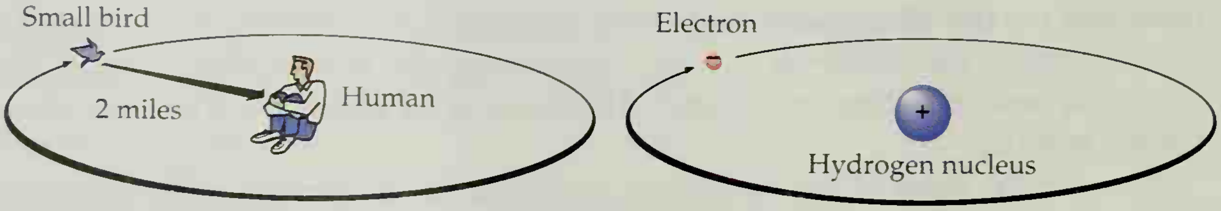


Figure 2.10
Relative distances and masses in the hydrogen atom.

As a chemical symbol for hydrogen, we use the capital letter H, which can represent either the element itself or a single hydrogen atom, depending on the context. Chemically, then, H can represent a single proton surrounded by a spherical shell containing a single electron as shown in Figure 2.9. If we wish to designate not only an atom of a particular element but its mass number and atomic number as well, we write the mass number (A) to the upper left of the atomic symbol and the atomic number (Z) to the lower left. For a hydrogen atom with a mass number of 1 and atomic number of 1, we write

$$\begin{array}{rl} \text{mass number } (A) \searrow & \\ \text{elemental symbol} \longrightarrow & {}^{1}_{1}\text{H} \\ \text{atomic number } (Z) \nearrow & \end{array}$$

With the definitions of mass number and atomic number in mind, we can easily determine the number of neutrons in an atomic nucleus by subtracting the atomic number from the mass number: $A - Z =$ neutrons. As an illustration, a common atom of the element fluorine has a mass number of 19 and an atomic number of 9. Thus, its nucleus is made up of 9 protons and $(19 - 9) = 10$ neutrons. Because all atoms must be electrically neutral, we know that there are as many electrons surrounding the fluorine atom's nucleus as there are protons within its nucleus, 9. Moreover, since the chemical symbol for fluorine is F, we can represent the atom as

$${}^{19}_{9}\text{F}$$

EXAMPLE HOW MANY NEUTRONS?

How many neutrons are there in the nucleus of an argon atom of mass number 40? (The atomic number of argon is 18.)

With an atomic number of 18, $Z = 18$ for argon. Since the mass number of this particular atom of argon is 40, $A = 40$. Knowing that the number of neutrons $= A - Z$,

$$\text{neutrons} = A - Z$$

$$\text{neutrons} = 40 - 18$$

$$\text{neutrons} = 22$$

The nucleus of this argon atom contains 22 neutrons.

QUESTION

The most common kind of lithium atom, atomic number 3, has a mass number of 7. How many protons are there in the nucleus of this lithium atom? How many neutrons? How many electrons surround the nucleus? Given that the chemical symbol for lithium is Li, show A, Z, and the symbol as we did in the example of fluorine. __________

2.6 Isotopes: Deuterium and Tritium

As we have seen, the atomic nucleus can contain neutrons as well as protons. An atom with one proton and, in addition, one neutron in its nucleus is an atom of hydrogen with a mass number of 2. It *must* be an atom of the element hydrogen because with one proton in its nucleus its atomic number is 1 and all atoms with an atomic number of 1 belong to the element hydrogen. Its mass number, though, is 2 since both the proton and the neutron contribute 1 amu each to the total mass.

Isotopes are atoms of the same element with different mass numbers.

Atoms that have the same atomic number (and therefore belong to the same element) but that differ in mass number are called **isotopes.** To state this a bit differently, isotopes of any particular element all have the same number of protons (and therefore the same atomic number) but carry different numbers of neutrons in their nuclei (and therefore have different mass numbers). As an aid in differentiating between these two isotopes of the element hydrogen, the isotope of mass number 2 is called *deuterium*. Deuterium is the so-called "heavy hydrogen" used in the construction of the hydrogen bomb (Chapter 4).

Naturally occurring deuterium is extremely rare, with almost 6700 hydrogen atoms of mass number 1 for every deuterium atom that occurs in nature (Fig. 2.11). Because the ratio of the two isotopes overwhelmingly favors the atom of mass number 1, the word *hydrogen* commonly refers either to the naturally occurring mixture of the two, or simply to the isotope of mass number 1. Where confusion can occur, the term *protium* is used for the isotope of mass number 1. Furthermore, the symbol *D* represents specifically an atom of deuterium.

Naturally occurring hydrogen consists almost entirely of only the two isotopes, protium and deuterium. But it's possible to manufacture a third isotope, *tritium*, by adding a second neutron to the nucleus. Tritium, with a nucleus containing one proton and two neutrons, has a mass number of 3 and an atomic number of 1. Tritium is used along with deuterium to produce the explosive force of the hydrogen bomb. The hydrogen of the universe consists of about 99.985% protium, 0.015% deuterium, and just a trace of tritium.

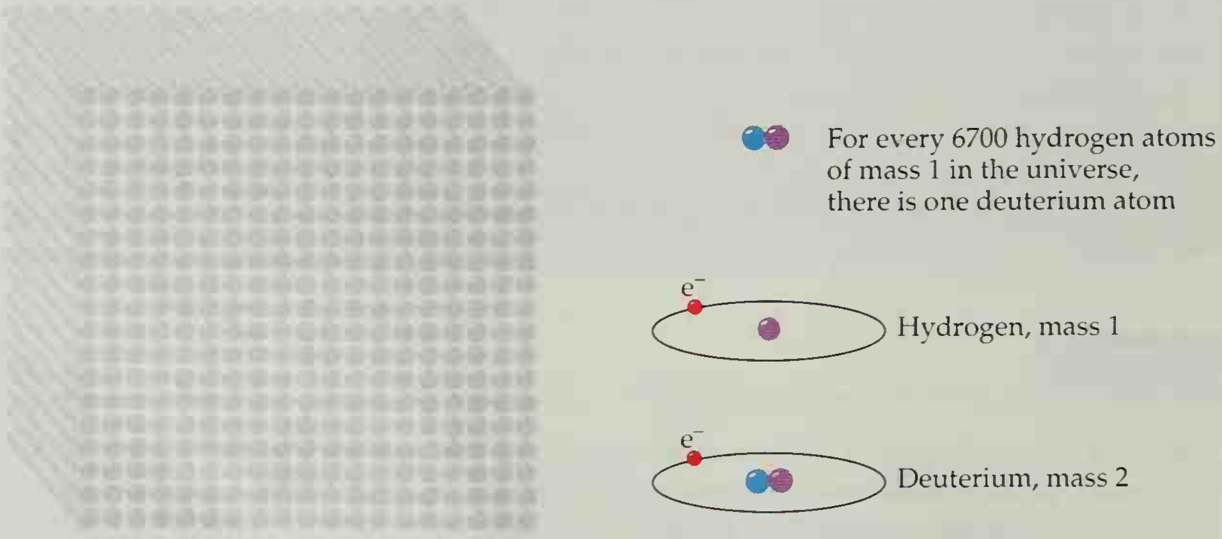


Figure 2.11
Relative abundance of deuterium.

QUESTION

As we've just seen, an atom with a nucleus consisting of *one proton* and *two neutrons* is tritium, an isotope of hydrogen. Is an atom with a nucleus consisting of *one neutron* and *two protons* still another isotope of hydrogen? Explain your answer. ________

2.7 Building up the Elements: Hydrogen through Neon

Although adding a neutron to an atomic nucleus increases its mass number and thereby generates a different isotope of the same element, adding a proton produces an entirely different element. (Adding a proton to an atomic nucleus isn't nearly as easy to do, in actual practice, as adding a neutron. In any case, what concerns us here isn't the specific procedure we might use for the addition, but rather the consequence that comes from adding a proton to an atomic nucleus.)

Adding protons, as we have seen, increases atomic numbers as well as mass numbers. Adding one proton to a hydrogen nucleus, for example, produces an atom of the element *helium*. Virtually all the helium atoms in the universe have two neutrons in their nuclei as well as two protons, so a helium atom's mass number is 4 and its atomic number is 2. With two positively charged protons in its nucleus, there are two negatively charged electrons in the surrounding shell. These two electrons completely fill this particular shell; no more electrons can enter it. We're familiar with helium as a gas used to fill balloons. Since helium is less dense than air, helium-filled balloons tend to rise upward into the atomosphere.

A third proton produces *lithium*, atomic number 3 and (for the most common isotope) mass number 7. Adding the proton to the nucleus requires

Helium-filled balloons.

A battery containing lithium.

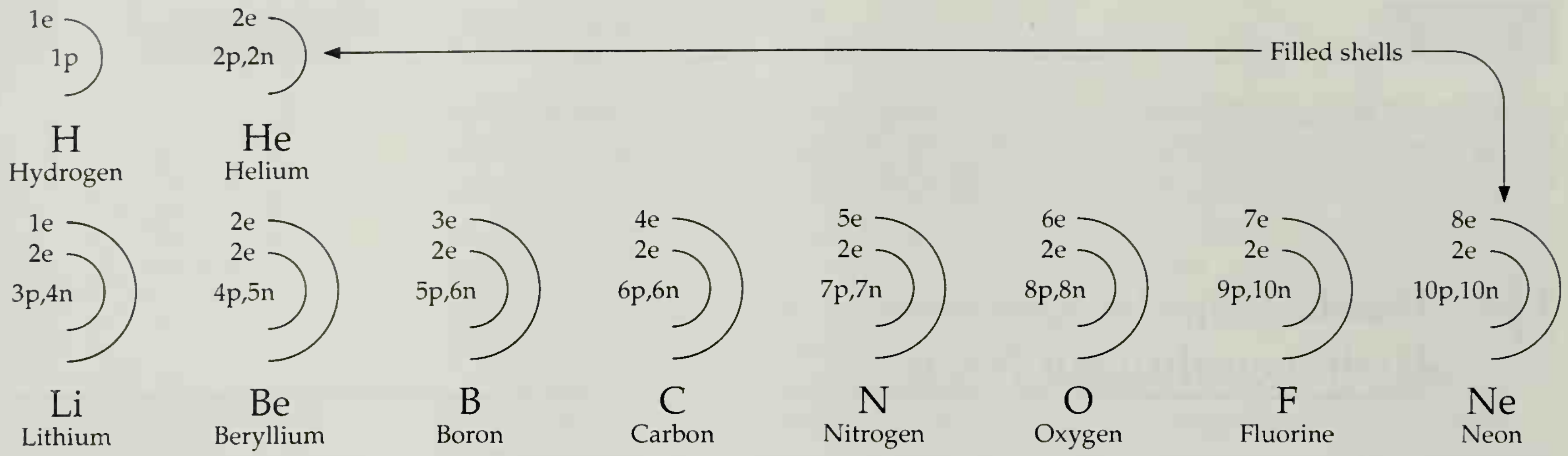


Figure 2.12

Names, symbols, electron structures, and compositions of nuclei of the first 10 elements.

TABLE 2.2 The First 10 Elements

Element	Atomic Number	Description
Hydrogen	1	Gas that burns in air; combines with oxygen to form water; more atoms of hydrogen in the human body than of all other elements combined
Helium	2	Unreactive gas; used medically to dilute anesthetic gases; used in lighter-than-air craft such as blimps and in balloons
Lithium	3	Reactive metal; forms hydrogen gas on contact with water
Beryllium	4	Strong but toxic metal; used in spacecraft and missile structures; alloying agent in tools, springs, and electrical devices
Boron	5	Nonmetal; component of boric acid, an antiseptic
Carbon	6	Nonmetal; found in all life; fundamental element of organic chemistry; occurs as graphite, soot, and diamonds; major component of coal, petroleum, and natural gas
Nitrogen	7	Gas that makes up about 78% (by volume) of our atmosphere
Oxygen	8	Gas necessary to all animal life; makes up about 21% (by volume) of our atmosphere
Fluorine	9	Extremely corrosive and reactive gas; compounds include fluorides used for hardening dental enamel, and chlorofluorocarbons (CFCs), used as refrigerants and formerly as spray can propellants
Neon	10	Gas of very low chemical reactivity; produces the glow of neon signs

Nitrogen and oxygen are the major elements of the atmosphere.

Neon glows as electrons pass through it.

adding a third electron to maintain electrical neutrality. Since the shell containing the first two electrons is now full and can hold no more electrons, the third electron goes into a second shell, larger than the first and concentric with it, as shown in Figure 2.7. Each of these electron shells occupied by the electrons that surround the nucleus is called a **quantum shell** and receives a *quantum number:* 1 for the shell closest to the nucleus (filled by two electrons), 2 for the next shell (which can hold a maximum of eight electrons), 3 for the next, and so forth. We use the term **electron structure** to indicate the distribution of electrons in the quantum shells surrounding a nucleus.

Each of the electron shells surrounding an atomic nucleus is a **quantum shell.**

The **electron structure** of an atom refers to the distribution of electrons in its quantum shells.

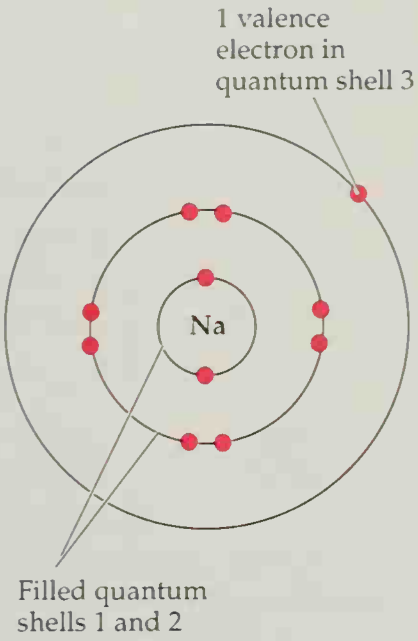
Lithium is a metal used in small, long-lasting batteries that power digital watches, calculators, and similar electronic equipment. Continuing the addition of protons to the nuclei and of electrons to the surrounding shells forms, in sequence, *beryllium, boron, carbon, nitrogen, oxygen, fluorine,* and *neon,* and completes the series of the first 10 elements. Figure 2.12 shows the names, chemical symbols, electron structures, and compositions of the nuclei for the first 10 elements; Table 2.2 describes some of their properties, sources, and uses.

QUESTION

How many quantum shells does the sodium atom, atomic number 11, have? (We've just noted that the second quantum shell can hold a maximum of eight electrons.)

2.8 More Electron Structures: Sodium through Calcium

In the neon atom the 10th proton is balanced by a 10th electron, which enters the second shell and completes that shell with its full complement of eight electrons. (Remember, there are two electrons in the first quantum shell of



every element except hydrogen.) Formation of *sodium* by addition of an 11th proton and a counterbalancing 11th electron places that new electron in the *third* quantum shell (Fig. 2.13). Adding more protons to the nucleus and more electrons to the third quantum shell produces, in succession, *magnesium, aluminum, silicon, phosphorus, sulfur, chlorine,* and *argon.*

Adding a proton to the argon nucleus and another electron, the 19th, produces *potassium* and begins filling the fourth quantum shell. *Calcium,* with atomic number 20, has two electrons in the first quantum shell, eight in the second, eight in the third, and two in the partially filled fourth. The first 20 elements are listed in Table 2.3 with their chemical symbols and electron structures.

TABLE 2.3 Electron Structures of the First 20 Elements

			Quantum Number of Shell			
Element	**Symbol**	**Atomic Number**	**1**	**2**	**3**	**4**
Hydrogen	H	1	1			
Helium	He	2	2			
Lithium	Li	3	2	1		
Beryllium	Be	4	2	2		
Boron	B	5	2	3		
Carbon	C	6	2	4		
Nitrogen	N	7	2	5		
Oxygen	O	8	2	6		
Fluorine	F	9	2	7		
Neon	Ne	10	2	8		
Sodium	Na	11	2	8	1	
Magnesium	Mg	12	2	8	2	
Aluminum	Al	13	2	8	3	
Silicon	Si	14	2	8	4	
Phosphorus	P	15	2	8	5	
Sulfur	S	16	2	8	6	
Chlorine	Cl	17	2	8	7	
Argon	Ar	18	2	8	8	
Potassium	K	19	2	8	8	1
Calcium	Ca	20	2	8	8	2

PERSPECTIVE: A Summary and a Foretaste

In this chapter we learned about atoms and elements, the fundamental structures and substances of chemistry and, indeed, of all the things of the world we live in. We saw that atoms are the smallest bits of the chemical elements that make up our universe; that all these atoms are similar in structure, formed of a nucleus and surrounding shells of electrons; and that they are formed of three subatomic particles, the protons and neutrons of the nucleus and the electrons of the surrounding shells. We also learned that although all atoms of any specific element must have the same number of protons in their nuclei, they may contain different numbers of neutrons and thus have different masses and exist as isotopes. We saw as well that as the number of protons in an atomic nucleus increases, the number of surrounding electrons keeps pace through the filling of the quantum shells surrounding the nucleus, in an orderly sequence.

Chapter 3 concludes our introduction to the foundations of chemistry. In it we'll examine some similarities that occur periodically in the behavior of elements as we continue to increase their atomic numbers. As we examine these periodic similarities we'll see how the interaction of electrons in the outermost shells of atoms allows individual atoms to form chemical bonds to each other and how these connections produce larger, more complex structures that we call molecules. In later chapters we'll learn that these structures range in size and shape from the small, simple molecules of the oxygen and water that sustain our lives, through the larger and more complex molecules of our foods and consumer goods, to the huge structures of the polymers and plastics of our consumer goods, and finally to the long, intricate, intertwined threads of the enzymes that allow our bodies to function and the DNA that forms the molecular basis of heredity.

EXERCISES

FOR REVIEW

1. Complete this statement with the words and phrases that follow. Each is used once.

______ are the smallest particles of an ______, a fundamental substance of chemistry and of the world, that can be identified as that element. All atoms consist of two parts: (1) a ______, which contains positively charged ______ and (except for ______, an ______ of hydrogen) they also contain electrically neutral ______; and (2) ______ which lie in ______ surrounding the nucleus. The number of protons in the nucleus defines and atom's ______ and is represented by the symbol ______. The sum of the protons and neutrons in the nucleus determines the atom's ______ and is represented by ______. As the atomic number of the atom increases, the number of electrons in the shells also increases so that the number of electrons always equals the number of protons and the atom remains electrically ______. The first quantum shell can contain a maximum of ______ electrons, the second a maximum of ______ electrons.

A
atomic number
~~atoms~~
eight
electrons
~~element~~
isotope
mass number
neutral
neutrons
nucleus
protium
protons
quantum shells
two
Z

Answers
IN BACK

2. Name an element that is

a. the major gas of the air we breathe
b. used in small, long-lasting batteries
c. used to harden the enamel of teeth
d. represented in the human body by more atoms than is any other element
e. present in graphite, diamonds, petroleum, and all living things

3. Of the first 10 elements, which are metals?

4. Question 3 mentioned "the first 10 elements." What does this phrase refer to?

5. How many different elements are currently known to exist?

6. In terms of the number of atoms present, hydrogen is the most abundant element in the universe and also in our bodies. What is the second most abundant element in the universe, again in terms of the number of atoms present? What is the second most abundant element in our bodies?

7. Given the atomic number and the mass number of an atom, how do we determine the number of protons in the nucleus? The number of neutrons in the nucleus? The number of electrons in the surrounding shells?

8. (a) Name the three isotopes of the element whose atomic number is 1. (b) What name do we give to a mixture of these three isotopes, collectively, when they are present in the same ratios as in the universe as a whole?

9. What is a name used for the isotope of hydrogen indicated by ${}^{3}_{1}H$?

10. What chemical symbol is used as the equivalent of ${}^{2}_{1}H$?

11. Name and give the chemical symbols for the elements with the first 10 atomic numbers.

12. Atoms of what element are used to define the atomic mass unit?

13. Can any isotope of any element have a mass number of zero? Explain your answer.

14. (a) What would remain if we removed an electron from a hydrogen atom? What charge would this particle bear? What would its mass be? (b) How do you think we could convert a sodium atom into one of the sodium cations discussed in Chapter 1?

15. Name

a. three elements that have only a single electron in their outermost quantum shell
b. two elements that have exactly two electrons in their outermost quantum shell
c. three elements with filled outermost quantum shells
d. one element that has only a single electron in its innermost quantum shell

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

16. Give the number of protons and the number of neutrons in the nucleus of each of the following atoms and the number of electrons in the first and second quantum shells: (a) ${}^{13}_{6}C$; (b) ${}^{10}_{5}B$; (c) ${}^{18}_{8}O$; (d) ${}^{40}_{19}K$ (e) ${}^{6}_{3}Li$.

17. (a) If we could unite a boron atom with a lithium atom to form a single new atom, what element would it belong to? (b) If we double the number of protons in an atom of carbon, with a mass number of 12, what element would the resulting atom belong to? (c) If we double the mass number of the atom of carbon described in part (b) but do not change its atomic number, what element would the resulting atom belong to?

18. Section 2.5 contains the statement that hydrogen atoms "make up two-thirds of all atoms in water, but just over 11% of the water's weight." Given that there are twice as many hydrogen atoms in water as there are oxygen atoms, and that virtually all the hydrogen atoms in water are ${}^{1}_{1}H$ and virtually all the oxygen atoms are ${}^{16}_{8}O$, how do you explain this apparent discrepancy?

19. Using 3×10^{-8} cm as the diameter of a gold atom and 3.3×10^{-22} g as its weight, calculate the weight of 1 cm^3 of gold. (You can start by finding how many gold atoms fit on a line 1 cm long; see Section 2.2.) How does your calculated value compare with the measured density of gold, 19.3 g/cm^3? Suggest some factors that might account for the difference.

THINK, SPECULATE, REFLECT, AND PONDER

20. Your answers to parts (a) and (b) of this exercise do not depend on whether the elements named exist as isotopes or on which isotope you

choose to consider. (a) Lithium, sodium, and potassium are all metals that react with water to liberate hydrogen gas. What, if anything, do atoms of each of these metals have in common? (b) Helium is an unreactive gas and neon is a gas of extremely low reactivity. What, if anything, do their atoms have in common?

21. Suppose we could combine one electron with one proton to form a single, new subatomic particle. What mass, in amu, would the resulting subatomic particle have? What electrical charge would it carry? What known subatomic particle would the resulting particle be equivalent to?

22. Suppose someone discovered a particle that consisted of a single neutron surrounded by a shell containing a single electron. Would you classify this as an atom? Would you classify it as an ion? Would it represent a new element? Explain your answers.

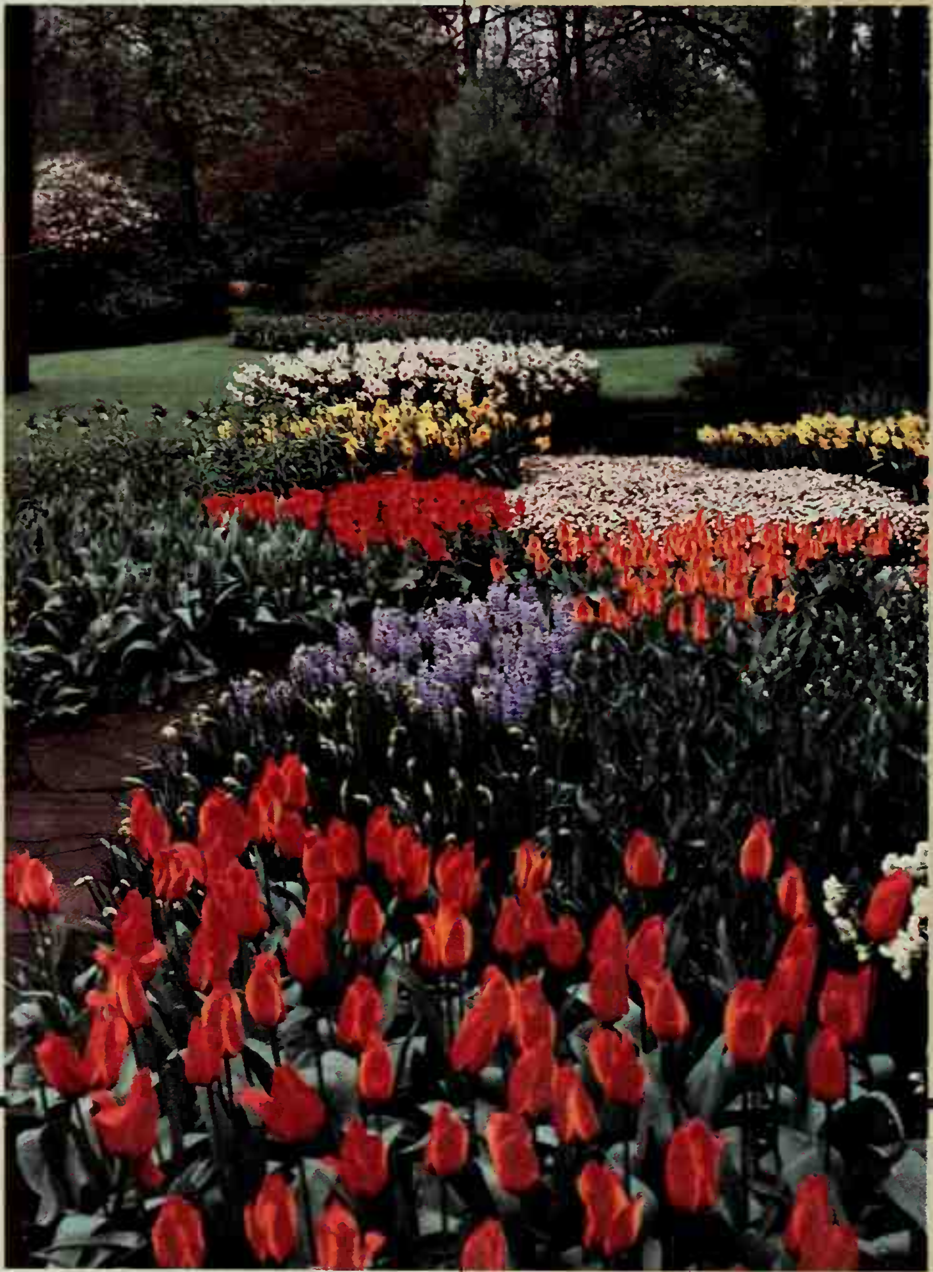
23. Suppose you have two spheres, one made of lead and one made of cork. They are standing next to each other at some spot on the surface of the earth. At that location each weighs 1 kg. Compare their masses at that location. Does one have a greater mass than the other? If so, which has the greater mass? Now move both spheres to one particular location on the surface of the moon and again compare their masses. Does one have a greater mass? If so, which one? Does one weigh more than the other on the moon? If so, which? Finally, leave the cork sphere on the moon and move the lead sphere back to its original location on earth. Again, compare both their masses and their weights.

24. The description of the atom that we have used in this chapter resembles in some ways our own solar system. What part of our solar system corresponds to the nucleus of an atom? What part corresponds to the electron shells surrounding the nucleus? What are some of the other similarities between the structure of the atom, as described in this chapter, and our own solar system? What are some of the more obvious differences?

Chemical Bonding

3

IONIC AND COVALENT COMPOUNDS



Flowers bloom periodically in the spring.

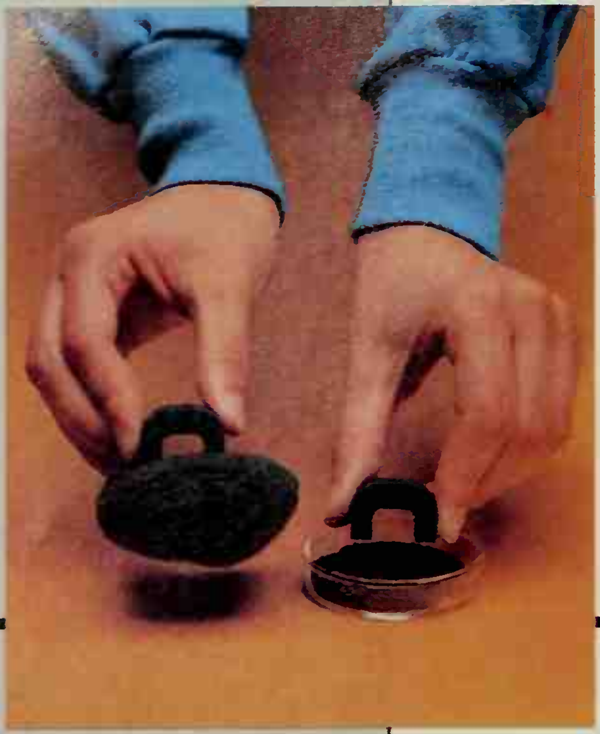


Figure 3.1
The attraction that iron has for a magnet isn't carried over into the iron oxides it forms as it rusts.

Scouring Pads and Kitchen Magnets

In this chapter we examine how and why elements combine to form compounds. We learn, too, that their characteristics can change as they join each other through chemical bonds. Dangerous or poisonous elements can form benign compounds, and the reverse can happen. Reasonably harmless elements can form toxic, corrosive, or otherwise hazardous compounds. An element seldom carries more than a few of its properties, if any at all, into the compounds it forms.

We see this in our daily lives. Carbon is the element that makes up the charcoal of the briquettes we use in backyard grills. It's a brittle, black solid that rubs off onto whatever touches it. Another element, oxygen of the air, is a gas that supports life and that's consumed by anything that burns. When we light charcoal briquettes, the elemental carbon of the briquette and the elemental oxygen of the air combine to produce heat and the compound *carbon dioxide*. Unlike carbon, carbon dioxide is a colorless gas. Unlike oxygen, carbon dioxide doesn't support life and won't keep a fire going. Indeed, carbon dioxide is widely used to put out fires. The characteristics of the carbon and of the oxygen are transformed as they combine to form carbon dioxide.

We can see this same sort of thing happening with the metal scouring pads we use for cleaning pots and pans. These are composed largely of iron that's drawn out into fine filaments and woven into pads that are often impregnated with a detergent. As wet pads of this sort stand in the open air, the iron in the filaments reacts slowly with the oxygen of the air to form reddish-brown oxides of iron we call rust. Let a wet scouring pad stand around for a few days and it rusts.

The element fluorine forms part of the inert, non-stick polymeric coating made from the compound tetrafluoroethylene. Although fluorine is an extremely reactive and hazardous element, the tetrafluoroethylene polymer that contains fluorine is stable, inert, and non-toxic.

Try this simple but effective demonstration of the change in properties of an element—iron, in this case—as it enters into a compound. Elemental iron is attracted to magnets. Touch a magnet to an iron scouring pad and feel the attraction they have for each other. You can use one of the small, strong magnets that holds notes, coupons, and so forth on the sides of refrigerators.

Now wet the scouring pad and let it stand in the open and rust away. As the days pass and the rust accumulates, the attraction between the pad and the magnet drops. Elemental iron is attracted to magnets, but it doesn't carry this characteristic into its compounds. The oxides of iron that form rust aren't attracted to magnets (Fig. 3.1).

Iron, oxygen, and carbon are elements we find easily in their free state in the world about us. In this chapter we'll concentrate our attention on two elements we don't often see as the free elements, sodium and chlorine. We'll focus our attention on them and on the compound they form when they react with each other: sodium chloride, our common table salt.

3.1 Table Salt Revisited

We entered our study of chemistry, at the beginning of Chapter 1, with a demonstration of a remarkable difference between two common chemicals, sodium chloride (table salt) and sucrose (table sugar). We saw that pure water is a very poor conductor of electricity, and although adding sucrose to water does nothing to improve its conductivity, adding sodium chloride does increase water's ability to conduct an electric current dramatically, causing the light bulb to burn brightly. That observation led us to classify substances as electrolytes and nonelectrolytes and introduced us to the chemical particles known as ions.

Now that we've learned something of elements and compounds, and of the ions and other chemical particles that make up our world, we'll return to sodium chloride, this time to contrast its properties to those of two *un*common chemicals, elemental *sodium* and elemental *chlorine*. In the discussions that follow, we'll use the term *elemental* to refer to pure elements themselves, not combined with any other element, either in a compound or any other way. With this definition, "elemental sodium" refers to pure, metallic sodium and "elemental chlorine" to pure chlorine gas, the forms in which we ordinarily find the pure elements themselves. Thus, although the element sodium is present in both the metal (as sodium atoms) and in the compound sodium chloride (as sodium cations), only a piece of the metal itself consists of *elemental* sodium. Similarly, the element chlorine is present in both elemental, gaseous chlorine and table salt, but only the gas itself consists of *elemental* chlorine.

As we proceed in this chapter we'll examine atoms and ions in more detail, we'll learn how atoms are converted into ions, and we'll learn about the two different kinds of bonds, *ionic* and *covalent*, that hold chemical particles together in the multitude of substances we find and use in our daily lives.

What's more, we'll learn that although the *sodium cation* of our table salt and the *sodium atom* of metallic, elemental sodium differ only in the number of electrons present in their most remote quantum shells (and, as a result, in the net electrical charge on each), this apparently small difference produces remarkable differences in their properties. And while the words "chlor*ide*," as in "sodium chloride," and "chlor*ine*," as in "chlorine gas," sound very much alike, the two chemical particles they represent could hardly be more different in the ways they behave.

QUESTION

The element of atomic number 53 is *iodine*, with the chemical symbol I. Iodine is an antiseptic available in commercial preparations in drugstores; *potassium iodide* is added to "iodized" table salt to protect against the condition known as "goiter" (Section 5.10). In which would you find (a) elemental iodine, (b) the I^- anion, and (c) the element iodine? ________________________

3.2 Sodium and Chlorine

We find elemental chlorine only rarely and elemental sodium not at all in the common substances of our everyday world, and for very good reasons. They are both extremely reactive and can be highly dangerous substances if they aren't used with care. Chlorine is capable of destroying living tissue and can be a health hazard and even deadly if it is inhaled in more than trace amounts. Because it kills bacteria, it is used in small quantities to eliminate infectious organisms from both swimming pools and public drinking water. It's also a very effective household bleaching agent. You can smell the odor of traces of elemental chlorine in the air near swimming pools and around open bottles of liquid household bleach, and you can taste it in the municipal drinking water of some regions. Released into the atmosphere in large volumes, it can kill plants and any animal that breathes it. Chlorine was one of the poison gases used in World War I.

Elemental sodium, a metallic solid. Elemental chlorine, a gas.

Chlorine illustrates the problem with trying to label chemicals as "good" or "bad" or as "beneficial" or "harmful" (Section 1.2). The same elemental chlorine that kills when it's used as a war gas saves lives when it's used to purify drinking water. It makes our lives easier and more pleasant as it rids swimming pools of bacteria and takes stains out of clothing. Released into the atmosphere in large quantities, it was used as a war gas; released judiciously into swimming pools and into drinking water, it helps prevent epidemics. The qualities of "good" and "bad" aren't properties of the chlorine itself, only of how we ourselves use it.

As for elemental sodium, the hazards of even small amounts of the metal far outweigh any benefits it might provide. If a piece of sodium the size of a pea comes in contact with water, it can ignite. A larger mass, perhaps the size of a walnut, explodes, as we'll see in Section 3.5. Elemental sodium has no uses among our consumer products.


Sodium reacts explosively with water.

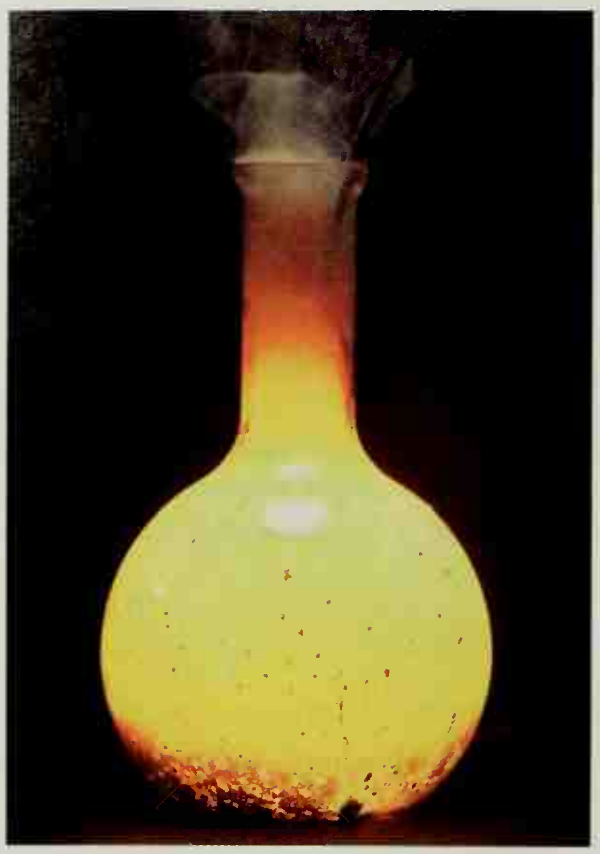
QUESTION

What compound forms when highly reactive, elemental sodium comes into contact with highly reactive, elemental chlorine? ______________________

3.3 Chemical Particles: Risks and Benefits

Sodium chloride, the compound that forms when elemental sodium reacts with elemental chlorine, is a relatively harmless electrolyte that many of us use daily to modify the taste of food. While it isn't completely without hazard—it's implicated as a contributing factor in high blood pressure, or *hypertension*, and when eaten in large quantities it can be deadly, especially to small animals, children, and infants—common table salt simply isn't in the same class as elemental sodium or chlorine. Yet it's composed of the same elements. Why both elemental sodium and chlorine should be so hazardous, and yet the sodium and chloride ions of their compound, sodium chloride, so benign, stems partly from the difference between an ion and an atom.

We should not assume because of this example that when elements themselves are hazardous their compounds will necessarily be harmless. The reverse can easily be true. Elemental nitrogen and oxygen, the principal gases of the air we inhale many times each minute, are themselves ordinarily entirely harmless to us, yet several of their compounds are quite hazardous. *Nitrogen dioxide*, for example, a compound containing twice as many oxygen atoms as nitrogen atoms, is partly responsible for the damage of acid rain (Section 10.16) and can produce a potentially fatal inflammation of the lungs if inhaled. The only generalization we can make is that no generalization is possible. There's no necessary connection between a hazard of an element and the chemical form it's in. Neither elements, compounds, atoms, ions, nor molecules are necessarily filled with either risks or benefits to us. In any case, both the risks and benefits we derive from them depend, as we have already seen, on how we use them.



The vigorous reaction of sodium with chlorine.

Common table salt, the product of the reaction of sodium with chlorine.

QUESTION

Name an element that is harmless or beneficial to us in its elemental form. Name a different element that can be hazardous in its elemental form. Now switch things around and name a hazardous compound of the harmless or beneficial element and a harmless or beneficial compound of the hazardous element. ________________

3.4 Valence Electrons

Several factors affect the properties of any particular atom or ion, including its atomic number, mass number, and electronic structure. Plutonium, Pu, element 94, may well be the most deadly of all the elements, regardless of mass number or electronic structure (Section 5.5). And while water, a compound of hydrogen and oxygen, is a necessity of life, drinking water in which deuterium atoms (^2_1H) have replaced the protium atoms (^1_1H; Section 2.6) can be fatal. Yet even as atomic number and mass number affect the properties of a chemical particle, electronic structure also plays a major role in its behavior.

The electron structures of sodium and chlorine, for example, are largely responsible for sodium chloride's ability to conduct an electric current. In considering the effects of electron structure we'll focus on the electrons in the outermost electron shell, which is known as the *valence shell*. It is these **valence electrons** that are so important, since *atoms tend to react so as to produce* *filled* **valence shells.** We'll examine some effects of this tendency after we first look at the connection between the number of valence electrons in an atom and the properties of the element it represents.

Valence electrons are the electrons of the **valence shell**, which is the outermost electron shell of an atom.

QUESTION

Name two elements of Table 2.2 with filled valence shells. What properties are common to them? ______

3.5 Periodicity

When characteristics repeat themselves again and again over time we say that they recur *periodically*, or that they are *periodic*. The seasons are periodic. By and large, summer's days are the warmest of the year; days are warmest, periodically, during the summer. Plants bloom, periodically, in the spring. Farm harvests come, periodically, during the fall. The sun also rises periodically.

If we examine the properties and behavior of all the elements (with the possible single exception of hydrogen, which is the first in the sequence of atomic numbers and something of a chemical maverick), we find that their properties repeat periodically, much as days grow warm or flowers bloom periodically from one year to the next. The properties of the elements also repeat themselves, but their repetition occurs over irregular sequences of atomic numbers rather than over regular periods of time.

Table 2.3, for example, shows that helium (atomic number 2), neon (atomic number 10), and argon (atomic number 18) all have filled valence shells, while Table 2.2 describes helium and neon as inert or virtually inert gases. That is, helium shows no tendency whatever to react with any other substance, whether it's an element or a compound. Helium certainly doesn't burn, for example. Neon is very nearly as unreactive as helium. Its chemical reactions are few and rare. Like neon, argon is a virtually inert gas. Similarly, krypton (36) and xenon (54) have filled valence shells and, like the others, are gases with extremely little reactivity. We would be correct in guessing that a filled valence shell is a mark of extraordinarily little chemical reactivity, or none at all, and that *any atom that has (or acquires) a filled valence shell often is (or becomes) quite inert.*

We can make one more generalization from the kind of data we find in Tables 2.2 and 2.3: Elements with the same numbers of electrons in their valence shells tend to behave in the same way. Lithium (atomic number 3), sodium (11), potassium (19), rubidium (37), and cesium (55), for example, have one valence electron each. All are metals and are all reactive, although some of these metals react with other substance much more vigorously than do others of the series. For example, each of them reacts with water at its own characteristic rate to produce highly flammable hydrogen gas. That's why, as we saw in Section 3.2, sodium ignites or explodes when it come into contact with water. Sodium, like the rest of the metals with only one valence electron, reacts with water to liberate the hydrogen of the water in the form of elemental hydrogen gas. With sodium, and all the other alkali metals except lithium, the heat released in the reaction often causes the hydrogen to ignite or explode.

QUESTION

What gas is produced when rubidium, Rb, reacts with water? What is the basis for your answer? ____

3.6 Atomic Weights and the Genius of Dimitri Mendeleev

Dimitri Mendeleev devised the first comprehensive periodic table of the elements.

Recognizing repetitions in properties similar to those we have just examined, Dimitri Mendeleev, professor of chemistry at the Technological Institute of St. Petersburg, Russia, devised an arrangement of the elements known as the Periodic Table. The youngest of 17 children, Mendeleev was born in Siberia in 1834. In his later years, during the last decade of the nineteenth century, he became the director of Russia's Bureau of Weights and Measures.

An exceptional teacher and extremely popular with his students at the Institute, Mendeleev was preparing in 1869 to write a chemistry textbook. As he was reviewing the properties of the 63 elements known at the time—today we recognize 109 (Section 1.4)—he realized that by organizing them in order of increasing *atomic weight* he produced, on a much greater scale, the same sort of periodic repetition of properties we have just described.

Because of their importance, we pause here to examine atomic weights briefly. An element's **atomic weight** is simply the average of the masses of

An early version of the periodic table.

TABLE I Distribution of the Elements in Groups and Series

Group	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			
Series 1	H	—	—	—	—	—	—				
" 2	Li	Be	B	C	N	O	F				
" 3	Na	Mg	Al	Si	P	S	Cl				
" 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
" 5	(Cu)	Zn	Ga	Ge	As	Se	Br				
" 6	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag
" 7	(Ag)	Cd	In	Sn	Sb	Te	I				
" 8	Cs	Ba	La	Ce	Di?	—	—	—	—	—	—
" 9	—	—	—	—	—	—	—				
" 10	—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au
" 11	(Au)	Hg	Tl	Pb	Bi	—	—				
" 12	—	—	—	Th	—	U	—				
	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	Higher oxides			
	—	RO	—	RO_2	—	RO_3	—	RO_4			
	—	—	—	RH_4	RH_3	RH_2	RH	Hydrogen compounds			

all of its isotopes, weighted for their individual abundances. For example, when we mix in the small amount of deuterium ($^2_1$H) present in the universe along with all the protium ($^1_1$H), the average weight of *all* atoms of atomic number 1 becomes slightly larger than 1 (the mass of protium alone). Thus, the atomic weight of hydrogen, the weighted average of all its isotopes (neglecting the trace of tritium present in the universe), is 1.008 amu.

The **atomic weight** of an element is the average of the masses of all of its isotopes, weighted for the abundance of each.

EXAMPLE CALCULATING ATOMIC WEIGHT

Calculate the atomic weight of chlorine from a knowledge of the abundances of its most common isotopes. The isotope of mass number 35 makes up 75.77% of all chlorine atoms, while the isotope of mass number 37 accounts for 24.23% (the remainder) of chlorine atoms.

To obtain the contribution of each isotope, weighted for its abundance, we multiply the mass of each isotope by the fraction of the total that each isotope represents. The isotope of mass 35 (75.77% of the total) thus contributes

$$0.7577 \times 35 \text{ amu} = 26.52 \text{ amu}$$

to the weight-averaged atomic weight of *all* atoms of the element chlorine. The isotope of mass 37 (24.23% of the total) contributes

$$0.2423 \times 37 \text{ amu} = 8.96 \text{ amu}$$

The weight-averaged atomic weight of chlorine is the sum of these two contributions:

$$\begin{array}{rl} & 26.52 \text{ amu} \\ + & \underline{\ 8.96} \text{ amu} \\ & 35.48 \text{ amu} \end{array}$$

which we can round off to 35.5 amu. For a review of the atomic mass unit (amu), refer to Section 2.4.

Although others had also noted the same sort of periodic repetition of properties even before Mendeleev's inspiration, none had pursued the idea as vigorously or in as much detail as the Russian chemist. He organized the known elements into a table in which, with a few exceptions, atomic weights increased regularly in the horizontal rows, from left to right, and elements with similar properties fell neatly into place in the table's vertical columns. To maintain a consistent periodicity in elemental properties he was forced to leave some of the boxes empty. He predicted that they would be filled by as yet unknown elements. Within 15 years three of the gaps were, indeed, filled through the discoveries of the elements gallium, scandium, and germanium, all of which proved to have the very properties he predicted from the locations of the vacancies. What's more, atomic weights of some of the elements Mendeleev had to place (apparently) out of the normal order in his table were later found to be incorrect. Newer, better values showed that he was, indeed, correct in his placement of those particular elements, and that they did not violate a sequence of (now corrected) atomic weights. It was the measured values of their atomic weights (as they were known at the time) that were in error, not Mendeleev's idea of periodicity.

QUESTION

The atomic weight of lithium (Li) is 6.94. The lithium isotope of mass number 7 is the most abundant of all lithium's isotopes, making up about 92.5% of all lithium atoms. What is likely to be the mass number of the second most abundant isotope of lithium? Explain your answer. ____________________

3.7 The Periodic Table

A **family** of elements consists of all the elements in any column of the periodic table.

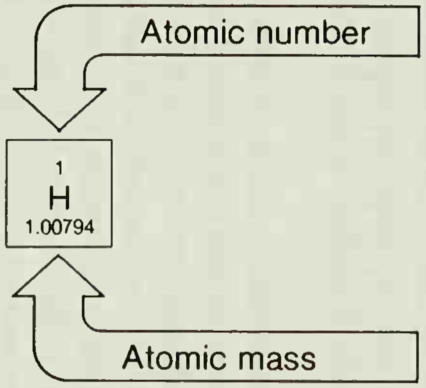
In the modern version of the periodic table (Fig. 3.2) the elements are organized in a sequence of increasing atomic *number* rather than atomic *weight*. Mendeleev, who lived from 1834 to 1907, had only atomic weights to work with; the concept of atomic numbers was not devised until 1913. In most modern versions of the table, the chemical symbol of each element appears in the center of the squares, with the atomic number above the symbol and the atomic weight below.

Now we're in a position to connect the number of valence electrons of an element (Section 3.4) with the element's position in the periodic table. We now know that each of the table's columns contains elements with the same numbers of valence electrons and that this is the basis of their chemical similarities. In recognition of these similarities we call all the elements in any individual column a **family** of elements. The leftmost family, consisting of lithium, sodium, potassium, rubidium, cesium, and francium, each with one valence electron, is the *alkali metal* family.

As we move from left to right within each row, valence shells of the atoms fill with electrons, from a single electron in the alkali metals to a full shell in the inert gases. The rightmost column, composed of gases with filled valence shells and with little or no chemical reactivity, is the *inert gas* or *noble gas* family, so called because of their almost complete lack of chemical association with the more common elements. Just to its left is a family of *halogens* consisting of fluorine, chlorine, bromine, iodine, and astatine. (*Halogen* comes from the Greek *hals*, meaning "salt" or "sea." The halogens readily form *salts*, which we discuss further in Chapter 10.) Elemental fluorine is extremely reactive; in combination with carbon it forms the plastic Teflon. Fluorine is also a component of chlorofluorocarbons (CFCs), which are used as refrigerants and which threaten to damage the ozone layer (Chapter 19). Along with its use as a bleach and disinfectant, chlorine is a component of synthetic rubber, *polyvinyl chloride* (PVC) and other plastics, and various pharmaceuticals. Bromine and iodine are also used in the manufacture of pharmaceuticals.

Because it concisely furnishes information about chemical symbols, atomic weights, atomic numbers, valence electrons, chemical families, and, to those familiar with its use, the reactivities of the elements, the periodic table provides one of the most valuable reference works in the entire study of chem-

PERIODIC TABLE OF THE ELEMENTS[a]



Periods	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases 0
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.00674	8 O 15.9994	9 F 18.99840	10 Ne 20.1797
3	11 Na 22.98977	12 Mg 24.3050											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.95591	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.93320	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92159	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc 98.9072	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.90447	54 Xe 131.29
6	55 Cs 132.90543	56 Ba 137.327	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.96654	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98037	84 Po 208.9824	85 At 209.9871	86 Rn 222.0176
7	87 Fr 223.0197	88 Ra 226.0254	89 †Ac 227.0278	104 Unq 261.11	105 Unp 262.114	106 Unh 263.118	107 Uns 262.12		109 Une									

*	58 Ce 140.115	59 Pr 140.90765	60 Nd 144.24	61 Pm 144.9127	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
†	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu 244.0642	95 Am 243.0614	96 Cm 247.0703	97 Bk 247.0703	98 Cf 242.0587	99 Es 252.083	100 Fm 257.0951	101 Md 258.10	102 No 259.1009	103 Lr 260.105

[a] Atomic masses are the 1985 values given in the Table of Atomic Masses and Atomic Numbers (opposite) but rounded, where appropriate to the fifth decimal place.

istry. Inside the covers of this book you will find a list of the data of the Periodic Table, alphabetized by the names of the elements, and a list of the names and symbols of the elements, alphabetized by the symbols.

QUESTION

Strontium (Sr), barium (Ba), and radium (Ra) are three members of the *alkaline earth metals* family of elements. What are the names and symbols of the other members of this family? ________________

3.8 Valence Shells and Chemical Reactivity

Combining a knowledge of the periodic table and of the reactions of the chemical elements produces the useful generalization we first saw in Section 3.4: *Atoms tend to react so as to produce filled valence shells.* Since the valence shells of the inert gases are already filled, these elements have virtually no tendency to react in any way with any other elements.

Each alkali metal, though, has a single electron in its valence shell. Losing that one valence electron to some other element leaves the alkali metal atom with a filled shell (the shell just below the one with the lone electron) and with the very same electron structure as a nearby inert gas. The halogens, such as chlorine, have valence shells that need only one more electron to be filled. Filling the shell by acquiring a single electron gives each of the halogens the same electron structure as a nearby inert gas.

(At this point we might ask why the sodium atom can't *gain seven* electrons to fill its outermost shell, and why a chlorine atom can't *lose seven* electrons to leave a lower, filled shell as its valence shell. We'll answer these questions in the next section.)

We'd be correct in expecting that metallic, elemental sodium would react with gaseous, elemental chlorine with the transfer of sodium's lone valence electron into chlorine's valence shell, giving both sodium and chlorine filled valence shells and inert gas electron structures. Our expectation is not only correct; it is explosively correct. Sodium and chlorine react violently, with the rapid release of a great deal of energy, to produce the very stable, very inert household commodity, sodium chloride, our common table salt (Fig. 3.3).

One important use for the periodic table now becomes clear. Understanding its construction allows us to begin predicting what elements will react with each other and what kinds of compounds they can form. Since each member of the alkali metal family contains only a single electron in its valence shell, and since each halogen can fill a valence shell by acquiring a single electron, any of the alkali metals can react with any of the halogens to form a compound by the simple transfer of a single electron from the valence shell of the alkali metal atom to the valence shell of the halogen. Potassium, for example, can react with any of the halogens to form a compound similar in many ways to NaCl. The results are KF, KCl, KBr, and KI. (Astatine, At, is

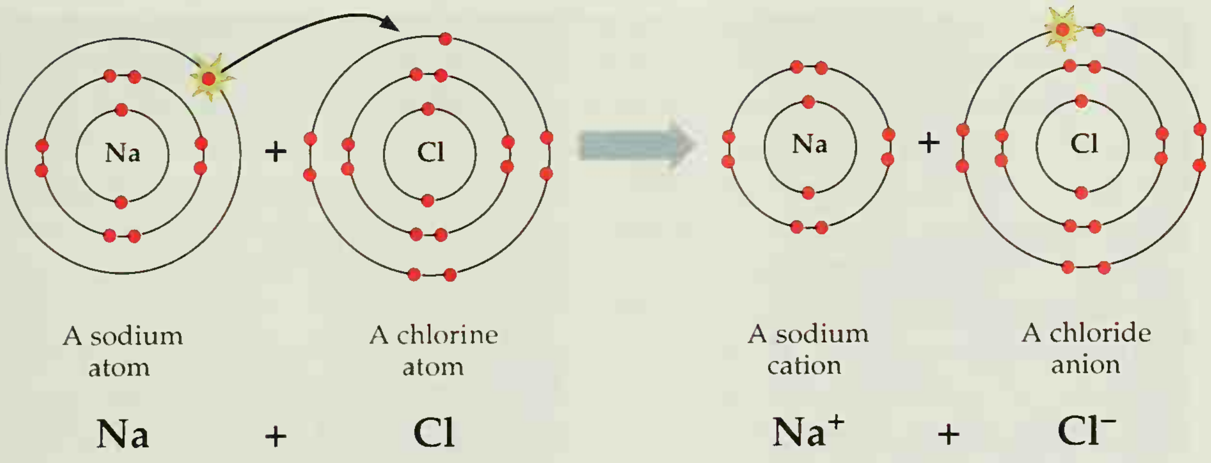


Figure 3.3
The reaction of sodium and chlorine to produce sodium chloride.

a very rare element, and although it is a member of the halogen family, we virtually never come across astatine or any of its compounds.) As a parallel illustration, chlorine reacts not only with sodium, but with the other alkali metals as well, to form LiCl, NaCl, KCl, RbCl, and CsCl. (Francium, Fr, and its compounds are about as rare as astatine and are easily ignored.)

QUESTION

(a) How many electrons must a magnesium atom lose to acquire a filled valence shell? (b) How many electrons must oxygen acquire to fill its valence shell? (c) Would you expect magnesium and oxygen to react with each other to form a chemical compound? ____________________

3.9 From Sodium Atoms to Sodium Cations, from Chlorine Atoms to Chloride Anions

As we've just seen, the transfer of one or more electrons between atoms converts the atoms into ions and results in the formation of **ionic compounds,** which are compounds composed of ions. Sodium chloride (Fig. 3.3) is just such an ionic compound, formed when elemental sodium and elemental chlorine react with each other, and in other ways as well. (The suffix *-ide* of *chloride* tells us that we are dealing with an anion. Fluor*ide*, chlor*ide*, brom*ide*, and iod*ide* are the names of the hal*ide* anions. The *-ine* suffix applies to the names of the elements and to the elemental forms themselves, as in fluor*ine*, chlor*ine*, etc.)

Ionic compounds are compounds composed of ions.

A sodium *atom* contains 11 protons within its nucleus and 11 electrons in the surrounding shells. The negative charges of these 11 electrons counter the 11 positive charges of the protons. Loss of the single electron from its third quantum shell leaves the sodium atom with only 10 electrons (in two quantum shells) to counterbalance the 11 nuclear protons. This leaves sodium with a net excess of one proton and thus a net electrical charge of 1+. On reaction with chlorine, then, the sodium atom loses one electron and is converted to a sodium cation, Na^+. We might ask, as in the preceding section, why the sodium atom can't just as well *gain seven* electrons and thereby fill its outermost shell. If it did, the resulting ion would contain an excess of seven electrons over protons and thus bear an electrical charge of 7−. Since like electrical charges repel each other (and opposite electrical charges attract), the accumulation of seven negative charges on the same small particle would make it unstable. Losing a single electron and forming the Na^+ cation, with a single positive charge, produces a much more stable particle than the one that would result from a gain of seven electrons.

The Cl *atom* contains 17 protons in its nucleus and an equal number of electrons in three quantum shells. As the valence shell, which holds seven electrons in the Cl atom, becomes filled with an eighth electron acquired from some other atom, such as a sodium atom of this example, the Cl gains a net excess of one electron over its nuclear protons and is transformed from a chlorine atom into a chloride anion, Cl^-. Just as the *gain* of seven electrons would produce an unstable ion in the case of sodium, the *loss* of seven electrons by the chlorine would produce an unstable ion with a charge of 7+.

QUESTION

The electronic structure of the sodium cation (two electrons in the first quantum shell and eight in the second) resembles the electronic structure of what inert or noble gas element? The electronic structure of the chloride anion resembles that of what inert or noble gas element? ____________________

3.10 Table Salt, Crystals of an Electrolyte

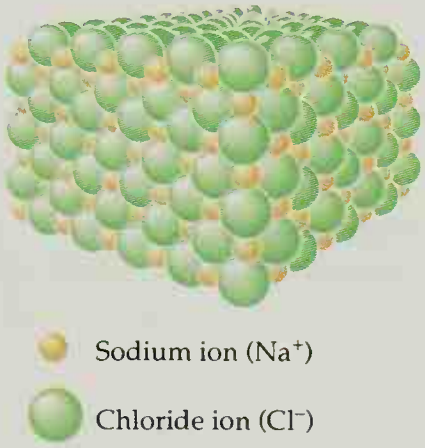


Figure 3.4
Part of a sodium chloride crystal.

A **crystal lattice** is the orderly, three-dimensional arrangement of the chemical particles that make up a crystal.

An **ionic bond** results from the attraction of oppositely charged ions.

The crystals of the sodium chloride we shake out of a salt shaker are made up of equal numbers of sodium cations and chloride anions. Crystals as a class are the well-defined, solid shapes that pure substances often form as their ions or molecules arrange themselves into a precise, regular, three-dimensional order. Crystals of sodium chloride result as the oppositely charged sodium cations and chloride anions attract each other and become organized into an extensive, orderly arrangement known as a **crystal lattice.** Figure 3.4 shows a part of this crystal lattice of NaCl. As this lattice extends outward in three dimensions it forms the well-defined shape of the crystals that appear, much enlarged, in Figure 3.5.

The force that holds the ions in place within the lattice comes from the mutual attraction of the oppositely charged cations and anions. It's called an **ionic bond** and it results in the formation of ionic compounds. (The formula NaCl does not tell us that sodium chloride is an ionic compound. To emphasize that fact we can write the formula as Na^+Cl^-.)

When sodium chloride dissolves in water the cations and anions separate from the lattice and from each other, enter the water solution, and provide the ions that carry an electric current between the poles in Figure 1.3. Crystals of table sugar (sucrose) consist of electrically uncharged molecules held in place in the lattice by forces much weaker than the ionic bonds of sodium chloride. When molecules of sucrose separate from their crystal lattice (Fig. 3.6) they don't provide ions and thus they don't conduct a current (Fig. 1.3).

Figure 3.5
Crystals of sodium chloride, an ionic compound and an electrolyte.

Figure 3.6
Crystals of sucrose, a covalent compound and a non-electrolyte.

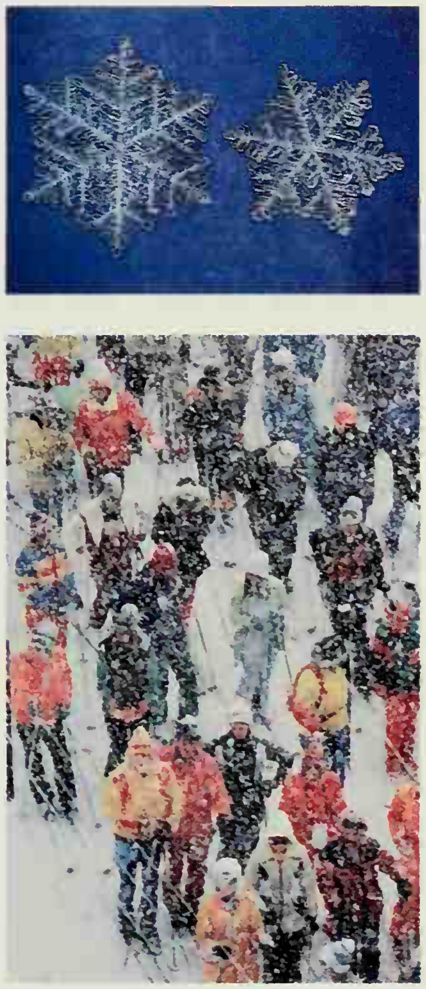


Figure 3.7

That's why the light bulb glows brightly when the electrolyte sodium chloride is added to the water, but not when the nonelectrolyte sucrose is added.

QUESTION

What do we call the structures, shown enlarged in Figure 3.7, that form as water crystallizes in the atmosphere in cold weather? ______________________

3.11 Chemical Formulas

Sucrose is a nonelectrolyte because it isn't made up of ions and doesn't provide any means for transporting an electric current across the water between the two wires of Figure 1.3. Sucrose, water and many other substances are made up of *molecules,* which we described briefly in Section 1.1 as groups of two or more atoms held together by chemical bonds, and which we examine in more detail shortly. While the ions of a crystalline ionic compound lie next to each other in a lattice that extends to the edges of the crystal, the atoms of a molecule are bound cohesively into a unit, the molecule, that has a well-defined size and shape and that exists as that same unit whether it's packed into a crystal or dissolved in a liquid like water or in a gas such as the air we breathe.

Water itself is made up of molecules that consist of two hydrogen atoms and one oxygen bound firmly to each other through chemical bonds. These three atoms exist as a molecular unit of specific size and shape no matter whether the water is in the form of ice, liquid water, or steam. To show the numbers of hydrogen and oxygen atoms in a water molecule we write the chemical formula of water as H_2O, with the subscript 2 indicating the presence of two hydrogen atoms and an implied subscript 1 at the oxygen, which indicates only a single oxygen. Sucrose, too, is made up of molecules, but it contains hydrogens and oxygens in numbers much larger than in water, and carbons as well. Sucrose molecules have the formula $C_{12}H_{22}O_{11}$, which indicates that 12 carbon atoms, 22 hydrogens, and 11 oxygens make up a molecule of sucrose. We'll discuss the forces that hold molecules together as a third kind of chemical particle (in addition to atoms and ions) in Section 3.13, after we examine chemical formulas in more detail.

A **chemical formula** is a sequence of chemical symbols and subscripts that shows the elements that are present in a compound and the ratio of their ions in a lattice or the actual number of their atoms in a molecule.

The **chemical formula** of a compound provides us with two pieces of information:

1. It tells us what elements are present.
2. It gives us the ratio of their ions or the actual numbers of atoms of each element present in a molecule.

The chemical formula for sodium chloride (NaCl), for example, tells us that both sodium and chlorine are present, and that they are present in a one-to-one ratio. The chemical formula H_2O tells us that two hydrogen atoms and one oxygen atom make up a water molecule. Both sodium chloride and water are **binary compounds**, made up of two different elements.

A **binary compound** is made up of two elements.

Two general rules are helpful for writing chemical formulas:

1. For compounds made up of ions, whether they are binary or contain more than two elements, write the cation first, then the anion. The cations of these compounds usually come from the alkali metal or the alkaline earth families of the periodic table (Section 3.7). The anions often come from the halogen family or the family beginning with oxygen. For these, name the cation first and then the anion, with the suffix *-ide* for the anion. For example, CaF_2 is *calcium fluoride*, Li_2O is *lithium oxide*, and SrS is *strontium sulfide*.
2. For molecules containing carbon (Chapter 7), write carbon first, hydrogen second, and then the other elements present in alphabetical order. (The names of many of these compounds don't follow any simple rules.) $CHCl_3$ (chloroform, an industrial solvent), $C_{12}H_{22}O_{11}$ (sucrose), $C_{16}H_{13}ClN_2O$ (the relaxant Valium, known chemically as diazepam), and $C_6H_8N_2O_2S$ (sulfanilamide, the first of the sulfa drugs) are examples.

EXAMPLE CATIONS COME FIRST

Name the compounds Cs_2O and $BaCl_2$.

Since Cs is written first in the formula Cs_2O, it represents the cation *cesium* (Table 3.2). Then comes O, representing the anion of the element oxygen and providing the word *oxide*. The full name of Cs_2O is *cesium oxide*.

For $BaCl_2$ we have the cation *barium* and the anion of the element chlorine, *chloride*. The name of $BaCl_2$ is *barium chloride*.

QUESTION

Name (a) MgI_2, (b) BeS, and (c) K_2O. Write the formula of a molecule of *urea*, a compound that we excrete to rid our bodies of excess nitrogen and that is composed of one carbon, one oxygen, two nitrogen, and four hydrogen atoms. ____________

3.12 Valence and Chemical Formulas

The ratio of ions in a binary, ionic compound (and therefore its chemical formula as well) depends on the valence of the elements it contains. We've seen that sodium loses and chlorine gains one electron each, so they combine in a one-to-one ratio in NaCl.

Unlike sodium, the element calcium has *two* electrons in its valence shell. In its reaction with chlorine, each calcium atom can transfer *two* valence electrons to chlorine atoms. Since each chlorine atom still needs only a single electron to fill its valence shell, *one* calcium atom can combine with *two* chlorine atoms in the ionic compound *calcium chloride* (Fig. 3.8). To show the association of *two* chloride anions with *one* calcium cation we write the chemical formula of calcium chloride as $CaCl_2$.

In addition to defining the outermost shell of electrons in an atom, we use the term *valence* to describe what we might call the "combining power" of an element. For ions, this is the same as the numerical value of their charge, regardless of its sign.

With the ability to lose or accept a single electron, both sodium and chlorine form ions with a valence of 1; calcium's valence is 2. In this same vein, magnesium has two electrons in its valence shell and has a valence of 2. Oxygen, which needs two electrons to complete its valence shell, also has a valence of 2.

Like a calcium cation, a magnesium cation can combine with two chloride anions to form *magnesium chloride*, $MgCl_2$. Combinations with this ratio of cation and anion can occur between any member of the alkaline earth family and any halogen. Beryllium and fluorine, for example, can combine to form *beryllium fluoride*, BeF_2.

Similarly, one oxygen atom can accept both electrons from a single atom, or one from each of two individual atoms. In the question at the end of Section 3.8, for example, we saw that a single oxygen atom can accept two electrons from the valence shell of a single magnesium atom to form *magnesium oxide*,

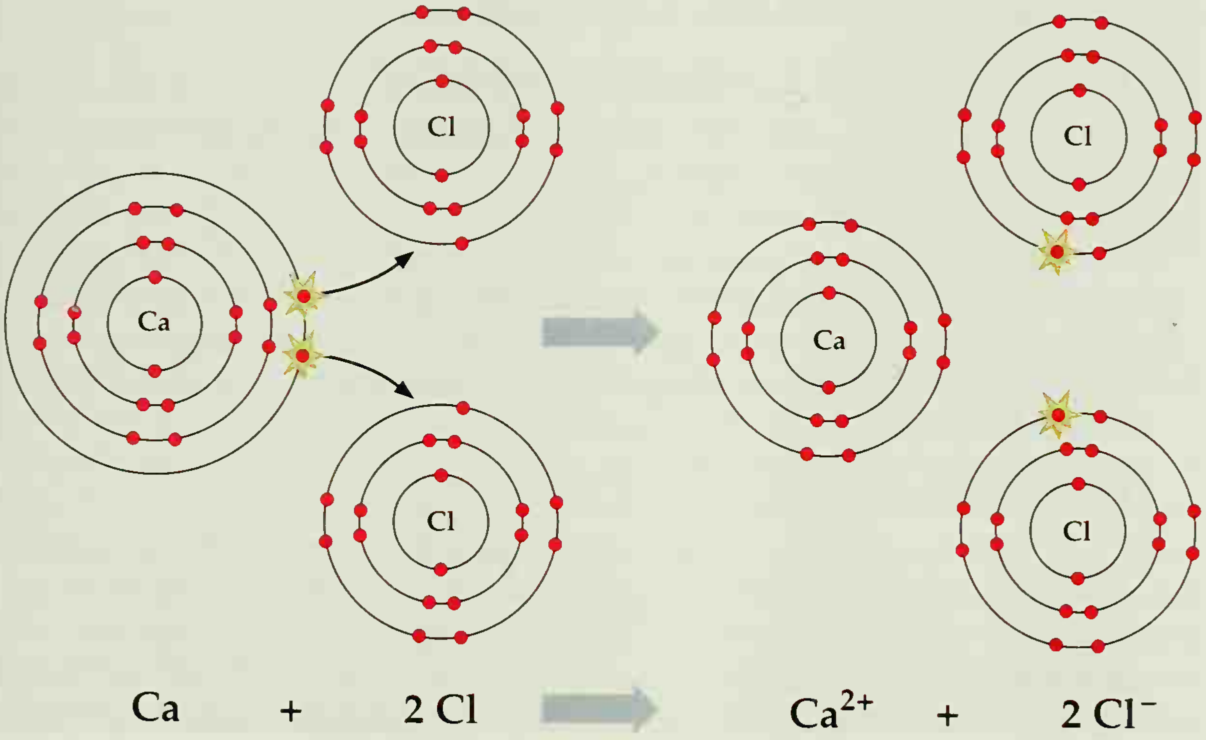


Figure 3.8
The reaction of calcium and chlorine.

MgO. In another example, oxygen can combine with one calcium atom to form the compound *calcium oxide*, CaO. In these examples both the magnesium atom and the calcium atom lose two electrons from their valence shells to form a magnesium cation, Mg^{2+}, and a calcium ion, Ca^{2+}. In each case the oxygen acquires two electrons to form an oxide anion, O^{2-}. By a similar process two sodium atoms can react with one oxygen to produce *sodium oxide*, Na_2O.

The subscripts reflect the fact that the net electrical charge of all the ions combined must be zero. In practice this means that the total number of positive charges provided by the cation(s) must equal the total number of negative charges brought by the anion(s). This occurs when

$$\text{cation subscript} \times \text{cation charge} = \text{anion subscript} \times \text{anion charge}$$

Notice that we ignore the sign (+ or −) of the charge here and concern ourselves only with the numerical value of the charge. The simplest case occurs when the cation and the anion electrical charges are equal, as in NaCl, MgO, and CaO. If the charges are equal, the subscripts must be equal, so we simply use (an implied) *1* for each.

EXAMPLE CHARGES MUST EQUAL

Write the chemical formulas of calcium chloride, sodium oxide, and aluminum oxide.

In the first case the charge on the calcium cation is 2+, while the charge on the chloride anion is 1−. Here we have

$$1 \text{ (the } Ca^{2+} \text{ subscript)} \times 2 \text{ (the } Ca^{2+} \text{ charge)} = 2 \text{ (the } Cl^- \text{ subscript)} \times 1 \text{ (the } Cl^- \text{ charge)}$$

$$2 = 2$$

The formula is $CaCl_2$.

For the compound of sodium and oxygen,

$$2 \text{ (the } Na^+ \text{ subscript)} \times 1 \text{ (the } Na^+ \text{ charge)} = 1 \text{ (the } O^{2-} \text{ charge)} \times 2 \text{ (the } O^{2-} \text{ charge)}$$

$$2 = 2$$

Once again, 2 = 2 and now the formula is Na_2O.

When aluminum reacts with oxygen, the aluminum loses three valence electrons (rather than gaining 5) and acquires a charge of 3+. Oxygen gains two valence electrons and acquires a charge of 2−. For aluminum oxide,

$$2 \text{ (the } Al^{3+} \text{ subscript)} \times 3 \text{ (the } Al^{3+} \text{ charge)} = 3 \text{ (the } O^{2-} \text{ subscript)} \times 2 \text{ (the } O^{2-} \text{ charge)}$$

$$6 = 6$$

and we have Al_2O_3.

In each of these formulas the product of (valence × subscript) of one ion equals the product of (valence × subscript) of the other. Knowing the formula and the valence of one of the ions allows us to calculate the valence of the other. Normally, the valence of hydrogen, the alkali metals, and the halides is 1, and the valence of the alkaline earths and oxygen is 2.

EXAMPLE CALCULATING VALENCE

Calculate the valence of lead in the compound PbO_2.

For lead dioxide, PbO_2, a compound used in the lead-acid batteries of automobiles (Chapter 6), we can calculate the valence of the lead as follows:

$$1 \text{ (the implied Pb subscript)} \times \text{(the valence of Pb)} = 2 \text{ (the O subscript)} \times 2 \text{ (the valence of O)}$$

$$1 \times \text{(the valence of Pb)} = 4$$

The valence of the lead in PbO_2, then, is *4*. Since the oxygen carries a negative charge, the Pb ion must exist as Pb^{4+}.

QUESTION

What is the valence of (a) platinum in PtO_2, a compound used in the catalytic converters of automobiles (Chapter 8); (b) copper in Cu_2O, a compound used as a red pigment in glass and ceramics; and (c) mercury in HgS, a pigment used in plastics, paper, rubber, and other commodities? ____________________

3.13 Water, a Covalent Compound

As we saw in our work with the light bulb at the opening of Chapter 1, neither sucrose nor water is a good conductor of electricity. It follows that neither one can be composed primarily of ions. Water, whose molecules are much simpler than those of sucrose, offers a good example of chemical bonding in nonionic compounds.

As shown by the formula H_2O, water's molecules are formed of two hydrogens and one oxygen. Since water is not a good electrolyte, some force other than ionic attraction must bond the hydrogens to the oxygen. That force is the **covalent bond;** we will now see how it forms.

A covalent bond consists of a pair of electrons shared between two atoms.

Hydrogen does not release its lone valence electron to oxygen as easily as sodium loses its valence electron to chlorine. As a result no full transfer of electrons from one atom to another takes place in the formation of water, and so ions don't form as they do in sodium chloride. Instead, the oxygen and the hydrogens of water *share* their valence electrons to acquire filled valence shells. As shown in Figure 3.9, two hydrogens, each with one valence electron, and one oxygen, with its six valence electrons, combine through the

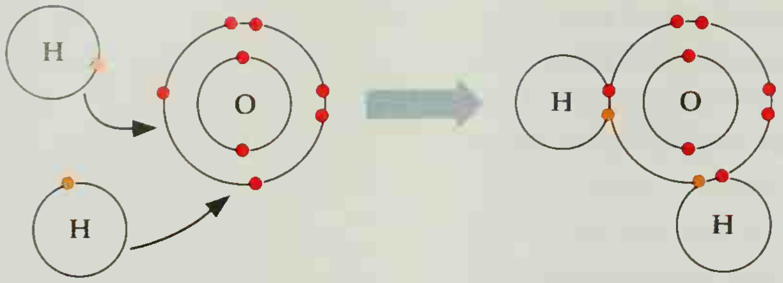


Figure 3.9
Covalent bonding in H_2O.

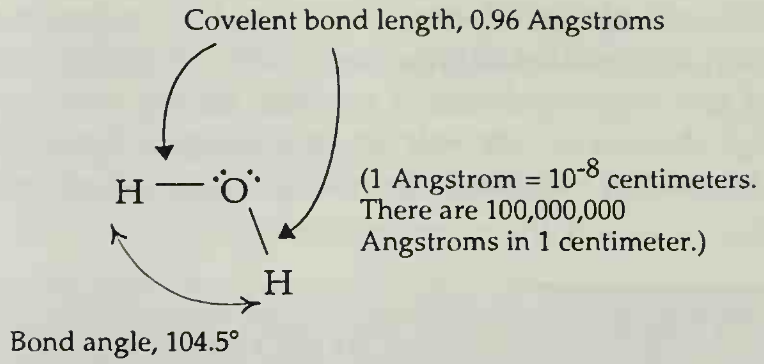


Figure 3.10
The structure of the water molecule.

sharing of two pairs of electrons. Each hydrogen, by sharing one of oxygen's electrons, acquires a filled valence shell of two electrons. The lone oxygen, by sharing one electron from each of the two hydrogens, also fills its valence shell. The elements of the water molecule, then, are held together by the sharing of two pairs of electrons. Each pair consists of one electron from the valence shell of a hydrogen and one electron from the valence shell of the oxygen.

A shared pair of electrons constitutes a covalent bond, which can be represented as a pair of dots (H:O:H) or, more often, as a dash (H–O–H). Unlike crystals of an ionic compound, which are aggregates of enormous numbers of cations and anions held together by electrostatic forces (Fig. 3.4) molecules are discrete, often relatively small chemical structures held together by covalent bonds (Fig. 3.10). **Molecules** have distinct sizes and shapes. In contrast, ionic compounds, as we saw in Section 3.10, are formed of ions that exist in orderly lattices extending in all directions to the surfaces of their individual crystals. Covalent compounds consist of discrete molecules; ionic compounds consist of vast crystal lattices. And, as we have seen, while the chemical formula of an ionic compound shows the ratio of its ions, the chemical formula of a covalent compound shows the actual numbers of atoms that make up each of its molecules. The chemical formula of a covalent compound is often called its **molecular formula.** Knowing the molecular formula of a compound, we can calculate its **molecular weight**, which is simply the sum of the atomic weights of all of the atoms in each of its molecules.

A **molecule** is a discrete chemical structure held together by covalent bonds.

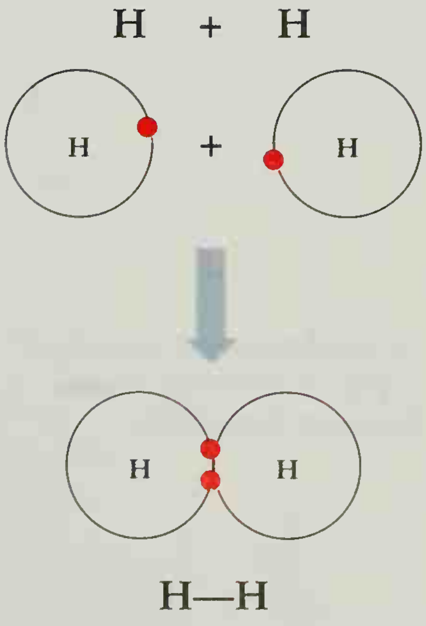
A **molecular formula** is the chemical formula of a covalent compound.

The **molecular weight** of a compound is the sum of the atomic weights of all of the atoms in each of its molecules.

Generally, different elements that fill their valence shells by the gain or loss of one or two electrons and that lie far from each other in the periodic table form ionic bonds with each other. Other elements, including those of the same chemical family, occupying the same vertical column, generally form covalent bonds with each other. Hydrogen, which we called a maverick element in Section 3.5, usually forms covalent bonds with other elements. These are, of course, no more than useful generalizations. Exceptions do occur, some of them quite important.

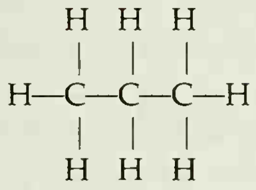
Of all molecules, hydrogen, H_2, is the simplest. It's made up of two hydrogen atoms, each sharing its single electron with the other and each thereby filling its valence shell with two electrons, which form the covalent bond (Fig. 3.11). With two atoms composing each of its molecules, hydrogen is *diatomic.* Other diatomic molecules include those of elemental nitrogen, N_2, oxygen, O_2, and all the halogens, F_2, Cl_2, Br_2, and I_2.

Figure 3.11
Formation of a molecule of H_2.



QUESTION

A molecule of *propane*, the fuel of liquid propane gas supplied by tanks to outdoor grills, trailers, and many homes, has the structure



$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & \\ & & H & & H & & H & \end{array}$$

(a) What is the total number of covalent bonds in propane? (b) What is the total number of *shared* electrons in propane? (c) What is the molecular formula of propane? ________________________________

A grill that burns propane gas.

3.14 Hydrogen Halides and the Halogens

We've seen that a hydrogen atom does not release its electron to the oxygen of water, but rather shares it in a covalent bond. Similarly, the hydrogen of a *hydrogen halide*, a compound of hydrogen and a halogen, does not release its electron to the halogen atom, but shares it instead. Figure 3.12 shows the result for *hydrogen chloride*. With this sharing, both the hydrogen and the halogen atom have filled valence shells. We can write the resulting molecule as HCl or, to emphasize the covalent bond, H—Cl.

Something similar results when two halogen atoms react with each other. Chlorine atoms, for example, lack a single electron for a filled valence shell. The sharing of two electrons, one from the valence shell of each of two different chlorine atoms, gives each a filled shell and results in the formation of a covalent bond. The result is a diatomic chlorine molecule, Cl_2 or Cl—Cl (Fig. 3.13).

In their pure states, then, both the hydrogen halides and the halogens exist as diatomic, covalent molecules.

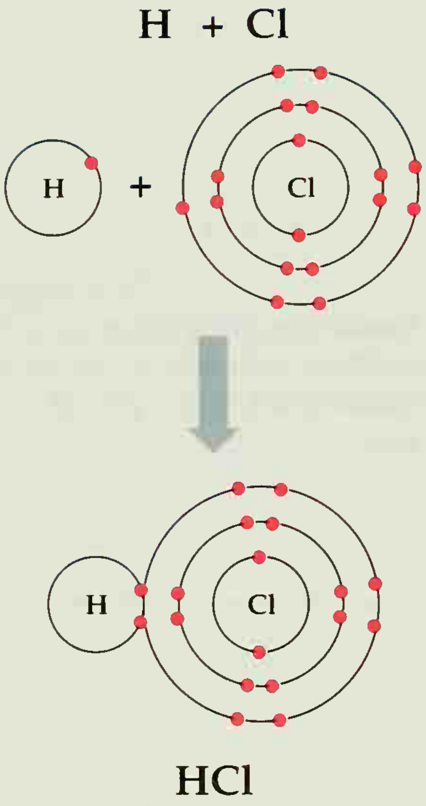


Figure 3.12

Formation of a molecule of HCl from a hydrogen atom and a chlorine atom.

QUESTION

Draw a molecule of fluorine, F_2, showing all of the electrons in all of the quantum shells. ________________________________

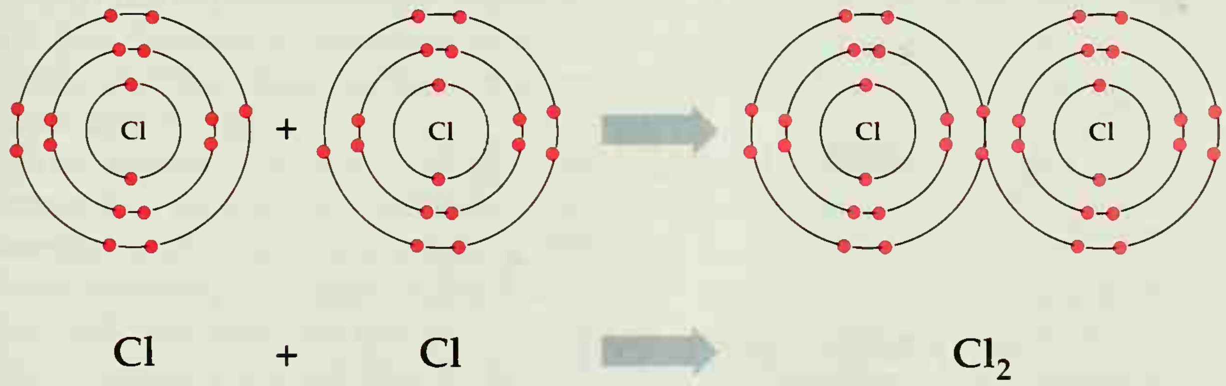


Figure 3.13

Two chlorine atoms combine to form a chlorine molecule.

3.15 Ionization, from Molecules to Ions

Things are not entirely as simple as the previous sections might suggest. Sodium chloride, a fine electrolyte, is indeed an ionic compound, and sucrose is a nonelectrolyte that does indeed exist as covalent molecules (of very complex structure) both in its pure, solid, crystalline state and also when it's dissolved in water.

But water itself is a very weak electrolyte. Actually, pure water *does* conduct electricity, but only very poorly. Although pure, liquid water is composed almost (but not quite) entirely of covalent H_2O molecules, it does nonetheless contain a very small concentration of ions. What's more, while the hydrogen halides are, indeed, covalent compounds, composed of molecules in which the hydrogen is attached to the halogen by a covalent bond, if you dissolve a hydrogen halide, such as HCl, in water you'll find that it is a fine electrolyte and, like the sodium chloride of Chapter 1, carries an electric current through water quite nicely. As we conclude this chapter we'll examine how covalent compounds can become electrolytes.

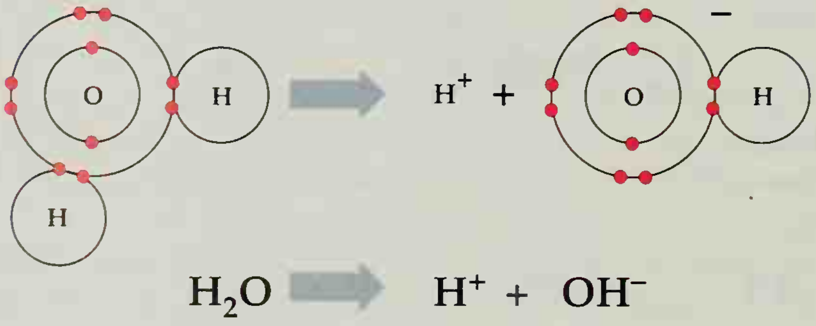
Although hydrogen is less efficient than sodium at releasing its valence electron, full electron transfers do take place to a very small extent between hydrogen and oxygen, and an occasional covalent water molecule, H_2O, can be transformed into an association of a cationic hydrogen ion, H^+, and a *hydroxide ion*, OH^-. This occurs as the hydrogen nucleus, a proton, leaves the electron pair that bonded it to the oxygen, with the oxygen keeping all of its electrons and also remaining bonded to the second hydrogen of the water molecule (Fig. 3.14).

Ionization occurs as a covalent molecule is transformed into a pair of ions.

The conversion of a covalent molecule into ions is known as **ionization.** In pure water ionization to a hydrogen cation and a hydroxide anion occurs to only a very small extent, which explains why water is such a poor conductor of electricity. At room temperature there is at any given moment only one pair of H^+ and OH^- ions for every 556,000,000 water molecules. For comparison, to produce the same ratio of Na^+ and Cl^- ions (one pair for every 5.56×10^8 water molecules) we could add 5 g of sodium chloride (one teaspoon of table salt) to 850,000 liters of water. That's about 225,000 gallons of water, enough to cover the entire playing surface of a football field to a depth of about 7.5 in.

With both the ionization and the reverse reaction—the recombination of ions into water molecules—occurring readily and rapidly throughout the liquid, there is always a dynamic *equilibrium* of the two processes that keeps the concentration of the ions constant at one pair of ions for every 5.56×10^8 water molecules. This equilibrium is symbolized chemically by two arrows.

Figure 3.14
Ionization of a water molecule.



$H_2O \rightleftarrows H^+ + OH^-$

Figure 3.15
The reversible ionization of water.

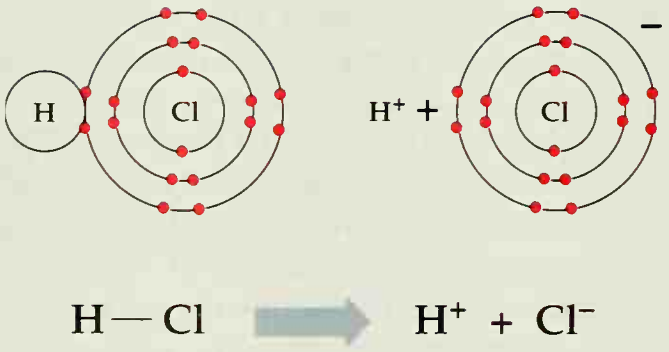


Figure 3.16
The ionization of a molecule of H-Cl to a hydrogen ion and a chloride ion.

One shows the ionization as the separation of a water molecule into a proton and a hydroxide ion. The other, reversed in direction, shows the recombination (Fig. 3.15).

While the hydrogen halides are all covalent compounds that exist as gases under ordinary conditions, all but hydrogen fluoride ionize completely when they dissolve in water. (HF ionizes only slightly in water, producing only a few H^+ and F^- ions.) Hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen iodide (HI) all ionize completely in water, each producing a hydrogen ion (H^+) and the associated halide ion (Fig. 3.16).

QUESTION

Like water, hydrogen peroxide (Fig. 3.17) also ionizes slightly to produce a hydrogen cation and an anion. What is the chemical structure of the anion resulting from the ionization of H_2O_2? Show the structure in two ways: (1) with pairs of electrons represented by pairs of dots and (2) with covalent bonds represented by dashes.

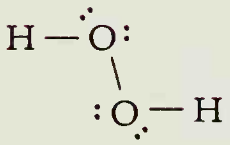


Figure 3.17
The hydrogen peroxide molecule, H_2O_2.

PERSPECTIVE: How Do We Know?

With this chapter we conclude laying the foundation for our continuing study of chemistry. It's a good point to stop, reflect for a moment, and ask, "How do we know?" How do we know that the hydrogen halides are all formed of covalent molecules, and that HCl, HBr, and HI ionize completely when they dissolve in water? How do we know that "at room temperature there is at any given moment only one pair of H^+ and OH^- ions for every 556,000,000 water molecules" (Section 3.14)? How do we know, for that matter, that atoms exist, that they have nuclei at their cores and electrons in their shells, and that there are such things as protons and neutrons? How do we know any of this?

The answer is that we ask experimental questions of nature and we interpret the answers so that they make as much sense as possible. That, in essence, sums up the scientific method we examined in Chapter 1. At its heart, *chemistry is an experimental science*. There's no way in the world to know that ordinary table salt will cause a light bulb to light up and that table sugar won't, unless someone tries it. The results of that experiment and others like it tell us all we know of table salt and everything else. There's no other way to learn about our physical universe except through the experimental questions we ask and the answers we get from them.

In the remainder of this book we're going to learn of the results of experimental questions others have asked, and of the answers they got and of the theories that these answers eventually coalesced into. Sometimes we'll follow the reasoning that leads to our current view of the world, as it exists today. Occasionally we'll examine the experimental tests themselves that lead to this view. In every case, though, what we learn comes from real tests, real experiments, real questions that people through the centuries have asked, and the hypotheses and theories that have grown from them.

In the next few chapters we'll examine more closely the chemistry of atoms, their nuclei, and the electrons surrounding the nuclei. We'll examine further the covalent bonds they form as well as many examples of the covalent molecules that are formed by these bonds. Initially, we'll examine all this with special emphasis on one of our major themes: how we obtain, store, and use chemical energy. We'll begin with the energy of the atomic nucleus and how we use it now, and how we may be able to use it even more effectively in the future to provide plentiful energy, to cure illness and save lives, and to learn more about our own past.

Then we'll move our focus outward from atomic nuclei to the electrons of their valence shells. We'll examine in detail both the fundamental chemistry and the more practical applications of the transfer of electrons from one substance to another and we'll see how this chemistry allows us to interconvert electrical energy and chemical energy, and to store electrical energy in the chemicals of batteries. Following that, we'll examine some of the covalent compounds of carbon and hydrogen that come from petroleum. We'll learn how we use them as sources of energy and what societal consequences they bring with them.

EXERCISES

FOR REVIEW

1. Complete this statement with the words and phrases that follow. Each is used once.

In its modern form the ______ is an organization of all the known elements, arranged in order of increasing ______. Elements that lie in the same ______ have similar ______, have the same number of ______, and belong to the same chemical ______. The table shows the element's chemical ______, atomic number, and ______, which is the average mass of all the ______ of the element, weighted for the ______ of each. The table is particularly useful for predicting the outcome of chemical reactions between ______ since their atoms tend to react so as to fill their ______. When atoms react by a complete ______ of electrons, the products are ______. When they react by ______ pairs of electrons, the result is a ______. While ionic compounds exist as crystals made up of extensive ______ of ions, covalent compounds are composed of discrete ______.

abundance
atomic number
atomic weight
column
covalent bond
elements
family
ions
isotopes
lattices
molecules
periodic table
properties
sharing
symbol
transfer
valence electrons
valence shells

2. Define, illustrate, or explain each of the following:

a. alkaline earth metal
b. binary compound
c. chemical family
d. chemical formula
e. covalent bond
f. halogen
g. ionization
h. molecular formula
i. molecular weight
j. molecule
k. valence electron

3. Which of the following are elements and which are compounds: (a) oxygen, (b) water, (c) chlorine, (d) sucrose, (e) hydrogen, (f) sodium chloride, (g) sulfur, (h) propane, (i) argon, (j) carbon

4. Which of the following consist principally of molecules, which principally of ions, and which principally of atoms: (a) water, (b) carbon, (c) sodium chloride, (d) propane, (e) lithium iodide, (f) sucrose, (g) potassium

5. Write chemical formulas for (a) lithium bromide, (b) calcium sulfide, (c) sodium sulfide, (d) beryllium oxide, (e) the chlorine molecule, and (f) the compound formed on reaction of silicon and hydrogen.

6. Write the chemical formulas of all the ionic compounds that could result from reaction of a mixture of lithium and potassium with a mixture of fluorine and bromine.

7. Name a commercial product that contains (a) elemental chlorine, (b) the iodide ion, (c) both the element nitrogen and the element chlorine, (d) the element fluorine, (e) the chloride ion, (f) the element sulfur, and (g) elemental iodine.

8. Where might you find (a) elemental oxygen, (b) elemental gold, (c) the element carbon, (d) sodium ions, (e) the element hydrogen, and (f) the elements carbon, hydrogen, nitrogen, and oxygen in a single compound?

9. What element has

a. an atomic weight of almost exactly 14
b. an atomic number of 16
c. one electron in its first quantum shell
d. three quantum shells, all three of which are filled with electrons
e. the electron structure 2 8 2
f. a valence shell filled with a total of two electrons
g. a total of two quantum shells, each of which is filled
h. a total of two quantum shells, with two electrons in its valence shell
i. twice as many electrons in its second shell as in its first

10. Each of the following pairs of elements reacts to form a binary compound. Which form an ionic compound and which form a covalent compound?

a. sulfur and oxygen
b. hydrogen and fluorine
c. barium and chlorine
d. sodium and bromine
e. nitrogen and oxygen
f. hydrogen and carbon
g. lithium and iodine
h. magnesium and oxygen

11. Write the chemical symbols of the following elements: (a) aluminum, (b) argon, (c) calcium, (d) carbon, (e) cesium, (f) fluorine, (g) gold, (h) hydrogen, (i) lead, (j) manganese.

12. Name the elements that the following chemical symbols represent: (a) Ag, (b) Be, (c) He, (d) I, (e) Kr, (f) Mg, (g) Na, (h) Si, (i) Zn.

13. How many electrons would an oxygen atom have to *lose* to obtain a filled valence shell? Why doesn't an oxygen atom lose these electrons, rather than acquire two, when it reacts with other elements?

14. (a) What are two properties that all elements in the same column of the periodic table as helium have in common?
(b) What are two properties that all elements in the same column of the periodic table as lithium have in common?

15. What would you expect to happen if you place a small piece of potassium metal into water?

16. What change occurs in the valence shells of elements as we move from left to right in any given row of the periodic table?

17. What change occurs in the valence shells of elements as we move down a column in the periodic table?

18. Why do elements in the same column of the periodic table show similar chemical behavior?

19. The element oxygen can exist in two molecular forms. In its most common form it exists as a diatomic molecule, O_2, but it can also exist as *ozone*, in which *three* atoms of oxygen combine to form a covalent molecule. Write the molecular formula of ozone.

20. Pure hydrogen chloride is a gas under ordinary conditions. Molecules of pure, gaseous hydrogen chloride consist of a hydrogen atom covalently bonded to a chlorine atom. When hydrogen chloride gas dissolves in water, the resulting solution easily conducts an electric current. As the hydrogen chloride molecules enter the water, what process occurs to generate an electrolyte?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

21. Give the valence of the cation in each of the following compounds: (a) SrF_2, (b) $ZnCl_2$, (c) $AlCl_3$, (d) CuO, (e) Fe_2O_3.

22. What is the total number of electrons being shared among all the covalent bonds of a molecule of *methane*, CH_4?

23. What would you write as the molecular formula for the nitrogen dioxide of Section 3.3? (*Di-* is a prefix meaning "two.") What is the valence of the nitrogen of this molecule?

24. Bromine's atomic weight is 79.9. Two isotopes make up virtually all the bromine in the universe. One, with a mass number of 79, makes up 50.69% of all the bromine atoms. What is the mass number of the other isotope?

25. The *permanganate* anion, MnO_4^-, bears a single negative charge. Knowing that oxygen fills its valence shell by acquiring two electrons, what do you calculate as the valence of the manganese atom in this ion?

26. What is the valence of neon?

THINK, SPECULATE, REFLECT, AND PONDER

27. Many compounds, such as carbon dioxide, CO_2, methane, CH_4, water, H_2O, and sucrose, $C_{12}H_{22}O_{11}$, exist as molecules. Hydrogen gas, H_2, also exists as molecules. Does this mean that the gas H_2 is a compound? Explain.

28. The covalent compound *acetylene*, the fuel of the oxyacetylene torch used by welders, has the molecular formula C_2H_2. The covalent compound *benzene*, a commercial solvent, has the molecular formula C_6H_6. Each of these compounds contains carbon and hydrogen atoms in a one-to-one ratio. Would it be correct to write the chemical formulas of each as CH? Explain your answer.

29. Elemental oxygen exists as a diatomic gas, O_2. How many electrons do the two oxygen atoms have to share between them to form this diatomic molecule? How many covalent bonds unite the two oxygen atoms of the O_2 molecule?

30. Arranging the elements in order of increasing atomic number also places the elements in order of increasing atomic weight, with a few exceptions. One of these appears in the sequence of tellurium (Te) and iodine (I). The atomic weight of tellurium (atomic number 52) is 127.6. The atomic weight of iodine (atomic number 53) is 126.9. How do you account for this?

31. Hydrogen chloride, HCl, exists as a gas composed of covalent molecules. If we dissolve this gas in water, the water conducts an electric current well. If we dissolve HCl in *benzene*, a solvent of molecular formula C_6H_6, the solution does not conduct an electric current. (Pure benzene does not conduct an electric current either.) What do you conclude from this observation?

32. The element carbon, as we will see later, forms the basis for all life as we know it. Science fiction writers sometimes speculate on the properties of different forms of life based on an element other than carbon. What element do you think they usually choose, and why? (Referring to Table 2.3 may help you answer this question.)

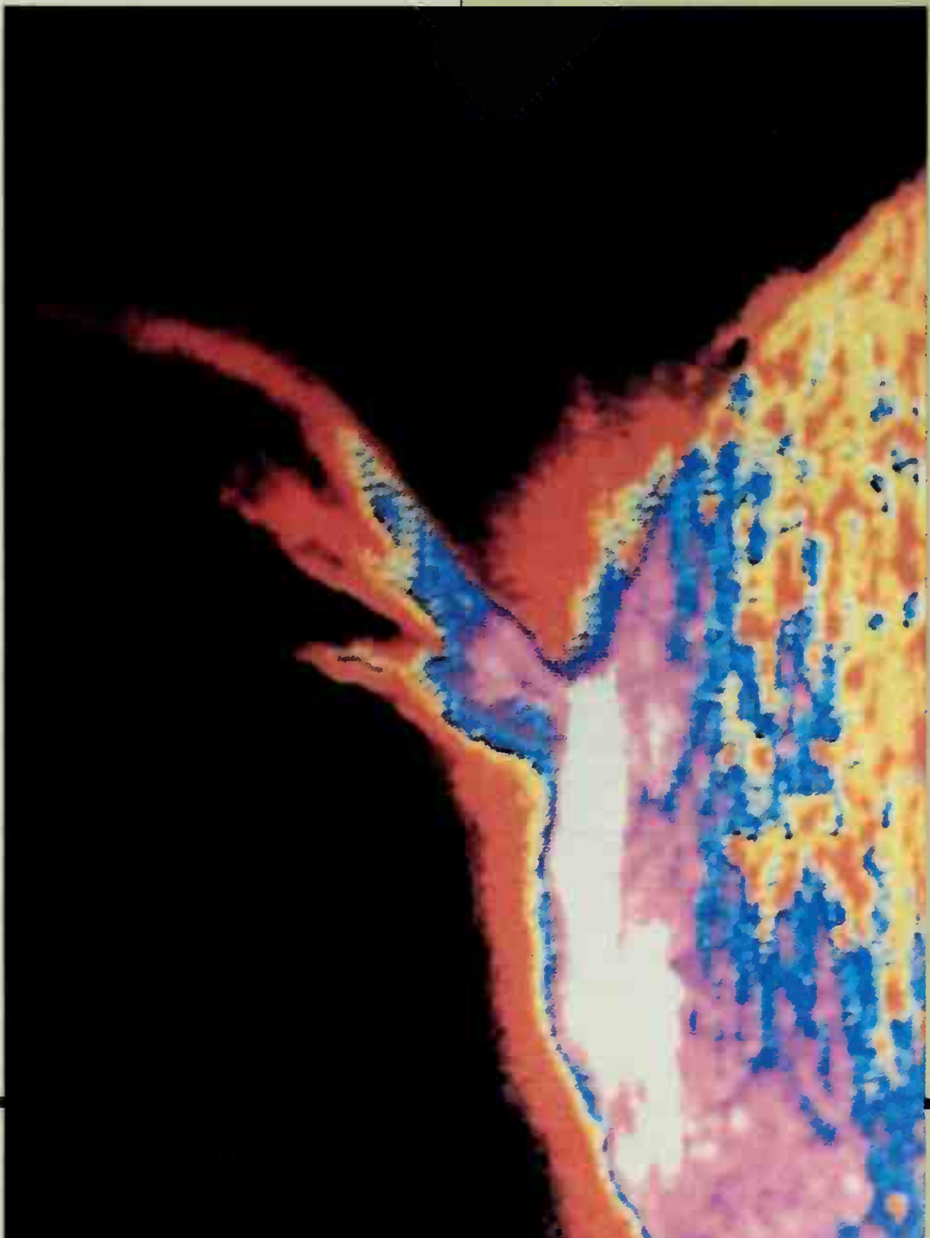
33. Some forms of the periodic table show hydrogen *twice*, once at the top of the column of the alkali metals and once again at the top of the column of the halogens. Suggest a reason for putting hydrogen into both families. (*Hint:* Consider the structure of the hydrogen atom and its similarities to the other elements of each of these families.)

34. Silver chloride, AgCl, is not soluble in water. Explain how you might be able to determine whether this is an ionic or a covalent compound. (*Hint:* Refer to Section 1.1.)

Discovering the Secrets of the Nucleus

4

FROM A PHOTOGRAPHIC MYSTERY TO THE ATOMIC BOMB



Nuclear reactions provide the sun's energy.

The world's first atomic explosion, July 16, 1945, at Alamogordo, New Mexico.

The Bomb

At 5:30 A.M., during a lull in a storm in the predawn darkness of July 16, 1945, near Alamogordo, New Mexico, the world's first atomic bomb was detonated. About 6 kg (13¼ lb) of plutonium exploded with the force of 20,000 tons of TNT. The resulting fireball, 10,000 times hotter than the sun, lit up the sky. An observer watching unprotected 20 miles away was temporarily blinded. People saw the light or felt the blast for hundreds of miles. It produced a cloud rising 8 miles, shaped like a mushroom. The hundred-foot steel tower holding the bomb vaporized and the desert sands below it melted to glass for half a mile. The power of the nucleus had been unleashed.

4.1 The Discovery of Radioactivity: How the Unexpected Exposure of a Photographic Plate Led to Two Historic Nobel Prizes

We begin our survey of energy and how we generate, store, and use it with an examination of the nucleus itself. In the chapter before you lies the story of atomic energy. It's a story that begins quietly, in a desk drawer of a laboratory in Paris in 1896, and comes to a close with the detonation of the first atomic bomb over the sands of Alamogordo in 1945 and the explosions of two more atomic bombs over the Japanese cities of Hiroshima and Nagasaki a few weeks later. As you read you'll learn some of the secrets of the nucleus, how they were discovered, and why they were first applied to a weapon of war.

In 1896 Antoine Henri Becquerel, a professor at the École Polytechnique, Paris and the son and grandson of physics professors, made an accidental discovery that led, within 50 years, to the construction and detonation of the first atomic bomb. This same discovery led still later to the use of the power of the nucleus in new, powerful methods for diagnosing and curing diseases, for establishing the age of civilizations and even of the Earth itself, and for providing energy to our homes and industries. Becquerel's discovery occurred while he was looking for a (nonexistent) connection between X rays, which had been discovered just the year before, and *phosphorescence*, a phenomenon that causes certain substances to glow visibly for a short time after they have been exposed to some forms of radiation, such as ultraviolet light.


Antoine Henri Becquerel. In 1903 he shared a Nobel Prize with Marie and Pierre Curie for the discovery of radioactivity.

Becquerel thought (incorrectly) that the generation of X rays might somehow be connected to phosphorescence, that phosphorescing substances might emit X rays as well as visible light. To learn whether they do, he conducted a series of tests based on the observation that crystals of uranium compounds phosphoresce after they have been exposed to sunlight. He placed a crystal of a uranium compound on a photographic plate well wrapped in black paper. He then placed the combination of the crystal and the wrapped plate in bright sunlight so that the ultraviolet component of the sunlight would induce phosphorescence. If the phosphorescing crystal also emitted X rays, he reasoned, these rays would penetrate the black paper and expose the photographic plate.

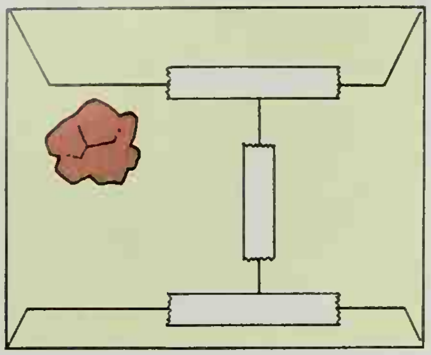

The Curie family: Marie Sklodowska, Irène, and Pierre. In 1911 Marie Curie received a second Nobel Prize for discovering the elements radium and polonium. Irène and her husband, Frédéric Joliot-Curie, shared the Prize in 1935 for producing radioactive isotopes of nickel, phosphorus, and silicon by artificial means.

Sure enough, when he developed the plate he found that it contained an exposed spot corresponding to the position of the crystal. Since Becquerel had already shown that a similarly wrapped plate placed in the bright sunlight but *without* the uranium compound on top of it would remain unexposed, he concluded (correctly) that the crystal of the uranium compound was responsible for the exposed spot and (incorrectly) that the crystal emitted X rays as it glowed with the visible light of phosphorescence.

The true source of the photographic image was revealed when a period of cloudy weather forced Becquerel to suspend his research. Without sunlight to induce the phosphorescence (and, Becquerel thought, the accompanying generation of X rays), he stored the crystal of the uranium compound in his desk drawer, near a well-wrapped, unexposed photographic plate that he also kept there. A few days later as he was developing other plates used in his work, Becquerel also developed this wrapped and presumably unexposed plate. To his amazement, it showed a distinct spot that indicated intense exposure. Something had penetrated the black paper and had caused a strong image to form on the plate even though it had never been exposed to phosphorescence or to X rays or to any other known form of radiation.

With additional experiments Becquerel soon found that this mysterious, penetrating radiation originated in the element uranium itself and had no connection whatever with ultraviolet light, X rays, or phosphorescence. Almost two years after the original discovery Marie Skłodowska Curie, a student of Becquerel's and often referred to more simply as Madame Curie, took up the study of this strange form of radiation. She gave it the name **radioactivity**, described many of its properties, showed that it was also emitted from elements other than uranium, and proposed that its origin lay in changes that occur within atoms themselves. It was this radioactivity that had penetrated through the black wrapping paper to form an image on the plate in Becquerel's

Radioactivity is the spontaneous emission of radiant energy and/or high-energy particles from the nucleus of an atom.



Placing a uranium compound on a wrapped sheet of film produces...

. . . an exposed spot on the developed negative.

desk drawer (Fig. 4.1). In continuing studies of radioactivity she and her husband Pierre, who had joined her in her work, soon discovered two additional radioactive elements, *radium* and *polonium*. Later work confirmed Marie Curie's ideas on the origin of radioactivity. Today we recognize that this form of radiation results from the spontaneous emission of radiant energy and/or high-energy particles from the nucleus itself.

In 1903 Marie Curie, a native of Poland, became the first woman to receive a Nobel Prize as she, Pierre, and Becquerel shared the award in physics for the discovery of radioactivity. In 1911 she again made history, this time by becoming the first person ever to receive the Nobel Prize a second time. This second prize was awarded in the field of chemistry for her discovery of the radioactive elements *radium* and *polonium*. Pierre, who might well have shared the honor with her, had been killed five years earlier when he was struck by a horse-drawn cart in the streets of Paris.

(In 1935 Marie and Pierre Curie's daughter, Irène Joliot-Curie, also received the Nobel Prize. For producing radioactive isotopes of nickel, phosphorus, and silicon by artificial means, Irène and her husband Frédéric Joliot shared the award in chemistry.)

QUESTION

(a) What was the function of the crystal of the uranium compound in Becquerel's investigations? (b) What was the function of the photographic plate wrapped in black paper? (c) What was the significance of the exposed spot on the wrapped photographic paper that was kept in the desk drawer, out of contact with sunlight?

4.2 Serendipity and Science

The story of the discovery of radioactivity provides a fine example of *serendipity*, which is the ability to make fortunate or happy discoveries quite unexpectedly and by accident. It was entirely by chance that the Paris weather happened to turn cloudy during Becquerel's investigations; lucky that he stored the uranium crystal and the photographic plate in the same drawer; and fortunate that he decided to develop the plate, even though he might have assumed that it had remained unexposed. And yet Becquerel had to be thoroughly prepared for the work he was doing to grasp the significance of the mysterious spot on the developed plate and to conclude that he had discovered a new form of radiation. What's more, he had to use the scientific method to confirm his discovery and to investigate its implications with additional experiments. We'll see other examples of serendipitous discoveries as we progress through our study of chemistry.

Notice that a serendipitous discovery depends on more than just luck. It requires the knowledge to recognize that something unexpected has happended and the skill to explore, explain, and extend the discovery. Louis Pasteur, the French chemist whose work led to the pasteurization of milk and other advances in the fields of chemistry and microbiology, pointed out that in making accidental discoveries of the kind we are talking about here, "chance favors only the prepared mind."

(The word *serendipity* itself was coined in 1754 by the English politician and writer Horace Walpole. It refers to the ability to make accidental discoveries similar to those of the characters of the fairy tale *The Three Princes of Serendip.*)

QUESTION

Was Columbus's discovery of the American continent an example of serendipity? If the American continent did not exist and Columbus had indeed reached the Orient by sailing westward, as he had expected, would that have been an example of serendipity? Explain your answers.

4.3 Radioactivity and Radioactive Decay

In 1899, three years after the discovery of radioactivity itself, the British physicist Ernest Rutherford showed that its rays consist of more than one form of radiation. He identified two kinds, which he differentiated by letters of the Greek alphabet: (1) the α-*rays* (*alpha rays*), easily stopped by paper, metal foil, or even a few centimeters of air (as well as by skin and lightweight clothing); and (2) the more penetrating β *rays* (*beta rays*). It takes a sheet of metal a few millimeters thick, a block of dense wood, or heavy clothing to stop β rays. A short time later a third component of the radiation was discovered, the γ *rays* (*gamma rays*). Even more deeply penetrating than either the α or β rays, γ rays pass through most substances with ease. Blocking them requires a shield made of many centimeters of lead or an even thicker wall of concrete (Fig. 4.2).

Ernest Rutherford was born in New Zealand and did much of his work with radiactivity, first at McGill University, Canada, and then in Manchester, England. His studies gave us our modern view of the atom as a chemical particle consisting of a dense, positively charged central nucleus surrounded by clouds of negatively charged electrons. In 1908 Rutherford received the Nobel Prize in chemistry for his contributions to our understanding of radioactivity.

Ernest Rutherford discovered α-rays and β-rays. He received a Nobel Prize in 1908 for his contributions to our understanding of radioactivity.

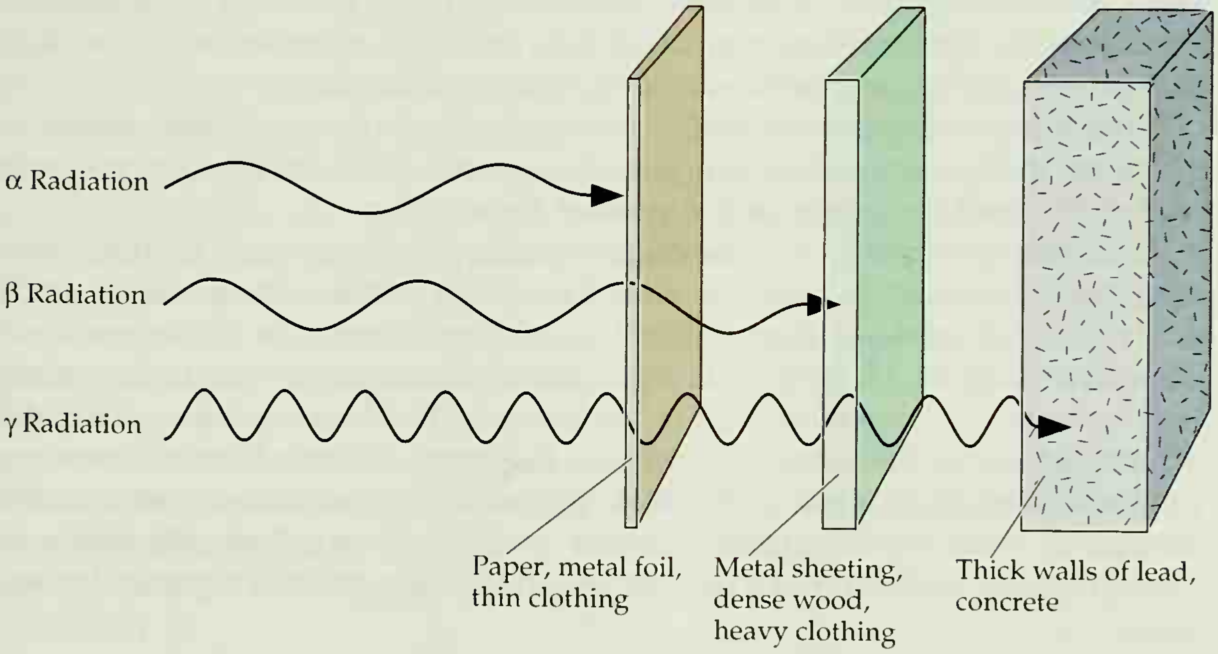


Figure 4.2

The penetrating power of radiation.

As a result of the work done by Rutherford and his students and co-workers, we now know that the radiation discovered by Becquerel comes directly from the nuclei of the atoms of radioactive isotopes. We also know that as the radioactive atoms emit these rays, their atomic numbers and mass numbers often change. (Sometimes only the atomic number changes, sometimes only the mass, sometimes both, and sometimes, but far less often, neither. We'll see an example of this last case in Chapter 5.)

Since each atomic number corresponds to a specific element (recall that the atomic number of hydrogen is 1; helium, 2; lithium, 3, etc.) radioactivity often results in the transformation of atoms of one element into atoms of (one or more) other elements.

Furthermore, if the newly formed nuclei are themselves radioactive they, too, emit radiation and are themselves transformed into still other nuclei until, eventually, the final product of a series of transformations is a *stable* or *nonradioactive* nucleus. The entire and sometimes intricate path followed in these transformations, from one radioactive atom to another and eventually to a stable atom, is called a chain or sequence of *radioactive decay*. As we've just seen, the radiation that accompanies this decay consists of α, β, and γ rays.

QUESTION

Radioactivity does considerable biological damage and can be harmful to living things. Of the three forms of radiation discussed in this section, the α, β, and γ rays, which would be the most hazardous to a person standing a few feet from a radioactive substance that emits all three of these forms of radiation? Which would be the least hazardous? ______________________________

4.4 Nuclear Notation

To follow the events of even the simplest path of radioactive decay and the changes that occur in the nucleus of an atom as a result of its radioactivity, and to understand the nature of α, β, and γ rays, we examine here a convenient form of notation that shows both the atomic number and the atomic mass of an isotope or a subatomic particle. With the particle's mass number written to the top left of its symbol, and its atomic number to the bottom left, we can see at a glance its mass and its total nuclear charge.

With subatomic particles that carry an electrical charge it's also useful to show the charge at the upper right of the symbol. Occasionally, we use only the symbol and its charge or the symbol alone.

With this system (Fig. 4.3) the common isotope of hydrogen, protium (Section 2.6), is written ${}^{1}_{1}H$, and the rarer deuterium (often written simply as D) is ${}^{2}_{1}H$. Neither of these two naturally occurring isotopes of hydrogen is radioactive. Tritium, a hydrogen isotope that is radioactive and occurs in nature only in extremely small quantities, is ${}^{3}_{1}H$. As additional examples, virtually all the helium in the universe occurs as the stable isotope ${}^{4}_{2}He$, with a mass of 4 and atomic number 2. Fluorine occurs almost exclusively as a stable isotope of mass 19 and atomic number 9, ${}^{19}_{9}F$. Somewhat simpler forms of notation, such as fluorine-19 or F-19, emphasize the mass of a particular isotope.

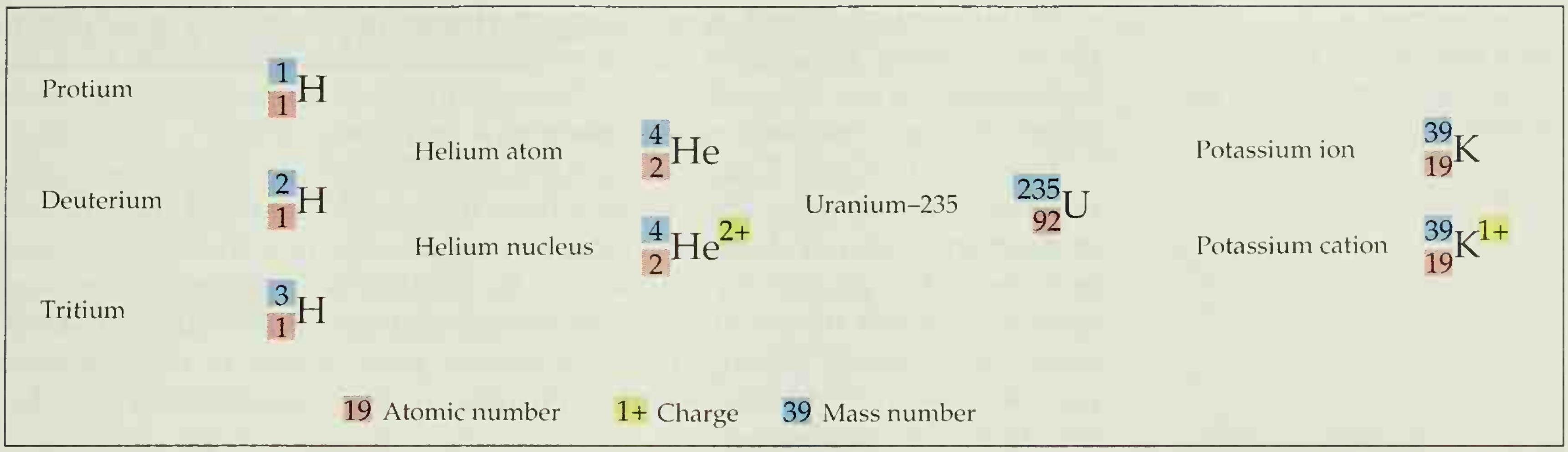


Figure 4.3
Notation showing atomic number, mass number, and charge.

Like hydrogen, many other elements can exist both in the form of stable isotopes and also as naturally occurring or manufactured radioactive isotopes, known as **radioisotopes.** About 98.9% of all carbon atoms, for example, exist as the stable isotope $^{12}_{6}C$, with another stable isotope, $^{13}_{6}C$, making up virtually all of the remainder. The existence of a trace of a naturally occurring radioisotope $^{14}_{6}C$, also known as *carbon-14, C-14,* or *radiocarbon,* allows us to date ancient objects, as we will see in Chapter 5.

A **radioisotope** is an isotope of an element that emits radioactivity.

QUESTION

How many neutrons are in the nuclei of each of the stable isotopes of carbon, $^{12}_{6}C$ and $^{13}_{6}C$, and in the radioisotope, $^{14}_{6}C$? (For help, see Section 2.5.) ____________

4.5 α Particles, β Particles, and γ Rays

This same notation helps describe α, β, and γ radiation. The α rays that Rutherford discovered are composed of streams of high-energy helium nuclei given off during radioactive decay and traveling at speeds of about 5% to 7% the speed of light. In effect, these rays consists of large numbers of fast-moving helium atoms stripped of their two surrounding electrons, or $^{4}_{2}He^{2+}$. Other ways of writing them are $^{4}_{2}\alpha$ and simply α.

α rays penetrate into and through matter only very poorly. With their two positive charges and their mass of 4 amu, the helium nuclei that make up these rays simply can't make much headway through the enormous numbers of atoms that make up any bit of matter. Frequent collisions with atoms cause the rays to be stopped easily, even by a thin sheet of paper as we saw in Section 4.4. In addition, since a nucleus that emits an **α particle** loses two protons and two neutrons, the atom losing the α particle drops by two units in atomic number and by 4 amu in mass.

Alpha particles are high-energy helium nuclei emitted by radioactive nuclei and traveling at 5% to 7% the speed of light.

β radiation consists of a stream of high-energy electrons traveling in a range of velocities, up to about 90% the speed of light. As each of the high-energy electrons that make up the β rays carries a charge of 1− and virtually no mass, the rays (and the particles that form them) are written as $_{-1}^{0}e$, $_{-1}^{0}\beta$, β^{-}, or simply β.

Beta particles are high-energy electrons emitted by radioactive nuclei and moving at up to 90% the speed of light.

With their high speed, single negative charge, and extremely small mass, the high-energy **β particles** pass through matter much more easily than do α particles and are stopped only by heavy clothing or thick walls. They have about 100 times the penetrating power of α particles.

The loss of a single β particle produces an *increase* of one unit in the atomic number of the nucleus. This follows from the requirement that the creation or destruction of net electrical charge can never occur in a chemical reaction or in any other process for that matter. No positive (or negative) charge can appear or vanish unless the opposite charge also appears or vanishes at the same time, usually through the formation of pairs of ions or of subatomic particles bearing opposite electrical charges, or their combination and destruction or neutralization.

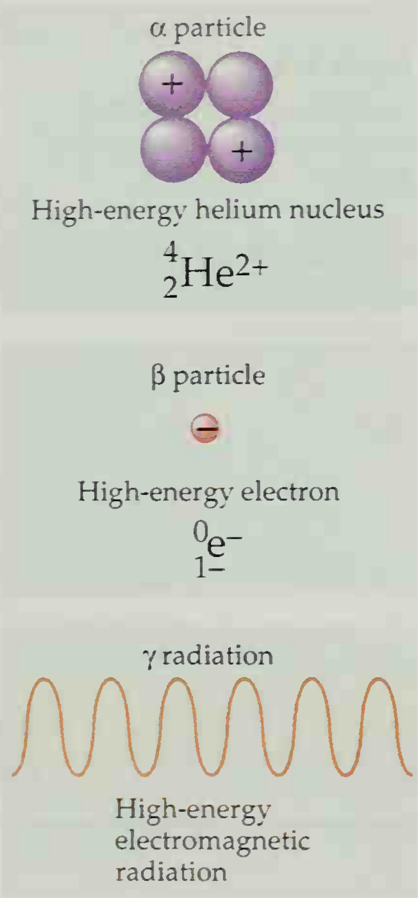


Figure 4.4

The components of α rays, β rays, and γ rays.

With this in mind we can see that if the nucleus of an atom *loses* a β particle, which carries a single unit of *negative* charge, then the nucleus must balance this loss of one unit of negative charge by simultaneously *increasing* in *positive* charge, again by one unit. For a physical picture of the ejection of a β particle from the nucleus, we can think of a neutron as a combination of a proton and an electron. Since the electron's mass is negligible compared with the mass of a proton or a neutron (Section 2.4), combining an electron with a proton (or removing an electron from a neutron) would hardly affect the mass of the particle. Moreover, as a union of one positive and one negative charge the combination would be electrically neutral, as a neutron indeed is. In effect, then, the loss of a β particle converts a neutron to a proton without substantially changing the total mass of the nucleus but nonetheless increasing in its atomic number by one unit.

Like visible light, radio and television waves, and X rays, the **γ rays** that constitute the third member of this set of radioactive emissions are a form of electromagnetic radiation. Because of their high energies (even greater than the energies carried by X rays) and their ability to penetrate deeply into matter, they can do considerable biological damage, as we'll see in Chapter 5. Without either mass or charge, γ rays are written $^{0}_{0}\gamma$ or simply γ.

The physical characteristics of these kinds of radiation help explain their very great penetrating power. Traveling with high energy at the speed of light and without either mass or charge, γ rays penetrate matter easily. Complete protection from their effects requires the use of thick lead or concrete shields. They have about 100 times the penetrating power of β rays.

In an interesting commercial application, γ rays are used to detect flaws in metal parts and structures in much the same way as X rays are used to detect and diagnose fractures in bones or cavities in teeth. A sample of the radioisotope cobalt-60, enclosed in a protective capsule, is placed in or near the metal part under examination. γ rays from the radioisotope pass through the metal and strike a sheet of photographic film on the other side. Developing the film produces an image that reveals flaws much as medical and dental X rays highlight fractures and cavities.

Gamma rays are a form of high-energy electromagnetic radiation. They have no mass and carry no electrical charge.

When high-energy α or β particles or γ rays collide with electrically neutral matter they can knock electrons away from atoms or molecules and generate pairs of ions. Along with other forms of radiation that are powerful enough to do this, including cosmic rays and X rays, these components of radioactivity are known as **ionizing radiation.** Figure 4.4 and Table 4.1 sum up their characteristics.

Ionizing radiation is any form of radiation capable of converting electrically neutral matter into ions.

TABLE 4.1 The Ionizing Radiation of Radioactivity

Radiation	Component	Symbols	Velocity	Penetrating Power
α rays	Helium nuclei	${}_{2}^{4}He^{2+}$, ${}_{2}^{4}\alpha$, α	5% to 7% of the speed of light	Low
β rays	Electrons	${}_{-1}^{0}e$, ${}_{-1}^{0}\beta$, β^-, β	Varies, up to 90% of the speed of light	Moderate
γ rays	Electromagnetic waves	${}_{0}^{0}\gamma$, γ	Speed of light	High

QUESTION

Write symbols for the α particle and the β particle showing their mass, their atomic number, and their electrical charge. ______________________

4.6 From Tritium to Helium, from Carbon to Nitrogen, from Uranium to Lead

We can now use our knowledge of nuclear radiation and its symbols to examine a few representative illustrations of naturally occurring radioactive decay. As we do, we'll use nuclear notation to write the kinds of equations that will help explain, here and in the next chapter, how the mysteries of the nucleus were explored, how the atomic bomb was built, and how we now use nuclear reactions in medicine, in commerce, and in the study of history.

Tritium, the simplest of all the radioisotopes, decays by β *emission* (the loss of a β particle) to form ${}_{2}^{3}He$, a stable isotope of helium:

$${}_{1}^{3}H \rightarrow {}_{2}^{3}He + {}_{-1}^{0}\beta$$

When the tritium nucleus loses the electron, one of the neutrons of its nucleus is transformed into a proton. Although its mass number remains unchanged at 3, the atom increases by one unit in atomic number and becomes the element helium (Fig. 4.5). Tritium itself is a key component of the hydrogen bomb. The combination of tritium with deuterium at extremely high temperatures provides the explosive force of one version of the hydrogen bomb (Section 4.15).

A container of radioactive material bearing the universal trident symbol for radioactivity.

Decay of carbon-14 also occurs with loss of a β particle. The result

$${}_{6}^{14}C \rightarrow {}_{7}^{14}N + {}_{-1}^{0}\beta$$

in this case is the transformation of a radioactive carbon atom into the most common isotope of nitrogen (Fig. 4.6). As in the case of tritium's decay, the

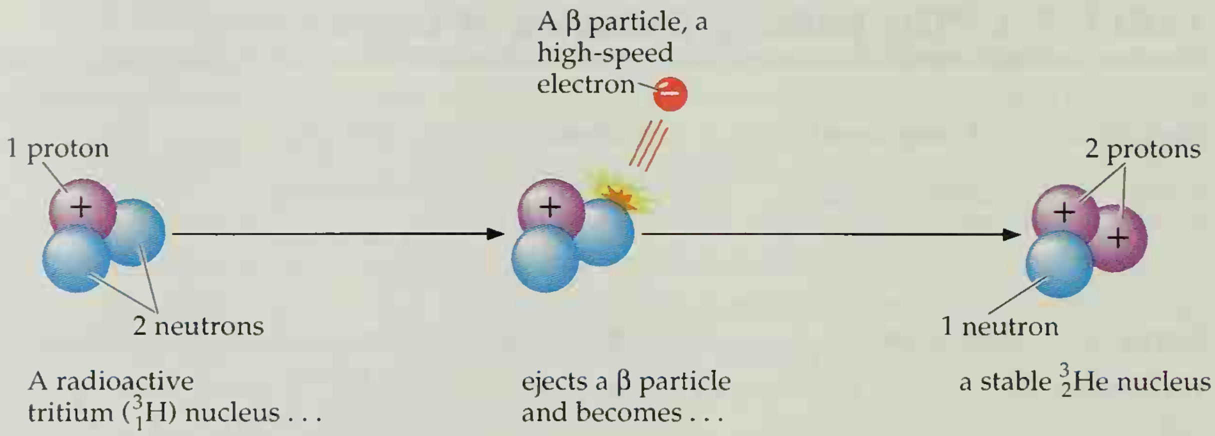


Figure 4.5
Radioactive decay of tritium.

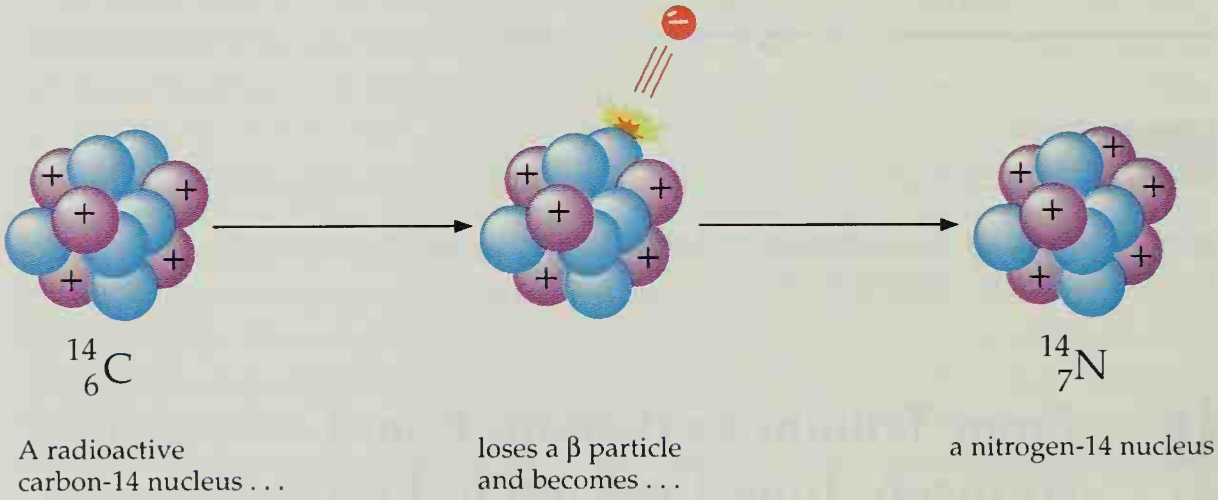


Figure 4.6
Radioactive decay of carbon-14.

mass of the nucleus remains unchanged while its atomic number increases by one unit. The radioactive decay of carbon-14 is useful for establishing the dates of ancient objects, as we'll see in detail in Section 5.14.

Uranium, which formed an image on the photographic plate in Becquerel's desk drawer and led him and the Curies to radioactivity, also provided the explosive force of one of the first atomic bombs. Its most common isotope, $^{238}_{92}U$, makes up over 99% of the uranium found in nature—mostly in *pitchblende*, an ore of the earth's crust—and represents the radioisotope of highest mass and highest atomic number of any found (in more than trace amounts) in nature. The radioactive decay of U-238 to thorium by loss of an α particle and emission of γ radiation represents the first step in one particular sequence of radioactive decay. Since the γ radiation that accompanies uranium's decay has neither mass nor charge and therefore doesn't affect the mass number or atomic number of any of the nuclei produced, it's often omitted from the equations. The equation for the decay of uranium to thorium is usually written as

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

Notice that

- The sum of the mass numbers to the left of the arrow, the 238 of the U-238, equals the sum of the mass numbers to the right of the arrow, 234 + 4.
- The sum of the atomic numbers to the left of the arrow, the 92 of the uranium, equals the sum of the atomic numbers to the right of the arrow, 90 + 2.

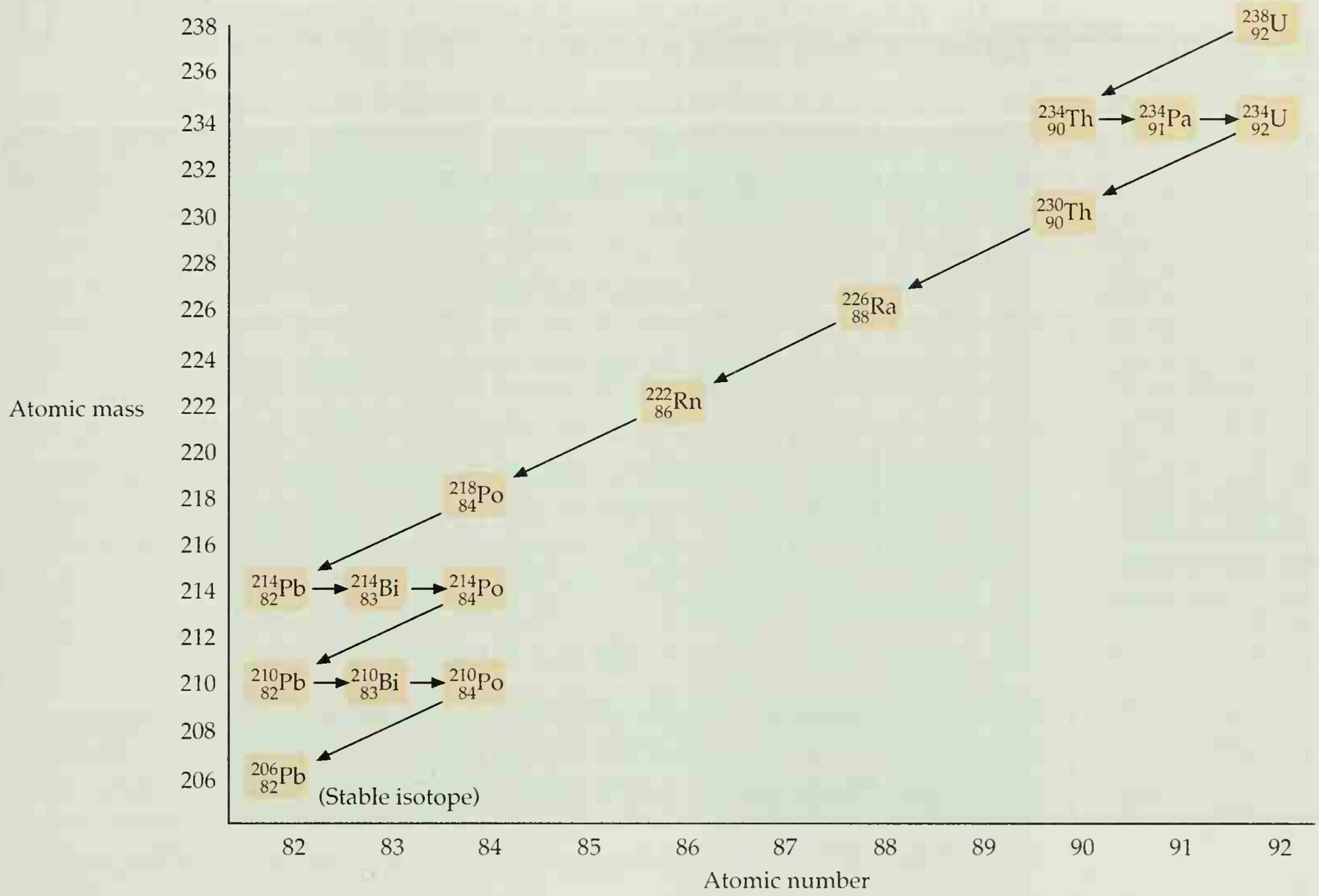


Figure 4.7
The sequence of radioactive decay from $^{238}_{92}U$ to $^{206}_{82}Pb$.

After 13 additional steps the entire chain finally comes to an end with the formation of a stable isotope of lead, $^{206}_{82}Pb$. The entire sequence appears in Figure 4.7.

Notice in Figure 4.7 that the radioactive element *radon* (Rn) is a transient part of this decay chain, forming from the radioactive decay of radium (Ra) and decaying, in turn, to polonium (Po). Radon itself is a gaseous element, a member of the inert family of elements of the periodic table.

There's concern that gaseous radon, formed by the decay of very small amounts of radioisotopes that occur naturally in some kinds of rocks and soils, may seep upward through the ground, enter homes and other buildings, and present an indoor pollution hazard. Ordinarily we might expect that any radon gas we inhale would leave our lungs with the following exhaled breath. Yet radioactive decay of radon while it's within our lungs would produce minuscule amounts of polonium and other radioisotopes that are solids rather than gases. These would not be exhaled, but would remain within our bodies, doing their biological damage through ionizing radiation (Chapter 5). There's still much dispute about whether radon actually constitutes a significant indoor hazard. Nevertheless, the simple possibility of harm from indoor radon has spurred the design and sales of various radon detectors for use in homes and other buildings.

(Other naturally occurring radioisotopes decay by paths different from the one shown in Figure 4.7. Uranium-235, for example, decays initially to thorium-231, by α emission, and then, through an additional 13 steps, to the stable lead-207. After a total of 15 steps, radioactive curium-245 ends up as a stable isotope of bismuth, Bi-209.)

The following example illustrates some of the steps in the sequence of radioactive decay shown in Figure 4.7.

EXAMPLE SUBATOMIC LOSS

What subatomic particle is lost from Ra-226 as it decays to Rn-222?

We can write the reaction that occurs here as

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + \text{subatomic particle}$$

Since the mass number drops by 4 and the atomic number drops by 2 as radium-226 is transformed into radon 222, the subatomic particle that is lost must be a combination of two protons and two neutrons. Thus, it must be a helium nucleus, which is the same in this case as saying that it is an α particle. The complete nuclear reaction is

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + \alpha$$

What subatomic particle is lost as radon-222 is converted to polonium-218?

Again, the equation

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + \text{subatomic particle}$$

shows us that a particle with an atomic number of 2 and a mass number of 4 is lost. It must once again be a helium nucleus. The complete equation is

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + \alpha$$

What subatomic particle is lost as bismuth-210 is converted to polonium-210 in the next-to-last step of the sequence shown in Figure 4.7?

Here the equation is

$$^{210}_{83}\mathrm{Bi} \rightarrow {}^{210}_{84}\mathrm{Po} + \text{subatomic particle}$$

Since there is no change in mass number and an *increase* by 1 in atomic number, an electron must have been lost from the nucleus as a β particle. The equation is therefore

$$^{210}_{83}\mathrm{Bi} \rightarrow {}^{210}_{84}\mathrm{Po} + \beta$$

QUESTION

What subatomic particle is lost by $^{210}_{84}\mathrm{Po}$ as it is converted into $^{206}_{82}\mathrm{Pb}$ in the final step of the decay sequence of U-238? Describe your reasoning. ______________________

4.7 Rutherford's Transmutation of Nitrogen

Although scientists could observe the changes that naturally occurring radioisotopes undergo, as Becquerel and the Curies had done, until 1919 no one had as yet planned and carried out an artificial nuclear transformation that would convert a *stable* isotope of one element into another element. In that year Ernest Rutherford, the British physicist who had earlier discovered the α and β rays (Section 4.3), published a report of the first artificial transformation of one element to another. By bombarding nitrogen-14, a stable (and the most common) isotope of nitrogen, with α particles emitted by radium, he transformed the nitrogen atom into an atom of oxygen. In the process, the nitrogen nucleus absorbs the two protons and two neutrons of the α particle and then loses a proton, all with a net gain of three in mass number and one in atomic number. The entire procedure results in a **transmutation** of one element into another:

Transmutation is the process of converting one element into another element.

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \rightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

As we saw for the decay of uranium-238 (Section 4.6), the sum of the mass numbers to the left of the arrow equals the sum of the mass numbers to the right, and the sum of the atomic numbers to the left equals the sum of the atomic numbers to the right. With his conversion of nitrogen into oxygen Rutherford had achieved the age-old dream of the transmutation of the elements.

One of the goals of *alchemy*, an ancient, mystical practice that preceded the science of chemistry and in many respects prepared its way, was a transmutation of one elemental substance into another. The alchemists sought especially to convert an inexpensive metal such as lead into precious gold. Through nuclear transformations much like Rutherford's the alchemical dream has by now been realized, but without creating the riches the ancients sought. Not only is expensive platinum (rather than lead) used as the starting metal, but the cost of the highly purified platinum needed for the modern transmutation is far greater than the value of the gold that's generated.

QUESTION

The conversion of platinum into gold has been achieved by bombarding platinum-198 with neutrons to produce platinum-199. This isotope, in turn, decays to gold-199 with the loss of a subatomic particle:

$$^{198}_{78}\text{Pt} + ^{1}_{0}n \rightarrow ^{199}_{78}\text{Pt}$$

$$^{199}_{78}\text{Pt} \rightarrow ^{199}_{79}\text{Au} + \text{a subatomic particle}$$

What subatomic particle is lost by the platinum as it becomes an atom of gold?

4.8 A Nuclear Wonderland

Jerome I. Friedman. In 1990 he shared a Nobel Prize with Richard E. Taylor and Henry W. Kendall for their experimental demonstration of the existence of quarks.

As this century has progressed, science has probed ever more deeply into the structure and behavior of the atom, continuously stripping away its secrets. Even today the nucleus is being revealed as a strange and complex world, seemingly no less bizarre than the one Alice found when she fell down the rabbit hole of Lewis Carroll's *Alice's Adventures in Wonderland*.

It's certainly not a world of fiction and imagination like Alice's. The nucleus is, after all, the very real chemical foundation of the real matter of our everyday world. It's a world, though, that seems to operate by a set of natural rules very much different from the sort we're accustomed to.

One of its most striking features, for example, is the ability of large numbers of protons (all positively charged) to remain closely packed in the stable clusters of the nucleus. In our more familiar world such a compact assembly of similarly charged particles would fly apart, propelled by the forces of electrical repulsion (Section 3.9). Yet most nuclei are stable; they follow laws of nature that operate most effectively in the nucleus and that we simply don't find at work in our more familiar, everyday world.

A **positron** is a subatomic particle that carries a charge of 1+ but is otherwise identical to an electron.

There are still other strange facets to the nuclear world. In addition to its relatively familiar protons, neutrons, and electrons, for example, the nucleus is also inhabited by other, more exotic species. Some, like the **positron,** appear briefly, the result of radioactive decay or high-energy collisions at the nuclear level, and then vanish in still other transformations. The positron is a positively charged particle, completely identical to an electron except for the sign of its electrical charge. We can write it as ${}_{1}{}^{0}_{+}e^{+}$ (Section 4.5). Positrons appear in some forms of radioactive decay and in several other nuclear processes. When one of them meets an electron the pair disappears in a burst of γ radiation. We'll meet the positron once again in Section 4.15.

Quarks are fundamental particles that compose larger subatomic particles such as protons and neutrons.

Another strange set of particles, the **quarks,** are among the truly fundamental particles of the universe. First proposed in 1964 to make sense of the large and growing number of subatomic particles being discovered, many of which are more fundamental even than the protons and neutrons of the nucleus, quarks remained hypothetical particles until a set of experiments begun in 1967 demonstrated their existence. For discoverying quarks, Jerome I. Friedman and Henry Kendall of the Massachusetts Institute of Technology and Richard I. Taylor of the Stanford Linear Accelerator Center shared the 1990 Nobel Prize in physics.

Gluons are subatomic particles that hold the quarks in their clusters.

Named for a word invented by the Irish writer James Joyce for his book *Finnegans Wake*, quarks are particles that combine in various ways to form still other subatomic particles, including protons and neutrons. It takes a set of three quarks, for example, to form a proton or a neutron. In the work that demonstrated the existence of quarks, Friedman, Kendall, and Taylor also found experimental evidence for still another strange particle, the **gluon,** which was proposed years earlier to account for the "glue" that holds the (then hypothetical) quarks together in their small clusters. The whimsy evident in the word *quark* and in its origin, and in *gluon*, appears repeatedly in terms used to describe quarks and their properties, classifications such as *color*, *flavor*, *charm*, and *beauty*, none of which has anything at all to do with the colors, flavors, charms, or beauties we find in our everyday world.

With one exception, the stranger particles and properties of the nucleus—its extraordinary behavior and its newly found particles with their unfamiliar colors, flavors, charms, and beauties—are beyond the scope of our examination here. That single, important exception, the one that we will examine, concerns the effect of neutrons on the stability of the nucleus. It is an effect that has led to the production of new, artificially produced radioisotopes, valuable in medical diagnosis and treatment, and it led as well to the construction of the atomic bomb.

4.9 Nuclear Fission

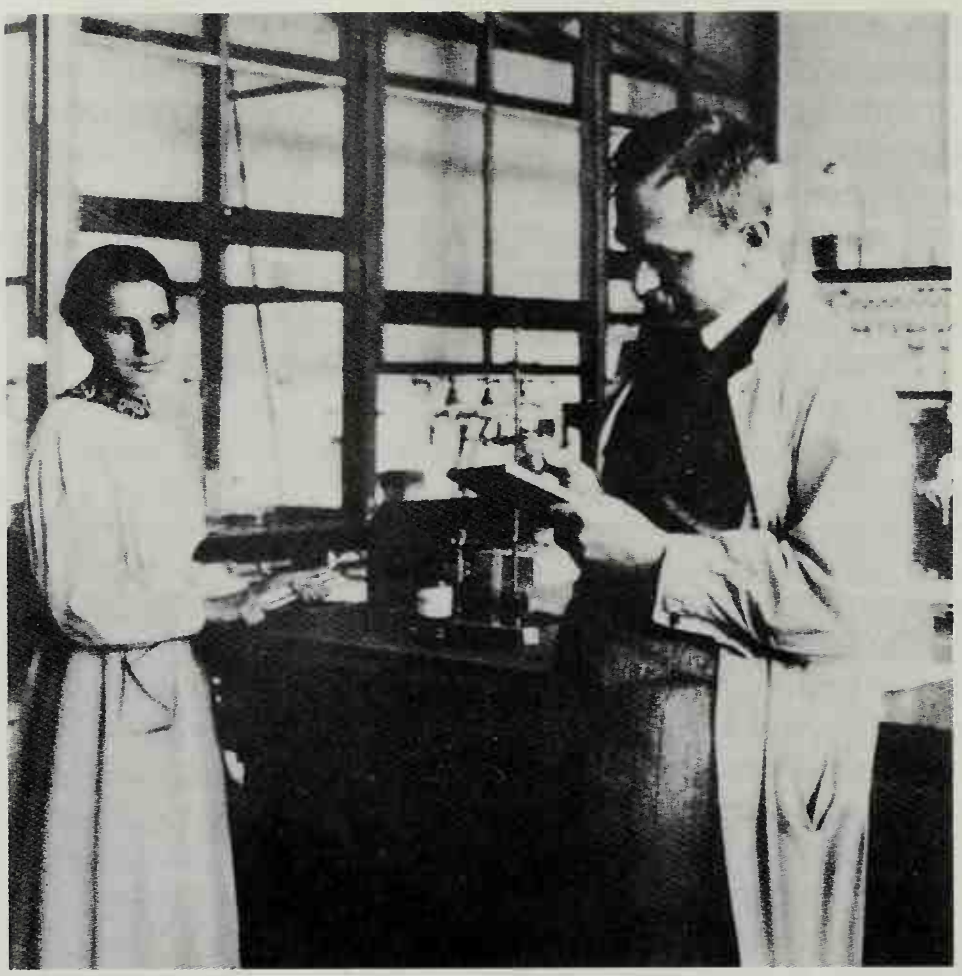
The stability of any particular nucleus depends, among other things, on the ratio of its neutrons to its protons. The ratio of greatest stability starts at about 1:1 (one neutron per proton) for elements with low atomic numbers, such as helium, and rises to about 1.5:1 for stable isotopes of mercury and lead. The most abundant (stable) isotope of lead, for example, $^{208}_{82}\text{Pb}$, contains 126 neutrons and 82 protons, which amounts to 1.54 neutrons for every proton.

With a few exceptions nuclei with ratios at or very near the ideal are stable, but those that lie beyond a narrow range are apt to decay. Thus, protium and deuterium are stable isotopes of hydrogen while tritium, with its ratio of two neutrons to one proton, is radioactive. Carbon-12 and carbon-13 are stable isotopes of carbon but carbon-14, with a higher ratio than either of the others, is radioactive. Adding a neutron to the nucleus of platinum-198 causes it to decay by β emission to gold-199 (see the question at the end of Section 4.7). One relatively simple way to destabilize a nucleus, then, is to increase its content of neutrons.

Although Rutherford had proposed the neutron as a nuclear particle as early as 1920, its existence wasn't observed experimentally until 12 years later, in 1932. (The neutron's discoverer, British physicist James Chadwick, received the Nobel Prize for physics in 1935.) In 1938, six years after the discovery of the neutron, an investigation of its effect on the nucleus of a uranium atom led to a new kind of nuclear transformation and to what would soon become an entirely new source of energy. The world was about to be changed.

The critical event occurred in 1938, almost exactly one year before the outbreak of World War II. Until then all of the changes either observed or produced artificially in atomic nuclei involved additions and losses of small particles: α particles, β particles, and protons. What's more, while some of the nuclear transformations released a bit of energy, others consumed more energy than they produced. All this changed in a laboratory in Berlin late in 1938. There Otto Hahn, a German radiochemist who would receive the 1944 Nobel Prize in chemistry for his discovery, bombarded uranium with neutrons. Among the products that he and a co-worker, Fritz Strassmann, isolated from the experiment was an isotope of barium, an atom with a little less than two-thirds the protons of a uranium atom and less than two-thirds uranium's mass number. This was an astonishing discovery, not easily explained on the basis of what was then known about the behavior of atomic nuclei.

Lise Meitner interpreted Otto Hahn's experimental observations as confirmation that he had split a uranium nucleus.



What had been dislodged from the uranium nucleus by increasing its ratio of neutrons to protons ever so slightly was not a few small, subatomic particles, not a couple of α particles or β particles or a proton or two, but fully a third of the entire nucleus. Something remarkable had happened to the nucleus. Once again, serendipity was at work.

Uncertain about how to interpret the generation of barium by the addition of neutrons to the uranium nucleus, but convinced of its significance, Hahn and Strassmann sent word of their discovery to Lise Meitner, a physicist who had worked with Hahn in earlier studies of radioactivity. Born in Austria, Meitner had fled to Denmark when the Nazis took power. Working with her nephew, Otto Frisch, she concluded that, rather than knocking some small subatomic particle out of the uranium nucleus, the neutrons had actually cleaved the nucleus of an atom of uranium into two or more large fragments, a transformation without precedent in all the previous studies of the atom. (A few weeks later Hahn and Strassmann came to the same conclusion as well.) It was Lise Meitner who coined the term **nuclear fission** for the splitting of an atomic nucleus.

Nuclear fission is the splitting of the atomic nucleus into two or more large fragments.

QUESTION

When an atom of uranium-235 is bombarded with neutrons one of the many fission reactions it can undergo produces barium and an additional element (as well as energy and additional neutrons), but no α particles or β particles. With this in mind, and with reference to the periodic table, name the additional element produced in this particular mode of fission. ______________________

4.10 A Chain Reaction, a Critical Mass

Soon it became clear that fission differs in one very important way from the other nuclear reactions known at the time. Fission releases enormous amounts of energy, far more than that released by the loss of a few small particles from a radioactive nucleus. With the remarkable discovery of nuclear fission and the recognition of the energy it might release, and with the coming of World War II, research on the atomic nucleus accelerated. If a *sustained* sequence of fission reactions could be maintained, consuming an entire package of fissionable material in an instant, the result might be explosive!

Uranium-235, a source of nuclear power.

Investigations quickly revealed that the most efficient uranium fission comes from the addition of a neutron to the isotope of mass 235, *uranium-235*, or *U-235*, rather than the more common U-238. More than 99% of all naturally occurring uranium is U-238; less than three-quarters of 1% occurs as the more fissionable U-235.

The cleavage of a U-235 nucleus can occur in many different ways and can produce any of numerous sets of products. It can, for example, produce tellurium, zirconium, and two neutrons (and energy)

$$^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{137}_{52}\text{Te} + {}^{97}_{40}\text{Zr} + 2{}^{1}_{0}n$$

or barium, krypton, and three neutrons (and, again, energy)

$$^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{140}_{56}\text{Ba} + {}^{93}_{36}\text{Kr} + 3{}^{1}_{0}n$$

or still other sets of products. Some 200 different isotopes representing 35 different elements result from the fission of U-235 atoms.

In addition to these various isotopes, the fission of U-235 also releases several neutrons as shown in the preceding equations. Any one (or more) of these could penetrate into another U-235 nucleus and continue the chain of energy-releasing fission reactions or start a new branch. Averaging over all the sets of products that result from the fission of U-235, one fission reaction produces about 2.5 neutrons. If each released neutron could cause the fission of another nucleus, every cleavage of *two* U-235 nuclei could release enough neutrons to split an additional *five*.

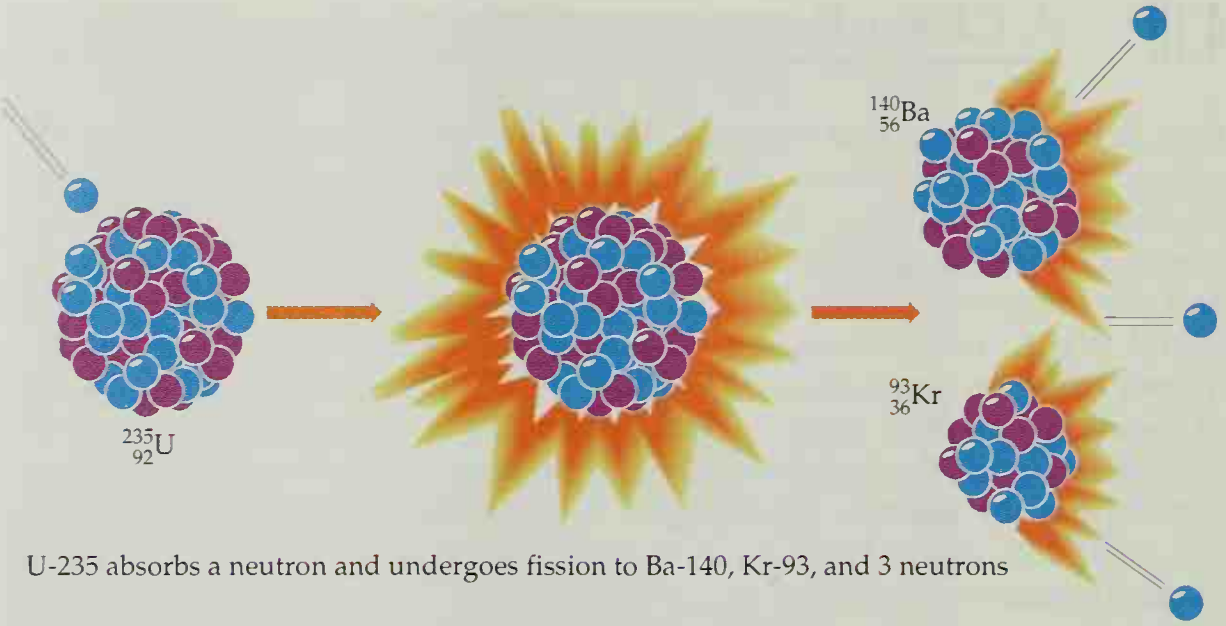
In this way the fission of a single U-235 atom could begin a cascading **chain reaction** that could consume all the U-235 present and release energy instantaneously in amounts never before achieved by humans. (The slow release of energy, even in very large amounts, can be tapped to obtain electrical, mechanical, or other kinds of power. The instantaneous release of immense amounts of energy is explosive.)

Thoughts quickly turned toward the new war and to the building of an atomic bomb that would convert the sudden release of energy from a rapid chain reaction into the immense explosive force of a devastating weapon. What was needed was a **critical mass** of U-235. This is the minimum mass of fissionable material needed to produce a self-sustaining chain reaction. It's reached when the mass of fissionable material becomes large enough to ensure that the released neutrons are, indeed, absorbed by other fissionable nuclei and that these released neutrons do produce a continuing chain of

A **chain reaction** is a continuing series of nuclear fissions that occurs when neutrons released in the fission of one atom cause the fission of additional atoms, which in turn release still more neutrons and produce still more fissions, and so on.

A **critical mass** is the minimum mass of fissionable material needed to sustain a chain reaction.

Figure 4.8
A typical fission reaction of U-235.



U-235 absorbs a neutron and undergoes fission to Ba-140, Kr-93, and 3 neutrons

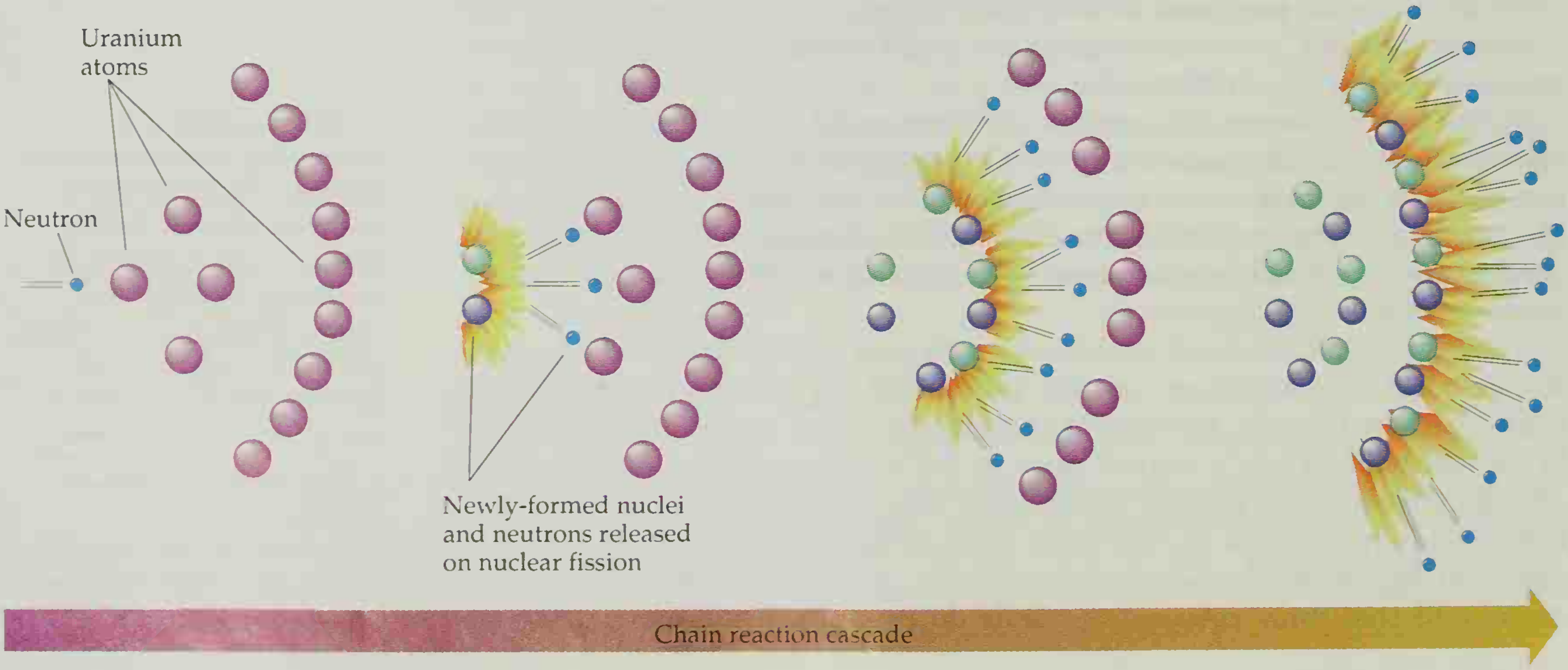
fission reactions and thereby generate and sustain an energy-releasing chain reaction. Figures 4.8 and 4.9 show a typical fission of a U-235 atom and the resulting chain reaction.

U-235 isn't alone in its ability to begin and sustain a chain reaction. Plutonium-239, a radioisotope that occurs in nature only in traces, can also generate a chain similar to that of U-235. The fission of Pu-239 is a bit more efficient and releases about 20% more energy than the fission of U-235.

QUESTION

(a) What is the advantage to using U-235 rather than U-238 as the fissionable material in building a fission bomb? (b) What is the disadvantage to using U-235 rather than U-238 as the fissionable material? ________________________________

Figure 4.9
Schematic diagram of the cascading effect of a typical chain reaction initiated by a single neutron.



4.11 The Manhattan Project

Spurred on by the recognition that a weapon as powerful as an atomic bomb could determine the outcome of the war, and with the fear that Germany might be making rapid progress toward the same goal, the United States set out to build the atomic weapon as quickly as possible. Complete control of the project and all the economic and political power to complete the work were given to the U.S. Army Corps of Engineers under the code name of the Manhattan Engineering District. The entire operation quickly became known more simply as the *Manhattan Project*. To provide the nuclear explosive several secret production facilities were constructed, the most successful of which were at Oak Ridge, Tennessee, and Hanford, Washington. The scientific center that actually designed and assembled the bomb itself was located at Los Alamos, New Mexico.

At Oak Ridge common uranium, a mixture of isotopes, was converted to its gaseous fluoride, UF_6 or *uranium hexafluoride*. The desired isotopic $^{235}_{92}\mathrm{UF}_6$ was separated from the more plentiful $^{238}_{92}\mathrm{UF}_6$ by taking advantage of subtle differences in the physical properties of the gases through a process known as *gaseous diffusion* (Fig. 4.10). The hexafluoride of the U-235 is 3 amu lighter in mass than that of the more common U-238 and its molecules move about a bit more rapidly than those containing the heavier isotope. As a result the lighter $^{235}_{92}\mathrm{UF}_6$ diffuses through extremely small openings of a porous barrier a little more quickly than the heavier $^{238}_{92}\mathrm{UF}_6$ (Fig. 4.10). Reconverting the isotopically pure $^{235}_{92}\mathrm{UF}_6$ to elemental uranium produces the pure metal.

Because of the importance of the bomb, because of the wartime urgency in its construction, and because the building of the atomic bomb was an entirely new event in human history, with little or no certain knowledge or established techniques that would ensure success, several different routes were followed simultaneously. With several paths taken at the same time, the failure of any one need not doom the project. As an alternative to U-235 as the explosive, for example, Pu-239 was manufactured at the Hanford plant. There, fissionable Pu-239 was generated by a controlled reaction that begins with the absorption of neutrons by U-238. This became the first large-scale

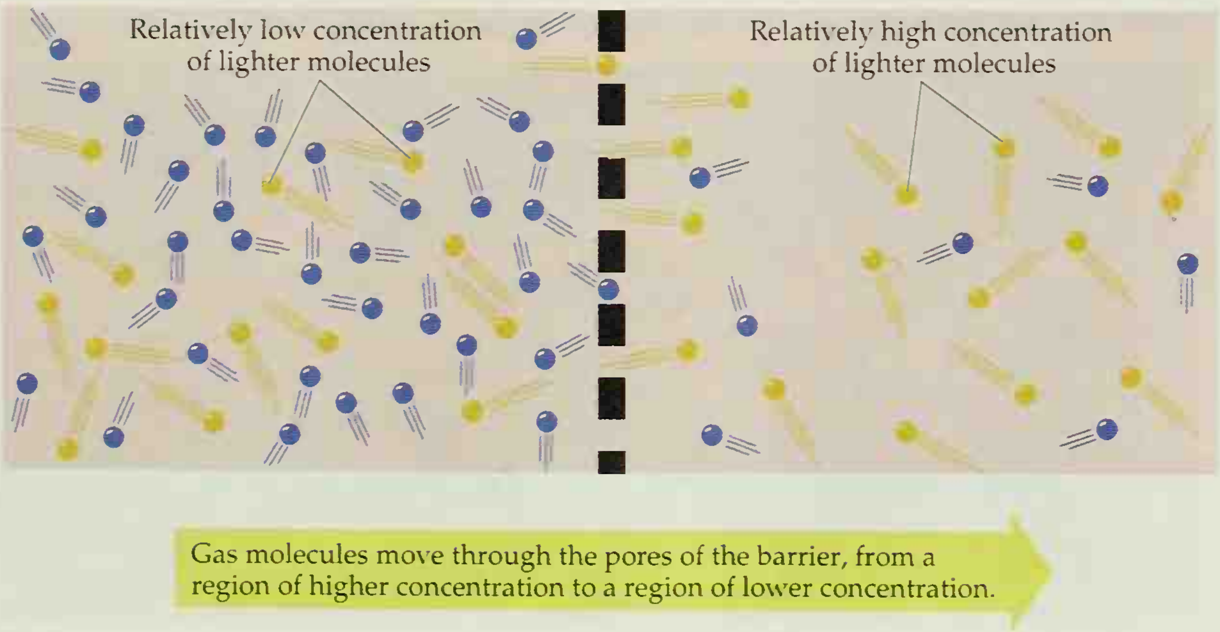


Figure 4.10
Enrichment by gaseous diffusion.

J. Robert Oppenheimer, the scientist who led the team that designed, assembled, and detonated the first atomic bomb.

The plant at Hanford, Washington, where plutonium-239 was manufactured for the atomic bomb.

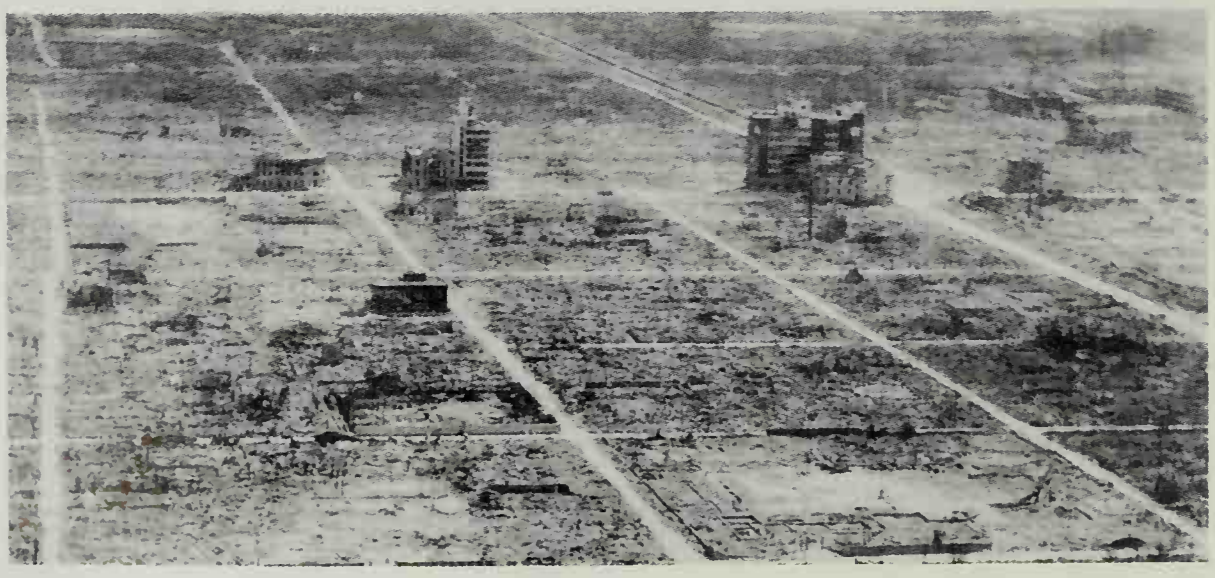
The first atomic bombs. The Plutonium bomb, which measured 3.25 meters (10.7 feet) long and 1.5 meters (5 feet) in diameter, was given the code name "Fat Man." The uranium bomb, 3 meters (10 feet) long and 0.7 meters (2.3 feet) in diameter, was called "Little Boy."

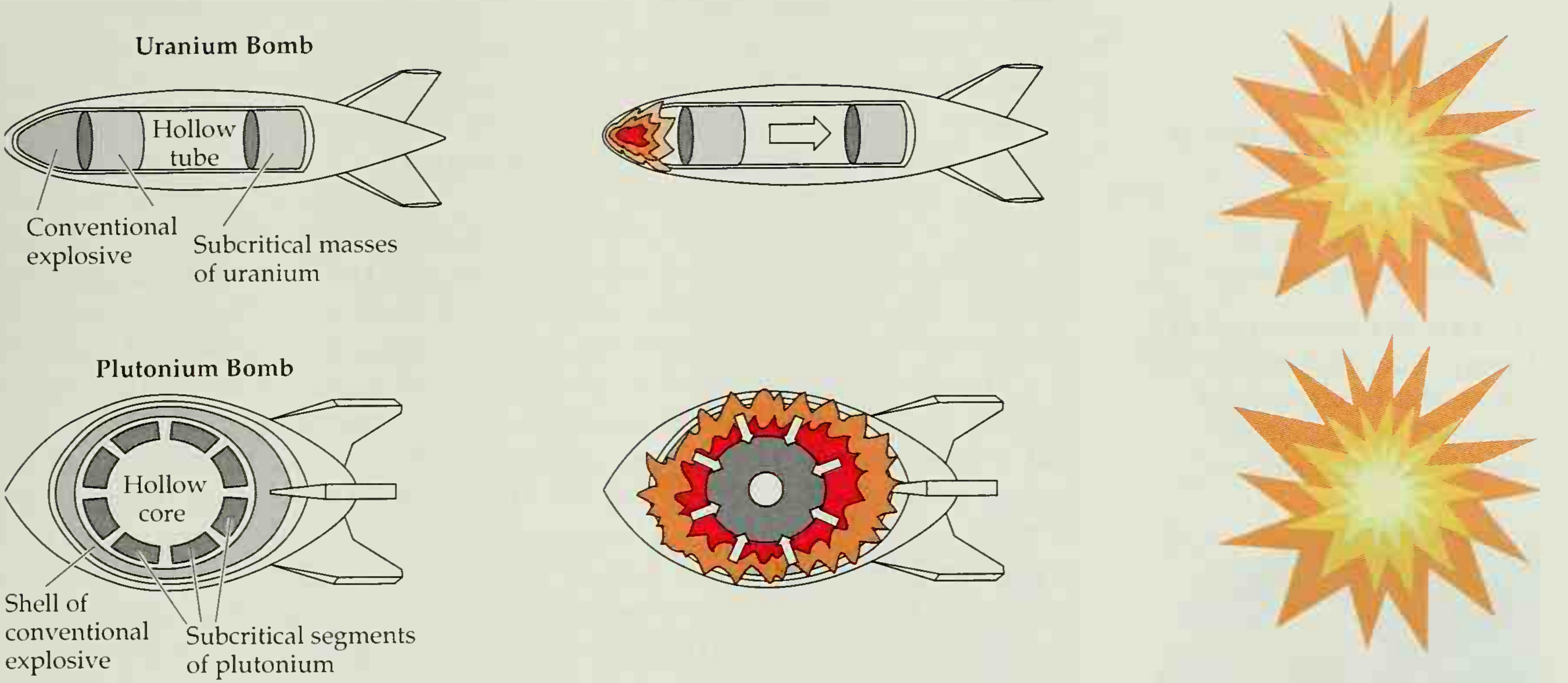
synthetic transformation of one element into another. The alchemists' dream had become reality on a massive, industrial scale.

With successful production of fissionable uranium and plutonium, the bomb itself could now be constructed. It would have to contain fissionable material in several small, subcritical portions that were well separated from each other to prevent the accidental formation of a single, explosive mass. In the absence of a critical mass no chain reaction could occur and so the bomb could not explode. The design of a bomb, then, hung on the mechanical act of bringing several small portions of uranium or plutonium together into a single, explosive mass suddenly and with enough force to keep it all together long enough to produce a critical mass and a nuclear explosion.

To detonate the fission bomb a conventional explosive charge would be used. As the subcritical fragments met under great force they would form the critical mass and produce the nuclear explosion (Fig. 4.11). Detonating the bomb would be a tricky matter, requiring the formation of a mass of fissionable material that would create an enormous explosion and yet not blow itself apart before it exhausted its nuclear energies. Finally the design seemed right, at least on paper. But whether it would all actually work was unknown. There had to be a test of a finished bomb.

Destruction caused by the uranium bomb at Hiroshima, August 6, 1945.





Conventional explosive compresses subcritical fragments into a critical mass...

... producing a nuclear explosion

Figure 4.11
The operation of fission bombs.

In the summer of 1945 a plutonium bomb was constructed at the Los Alamos laboratories and detonated in desert testing grounds just outside Alamogordo, New Mexico, as described at the beginning of this chapter. Following the successful test, a second bomb (a uranium bomb, a type never before detonated) and a third (another plutonium bomb, similar to the one used at Alamogordo) were exploded above the Japanese cities of Hiroshima and then Nagasaki on the mornings of August 6th and 9th. They destroyed the cities and killed or wounded an estimated 200,000 people. Victims who survived the initial blast and its immediate aftermath suffered for decades from delayed effects of the radiation.

The bombs were history's first atomic weapons. They produced unimaginable destruction and deaths, immediately from the blast and fireball and lingering from the lethal radiation. The uranium bomb dropped on Hiroshima exploded with a power equivalent to 13,500 lb of TNT. Destruction of the city was virtually total for a distance of over a mile from the center of the blast; temperatures of more than 3000°C incinerated buildings and people within 2 miles of the center. Seeing the blast and the mushroom cloud from the cockpit of the *Enola Gay*, the B-29 that dropped the bomb over Hiroshima, the copilot of the flight wrote in his journal, "My God, what have we done?" Within a few days Japan surrendered. World War II had ended.

We turn now to the source of this immense power and, in the next chapter, to how we have harnessed it for peace.

4.12 Energy, Mass, and Albert Einstein

The unimaginable power released by nuclear reactions, whether through the explosion of an atomic bomb in warfare or by the peaceful generation of electricity within the nuclear reactor of a power plant, comes from the conversion of mass itself directly into energy. In the chemical changes we examined in Chapter 1 and in the chemical reactions that are the subjects of the remaining chapters—reactions that involve the sharing and the transfer of valence electrons—we invariably observe the operation of two fundamental laws of chemistry. One, the **Law of Conservation of Mass,** recognizes that *mass* can neither be created nor destroyed as a result of chemical transformations. In a parallel fashion, the **Law of Conservation of Energy** holds that *energy* can neither be created nor destroyed as a result of chemical transformations. The first of these laws requires that there must be exactly as much matter (and therefore exactly as many atoms) among the combined products of a chemical reaction as in its combined reactants. Similarly, the second requires that the sum of all the energy present in the products (including any that is liberated as the reaction progresses) must equal the sum of all the energy in the reactants (including any that is added to produce the reaction). In brief, although matter can be converted from one substance (a reactant) to another (a product) it can neither be created nor destroyed; and although energy can be transferred or changed from one form to another, it can neither be created nor destroyed. These laws hold, to the limits of our ability to detect changes in mass and energy, as long as the nuclei of atoms remain intact.

The **Law of Conservation of Mass** states that mass can neither be created nor destroyed as a result of chemical transformations.

The **Law of Conservation of Energy** states that energy can neither be created nor destroyed as a result of chemical transformations.

But in reactions that take place at the subatomic level, radioactivity and nuclear fission, for example, we can observe both the formation and disappearance of matter and the formation and disappearance of energy as matter and energy are interconverted, one into the other. We can observe the conversion of matter into energy and the formation of matter from energy.

Albert Einstein. He derived the equation that relates mass and energy.

Albert Einstein, born in Germany in 1879, naturalized as an American citizen in 1940, and generally recognized as the most brilliant theoretical physicist of the 20th century, was the first to describe these interchanges in mathematical terms. He found that matter and energy are themselves equivalent and interconvertible in the mathematics of their behavior. He showed that a specific quantity of mass is equivalent to a specific quantity of energy, calculated through the equation $E = mc^2$. In Einstein's equation E represents energy, m represents mass, and c is the speed of light in a vacuum. For his work in this and other areas of physics, particularly on a phenomenon known as the photoelectric effect, Einstein received the Nobel Prize for physics in 1921.

(It was Einstein who, not quite a month before the outbreak of World War II and at the urging of fellow scientists, wrote a letter to President Roosevelt revealing to him the possibility of producing an atomic bomb. He took no part in the actual creation of the bomb.)

4.13 The Matter of the Missing Mass: Mass Defect and Binding Energy

Knowing that matter and energy are equivalent, and that a specific quantity of mass is equivalent to a specific quantity of energy, we're now in a position to find the source of the energy that binds the protons and neutrons into an atom's compact, dense nucleus and, in the next section, to examine the source of the energy released by fission.

We look at binding energy first, with illustrations drawn from atoms of He-4 and U-235.

EXAMPLE TOTAL MASS

Calculate the mass of an atom of helium-4 and an atom of uranium-235.

We start with the smaller atom, He-4. We might expect the total mass of the He-4 atom to be equal to the sum of the masses of the protons, neutrons, and electrons that compose it.

Using the values of Section 2.4, for protons, neutrons, and electrons

proton = 1.007 amu
neutron = 1.009 amu
electron = 0.0005 amu

we can calculate the mass of an atom of He-4. Knowing that the atomic number of He-4 is 2 and that its mass number is 4, we deduce that the He-4 atom has a nucleus composed of 2 protons and 2 neutrons and that there are 2 electrons in its electron shell. Thus, the subatomic particles that make up an atom of He-4 are

2 protons
2 electrons
2 neutrons

With a mass of 1.007 amu each, we expect the protons to contribute

$$2 \text{ protons} \times 1.007 \text{ amu/proton} = 2.014 \text{ amu}$$

With a mass of 0.0005 each, we expect the electrons to contribute

$$2 \text{ electrons} \times 0.0005 \text{ amu/electron} = 0.0010 \text{ amu}$$

With a mass of 1.009 each, we expect the neutrons to contribute

$$2 \text{ neutrons} \times 1.009 \text{ amu/neutron} = 2.018 \text{ amu}$$

Combining these individual contributions, we find that the calculated mass of the He-4 atom is

protons	2.014 amu
electrons	0.001 amu
neutrons	2.018 amu
	4.033 amu

The calculated mass of the He-4 atom is thus 4.033 amu. Notice that this is just a little larger than the mass number, which is simply the sum of all the protons and all the neutrons in the nucleus (Section 2.5). As we've seen, each proton and each neutron has a mass just a little larger than 1 amu.

For an atom of U-235 we might again expect the total mass to be the sum of the masses of all the subatomic particles that compose the U-235 atom. Once again using the values of Section 2.4 for protons, neutrons, and electrons we can calculate the mass of an atom of U-235. With the periodic table or a table of atomic weights and atomic numbers, we find that the atomic number of uranium is 92. Thus, there must be 92 protons in the nucleus and 92 electrons in the surrounding shells. Furthermore, since its mass number is 235, the total, combined number of protons and neutrons in the nucleus must be 235:

$$\text{protons} + \text{neutrons} = 235$$

With 92 protons in the nucleus, the number of neutrons in U-235 is

$$\text{neutrons} = 235 - 92 = 143$$

The subatomic particles that make up an atom of U-235 are thus

92 protons
92 electrons
143 neutrons

With a mass of 1.007 amu each, the protons contribute

$$92 \text{ protons} \times 1.007 \text{ amu/proton} = 92.64 \text{ amu}$$

With a mass of 0.0005 each, the electrons contribute

$$92 \text{ electrons} \times 0.0005 \text{ amu/electron} = 0.0460 \text{ amu}$$

With a mass of 1.009 each, the neutrons contribute

$$143 \text{ neutrons} \times 1.009 \text{ amu/neutron} = 144.29 \text{ amu}$$

Combining these individual contributions, we find that the calculated mass of the U-235 atom is

protons	92.64 amu
electrons	0.05 amu
neutrons	144.29 amu
	236.98 amu

We can round this off to 237.0 amu for the calculated mass of the U-235 atom.

As we've just seen, the calculated mass of the U-235 atom arrived at by adding up the masses of all the subatomic particles that compose it is 237.0 amu. Yet the actual mass of an atom of U-235, *as measured experimentally* (and

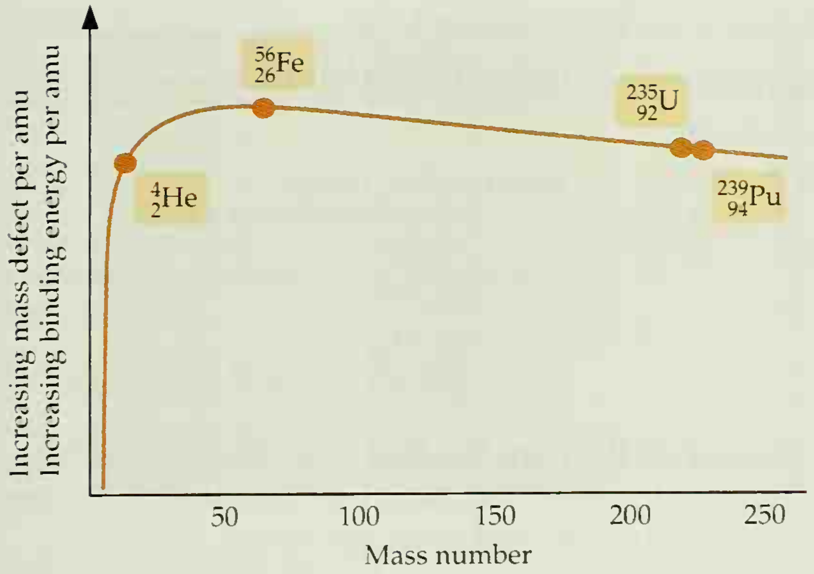


Figure 4.12

Mass defect and binding energy, per atomic mass unit.

also extremely accurately), is only 235.043924 amu, which can round off here to 235.0 amu. The difference between the calculated mass of all the protons, neutrons, and electrons present in an atom and the actual, *measured* mass is known as the atom's **mass defect.** The mass defect for the U-235 atom, then, is about 2.0 amu. For He-4, the measured mass is 4.003 amu and the mass defect is the difference between 4.033 amu (the calculated value) and 4.003 amu (the measured value), or 0.030 amu.

Where did the missing mass go? The answer is that the "missing" mass is still very much present in the atom, but it's contained in the atom *as energy*. For U-235 the energy equivalent of 2.0 amu, the difference between the sum of the masses of its individual particles and the mass of the whole atom itself, is the **binding energy** required to hold the nucleus of the U-235 atom together. This energy that holds the protons and neutrons together as the compact mass of an atomic nucleus, then, comes from the conversion into energy of a very small fraction of the masses of the subatomic particles that compose the atom. For He-4 the binding energy is the energy equivalent of 0.030 amu.

Similar calculations and measurements for atoms of other elements show that the mass defect per atomic mass unit (and therefore the binding energy per atomic mass unit as well) rises sharply as mass numbers increase, reaches its maximum at mass numbers of 50 to 60, and then drops slowly as mass numbers increase further (Fig. 4.12).

An atom's **mass defect** is the difference between the mass of the atom as a whole and the mass of all the individual protons, neutrons, and electrons that compose it.

The **binding energy** of an atom, the energy that holds the nucleus together as a coherent whole, is the energy equivalent of its mass defect.

QUESTION

Calculate the mass defect of an atom of Pu-239. The measured mass of an atom of Pu-239 is 239.05 amu. ______________________

4.14 The Energy of Uranium Fission

Now we can turn to the source of the energy released by nuclear fission, once again using the equivalence of mass and energy. We use the neutron-induced fission of U-235 to barium, krypton, and three neutrons as an illustration (Section 4.10):

$$^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{140}_{56}\text{Ba} + ^{93}_{36}\text{Kr} + 3^{1}_{0}\text{n}$$

Using accurately measured masses of the neutron and the atoms that take part in this reaction

Particle	Precise Mass (amu)
the neutron	1.009
U-235	235.044
Ba-140	139.911
Kr-93	92.931

we can calculate the total mass of all the particles that enter into this reaction (one U-235 atom and one neutron) and all the particles that result from the fission (one Ba-140 atom, one Kr-93 atom, and three neutrons).

EXAMPLE GONE FISSION

Calculate the difference in mass between the reactants and the products in the fission of U-235 just shown.

The reactants and their masses are

Particle	Mass
1 U-235 atom	235.044
1 neutron	1.009
Total	236.053 amu

The products and their masses are

Particle	Mass
1 Ba-140 atom	139.911
1 Kr-93 atom	92.931
3 neutrons	3.027
Total	235.869 amu

As a result of this particular fission reaction, there is a loss of mass equal to

total mass of reactants	236.053
− total mass of products	−235.869
mass lost	0.184 amu

This loss of 0.184 amu is the amount of mass that is converted into energy in the fission reaction of a single U-235 atom. Released instantaneously from a large mass of uranium, it's the source of the explosive power of the uranium bomb; released slowly, under the controlled conditions of a nuclear power plant, it's a source of commercial electricity.

TABLE 4.2 Energy Production in Terms of a 100-Watt Light Bulb

Energy Source	Approximate Amount of Time the Energy Would Keep a 100-Watt Light Bulb Burning
Complete conversion of 1 g of matter into energy	28,000 years
Fission of 100 g of U-235 (Section 4.12)	2300 years
Fission of 1 g of U-235	23 years
Efficient burning of 1 g of gasoline	8 minutes
Nutritional energy that 1 g of sugar (about a fifth of a teaspoon) provides to the human body	Slightly less than 3 minutes

From a different perspective, a loss of a little less than a tenth of a percent of the total mass of the reactants occurs in this particular U-235 fission.

the mass lost in the fission

↘

$$\frac{0.184\text{ amu}}{236.053\text{ amu}} \times 100 = 0.078\%,$$

the portion of the mass converted into energy

↗

the combined mass of the reactants: a U-235 nucleus and a neutron

If it were to proceed through this nuclear reaction exclusively, the fission of a kilogram of U-235, for example, would convert about 0.78 g of matter into energy. Naturally, this energy could be used to do useful work just as the energy of burning oil, gasoline, coal, or wood or of falling water is used. The energy released by nuclear reactions is no different from the energy released by any of these.

Although the conversion of about a tenth of a percent of a mass of uranium into energy might seem to be an inefficient way to produce energy, for a bomb or for a power plant, Einstein's equation shows otherwise. By use of the equation $E = mc^2$, it's possible to calculate the amount of work that can be accomplished by the energy equivalent to this lost matter. Table 4.2 presents a comparison of the lengths of time a 100-watt light bulb could be kept burning by this and other representative quantities of energy and includes a comparison with the amount of energy we get from gasoline and from the biological metabolism of ordinary table sugar. In Chapter 5 we'll examine the advantages and disadvantages of nuclear fission as a commercial source of energy.

QUESTION

Table 4.2 shows that the efficient burning of 1 g of gasoline could keep a 100-watt light bulb burning for 8 minutes. How long would the energy obtained by the complete conversion of the gram of gasoline directly into energy keep the bulb lit? ________

4.15 Another Bomb, with the Power of the Sun

Nuclear fusion is the process by which several nuclei of small mass combine to form a single nucleus of larger mass.

We've seen that in *nuclear fission* the nuclei of certain isotopes of relatively large mass split apart into smaller fragments, releasing energy in the process through the conversion of matter into energy. In **nuclear fusion,** a transformation resembling the reverse of fission, several atoms of small mass come together at extremely high temperatures, 10 million to 100 million degrees Centigrade, to form larger nuclei. As in fission, nuclear fusion also results in the conversion of matter into energy. The fusion of four hydrogen nuclei to a helium nucleus and two positrons (Section 4.8) produces the energy of the sun. As in all other reactions, this fusion reaction occurs with the preservation of electrical neutrality: the two positive charges of the ejected positrons are balanced by the two negative charges of two electrons lost from valence shells. (The four hydrogen atoms taking part in the fusion reaction contain a total of four valence electrons; the single helium atom produced has only two. Thus, two electrons are lost from valence shells as a result of the fusion.)

$$4\ {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\ {}^{0}_{1+}e^{+} + 2\ {}^{0}_{1-}e^{-}$$

Since oppositely charged positrons and electrons combine with each other, with each pair of these subatomic particles transformed into a pair of γ rays (Section 4.8),

$${}^{0}_{1+}e^{+} + {}^{0}_{1-}e^{-} \rightarrow 2\ \gamma$$

The sun's energy comes from a fusion reaction that converts hydrogen to helium.

the overall fusion reaction of the sun is

$$4\ {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 4\ \gamma$$

Gram for gram, this particular fusion of four protium atoms converts almost 10 times as much mass into energy as does fission of U-235. Clearly, a bomb powered by a fusion reaction would be far more powerful than the fission bombs dropped on Hiroshima and Nagasaki. As a practical matter, though, the fusion of four protium atoms occurs too slowly to produce an explosion. Instead, the more rapid combination of a deuterium atom with a tritium atom provides the power of one kind of *fusion bomb,* or *hydrogen bomb.* (Although fast enough to produce an explosion, this reaction isn't quite as efficient in its conversion of matter into energy as is the combination of four protium atoms. Nevertheless, the fusion of deuterium and tritium still produces more power per gram of material than does uranium or plutonium fission.)

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n$$

The detonation of a small fission bomb within the larger fusion bomb produces the temperatures of tens of millions of degrees needed for the fusion reaction to begin.

QUESTION

The fusion bomb just described uses both deuterium (${}^{2}_{1}\mathrm{H}$) and tritium (${}^{3}_{1}\mathrm{H}$) as fuel. The deuterium can be obtained by concentrating quantities of the isotope that occur naturally in the water molecules of seawater. The tritium needed for the reaction is produced by wrapping the fission detonator with a compound of ${}^{6}_{3}\mathrm{Li}$. This isotope of lithium reacts with neutrons generated by the fission explosion to produce a tritium atom and another particle:

$${}^{6}_{3}\mathrm{Li} + {}^{1}_{0}n \rightarrow {}^{3}_{1}\mathrm{H} + ?$$

What is the additional particle produced in this reaction? Use the masses and the atomic numbers of the neutron and the lithium and hydrogen isotopes given in the equation to arrive at your answer. (*Hint:* Review Section 4.6.) ____________________

PERSPECTIVE: The Uses of the Atom

In this chapter we began the story of atomic energy in 1896 with the serendipity of Antoine Henri Becquerel as he examined an unexpected image on a photographic plate. We followed its path from the discovery of radioactivity to the development of a bomb that explodes and incinerates with the power of the sun. We saw that the recognition of nuclear fission as a means for creating a bomb of unprecedented destructiveness came at the outbreak of a war that threatened the very existence of our own civilization. We saw, moreover, that we appeared to be in competition with Germany in harnessing the power of the atom to war, and that building a successful atomic bomb as quickly as possible might have meant the difference between victory and defeat.

Today many other nations have or are believed to have nuclear weapons, including the Soviet Union, Great Britain, France, and China. Because of the destructive horror of the weapons, they are now regarded as unconventional weapons of war. To prevent their spread to still other nations throughout the world, more than a dozen countries have signed a nuclear nonproliferation treaty promising not to assist nonnuclear countries in getting or building nuclear arms. Moreover, major nations of the world have agreed through treaties not to introduce nuclear weapons into outer space and not to test them in space, in the atmosphere, or under water. Today only underground nuclear testing is permitted by treaty.

The prohibition of nuclear testing above ground is particularly important since the detonation of a nuclear weapon releases radioactive debris in the form of fine particles that contaminate the atmosphere and the oceans. When formed in the atmosphere this radioactive dust disperses and settles to the earth as radioactive **fallout.** This fallout is particularly dangerous since it settles on croplands as well as other regions and can enter our own bodies as we ourselves eat the contaminated crops and the parts and products of animals that also feed on them. Widespread testing and destruction of food supplies are sometimes carried out when fallout is released through accidents at nuclear power plants. We'll examine this more closely in Chapter 5.

Fallout is fine radioactive debris that is released into the atomsphere by nuclear explosions and accidents and that settles to the earth.

In this chapter we have examined the story of nuclear energy through its first application in weapons of destruction. Although the energy released by nuclear fission was first applied to warfare, that same energy of the nucleus, like the energy of fire, electricity, falling water, high explosives, and all the other forces we can control, serves us well or badly only in the ways we choose to use it. In Chapter 5 we'll learn how we use nuclear reactions in peace to generate electrical power, to cure illness, and to advance our understanding of our own history.

EXERCISES

FOR REVIEW

1. Complete this statement with the words and terms that follow. Each is used once.

Antoine Henri Becquerel discovered the phenomenon of ______, which occurs when the nucleus of a ______ emits an ______, a ______, and/or a ______. Each of these forms of radiation can cause the ionization of matter and so each is an example of ______. When an atomic nucleus loses either an α particle, which is a high-energy ______, or a β particle, which is a high-energy ______, the nucleus undergoes a change in its atomic number and becomes transformed into a nucleus of a different element in a process known as ______. If the newly formed isotope is also radioactive, it too emits radiation and is transformed into still another element. Eventually, after a series of these transformations, a nonradioactive ______ is formed and this ______ comes to an end.

α particle
β particle
γ ray
chain of radioactive decay
electron
helium nucleus
ionizing radiation
radioactivity
radioisotope
stable isotope
transmutation

2. Complete this statement with the words and terms that follow. Each is used once.

The first atomic weapons—the bombs tested at Alamogordo, New Mexico, and those dropped on Hiroshima and Nagasaki—derived their explosive power from the conversion of ______ into ______ through the process of ______. The first atomic bomb detonated was made of ______, an artificially produced isotope that does not occur naturally (in more than trace amounts). The bomb dropped on Hiroshima contained ______, which was separated from its more common isotope, ______, by the process of ______. Each of these weapons was detonated by setting off a conventional explosion that compressed several small pieces of the metal into a ______ and set off a ______, which produced the nuclear blast. Still another kind of nuclear weapon, which harnesses the power of the sun, relies on ______ for its energy. In one form, ______ and ______ nuclei come together at very high temperatures to produce ______ and release nuclear power.

chain reaction
critical mass
deuterium
energy
gaseous diffusion
helium
matter
nuclear fission
nuclear fusion
plutonium-239
tritium
uranium-235
uranium-238

3. Each of the following scientists or groups of scientists in the left-hand column received a Nobel Prize for contributing to our understanding of the structure and properties of the atomic nucleus. Match each of these individuals or groups with one of their major accomplishments (often, but not in every case, the one for which the prize was awarded) shown in the right-hand column.

5 a. A. H. Becquerel
3 b. James Chadwick
4 c. Marie Curie
1 d. Albert Einstein
6 e. Otto Hahn
2 f. Ernest Rutherford

1. derived the equation $E = mc^2$
2. discovered α and β rays
3. discovered the neutron
4. discovered nuclear fission
5. discovered radioactivity
6. discovered radium and polonium

4. Place the following events in chronological order, with the first event leading the list:

1945 a. detonation of the first atomic bomb
1899 b. discovery of α, β, and γ rays
1932 c. discovery of the neutron
1939 d. discovery of nuclear fission
e. discovery of radioactivity 1896
1919 f. the first planned, successful transmutation of an element

5. In the process of unlocking the secrets of the nucleus and in the story of the atomic bomb, what important event or process is associated with each of the following cities?

a. Alamogordo, New Mexico
b. Berlin
c. Hanford, Washington
d. Los Alamos, New Mexico
e. Oak Ridge, Tennessee
f. Paris

6. a. What element was the first one found to be radioactive?
b. What element was the first one found to undergo nuclear fission?
c. What radioisotope was the first to be produced artificially on an industrial scale?
d. Why was the element of part (c) produced in such large quantities?
e. What element is produced on the sun through a nuclear fusion reaction?
f. What isotope forms the final, stable product of the chain of radioactive decay that starts with U-238?
g. What element forms when carbon-14 undergoes radioactive decay?
h. What element forms initially on radioactive decay of radon?
i. What element served as the starting material for the first planned, successful, transmutation of one element into another?
j. What element was produced as a result of the first planned, successful transmutation?

7. What one characteristic is common to all end products of all possible chains of radioactive decay?

8. How does the ratio of neutrons to protons in an atomic nucleus affect the stability of the nucleus?

9. A *neutron bomb* is a proposed nuclear weapon that would explode with very little force (and therefore do little physical damage to buildings and equipment) but would release immense amounts of neutrons as ionizing radiation that would disable and kill troops and civilians. Which would you expect to penetrate matter more effectively: (a) a beam of high-speed neutrons or a beam of γ radiation? (b) a beam of high-speed neutrons or a beam of α radiation? Give reasons for your choices.

10. (a) What results from the collision of an electron with a positron? (b) Explain why this is an example of the conversion of mass into energy.

11. Protons and neutrons are the particles that make up the atomic nucleus. What particles make up protons and neutrons?

12. Describe a commercial use for γ radiation that is *not* a medical application.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

13. Using the form of notation shown in Figure 4.3 and (if needed) data obtained from the periodic table or lists of atomic symbols, atomic numbers, and mass numbers, write complete symbols for (a) radon-222, (b) carbon-13, (c) the most common isotope of lithium, (d) the isotope of chlorine of mass number 37, (e) an atom containing 43 protons and 56 neutrons, (f) a helium nucleus, (g) a proton, (h) a γ ray, (i) a β particle, (j) a chloride ion, and (k) a sodium ion.

14. (a) When a radioactive nucleus ejects an α particle, both the atomic number and the mass number decrease. By what quantity does each decrease? (b) When a radioactive nucleus ejects a β particle only one of these (atomic number or mass number) changes. Which one? Does it increase or decrease? By what quantity?

15. (a) What effect does ejection of a γ ray have on atomic number? On mass number? (b) What effect does ejection of a positron have on atomic number? On mass number?

16. Tritium is a radioactive isotope of hydrogen. Explain why tritium *cannot* decay with the loss of an α particle.

17. What form of radioactivity, if any, occurs with an *increase* in the mass number of the radioactive nucleus? Explain.

18. The experimentally measured mass of an atom is always less than the mass calculated as the sum of the masses of all the protons, neutrons, and electrons that compose it. Why?

19. Per unit of atomic mass, Fe-56, the most common isotope of iron, has one of the greatest mass defects and one of the highest binding energies of all atoms.

a. Given that the experimentally measured atomic mass of this isotope of iron is 55.9349, calculate its mass defect. The atomic number of iron is 26.
b. What is the mass defect of Fe-56 per atomic mass unit?
c. What is the mass defect of U-235 per atomic mass unit? (See Section 4.13.)
d. Which has the greater binding energy per atomic mass unit, Fe-56 or U-235?

THINK, SPECULATE, REFLECT, AND PONDER

20. Describe one difference between the way the laws of the physical universe operate within the nucleus and the way they operate in our everyday world.

21. Describe Becquerel's use of the scientific method as he sought to establish a connection between phosphorescence and X rays. How did he explain the observation of an exposed spot on the photographic film that had been wrapped in black paper and kept in a drawer with the crystal of the uranium compound, out of contact with sunlight? How did this observation affect the idea that a phosphorescing substance emits X rays along with visible light? If Becquerel wished to continue his investigation of a connection between phosphorescence and X-ray emission, what test(s) might he have used next?

22. Give an example of a discovery (other than the discoveries of radioactivity, nuclear fission, and the American continent; see the question at the end of Section 4.2) made through serendipity. The example you use may come from outside the field of science.

23. Contrast and compare the use of serendipity and the use of the scientific method in making discoveries. Can the two work in common in making discoveries or must the use of one exclude the use of the other?

24. In the operation of the scientific method the questions that scientists ask of the universe (in their experiments) are almost always based on something already known of the universe. The questions are chosen carefully, so that there is a good chance that the answers (the results of the experiments) will yield interesting or important information. With this in mind, why do you think that Otto Hahn chose to bombard uranium nuclei with neutrons rather than with α or β particles?

25. It has been suggested that in areas with certain kinds of soil and underground rock and mineral deposits, it may be more hazardous to live in a house that is well sealed against drafts than in one with loose-fitting doors and windows that allow a continual flow of air into and out of the house. Suggest a reason why this may be so.

26. Explain why radioactivity is hazardous to humans.

27. The first significant application of newly discovered nuclear energy was in the construction of an atomic bomb. Suggest a reason why this was so.

28. Nuclear weapons tests in space, in the atmosphere, and in the ocean are prohibited by international treaty, but underground tests are still permitted. Why are underground tests of nuclear weapons considered to be different from the other tests?

29. Detonations of high explosives such as dynamite and TNT are used for peaceful purposes, in demolition and in construction, for example, as well as in weapons of war. Suggest and describe peaceful uses for detonations of fission or fusion nuclear explosives.

30. As we saw in Question 9, a neutron bomb produces a very small blast when it explodes, but instead releases very large numbers of neutrons. Would you classify a neutron bomb as a more humane weapon or a less humane weapon than a uranium bomb of the power that exploded over Hiroshima? Explain.

31. As we saw in Section 4.9, Otto Hahn and Fritz Strassmann carried out certain experiments on uranium late in 1938 in Berlin, and Lise Meitner identified the results of these experiments as newly discovered nuclear fission, a process that could release incredible amounts of energy. In September 1939, Germany invaded Poland and World War II began. Not quite a month before the outbreak of war, and believing that Germany was working toward the development of an atomic bomb, several scientists persuaded Albert Einstein to write a letter to President Roosevelt, as we have seen in Section 4.12, revealing the possibility that such a bomb might be built. Assume that you are a nuclear scientist living in August 1939. You are aware of the possibility of building a bomb of such devastating power, and you are also aware of the events taking place in Europe and of the implications they hold for our form of society. Would you have joined other scientists in urging Einstein to write his letter or would you have urged that he not write it? Explain your answer.

32. Assuming that the nations of the world will continue to maintain military forces and arm themselves with weapons of war, do you think that nuclear weapons ought to be an accepted part of a nation's arsenal of weapons? Do you think that all nations ought to renounce the use of nuclear weapons, destroy any and all that they now possess, and refrain from building or helping others to build more? If you think that nations ought to maintain nuclear weapons, do you think these weapons ought to be considered as conventional weapons, like bullets, shells, high-explosive bombs, and mines, or that they ought to be considered to be unconventional weapons, like nerve gas, poison gas, and the biological weapons of germ warfare? Give your reasons for answering as you do.

33. One of the motives for dropping atomic bombs on Japan at the end of World War II was to save the lives of American troops who might otherwise have had to invade the home islands of Japan. There is still dispute about whether such an invasion would have been necessary. Regardless of the likelihood that such an invasion might have been required, suppose that one would indeed have been necessary and that the lives of American troops would have been lost as a result. Suppose you had been president of the United States in 1945 and that the best military estimates were that dropping the bombs would save the lives of *1 million* U.S. troops. Knowing what you do now of the effects of the bombs that dropped on Hiroshima and Nagasaki, would you have authorized their use? Suppose that the best estimates were that Japan was lightly defended and that our troops were so well prepared and that no more than *10* U.S. lives were likely to be lost. Under those conditions, would you have authorized the use of nuclear weapons? If you would have authorized their use at the level of 1 million casualties, but not at a level of 10, can you cite a specific number of casualties that would have been a dividing line between your decision to authorize and your refusal to authorize the use of the atomic bombs? Explain why you answer as you do.

25. It has been suggested that in areas with certain kinds of soil and underground rock and mineral deposits, it may be more hazardous to live in a house that is well-sealed against drafts than in one with loose-fitting doors and windows that allow a continual flow of air into and out of the house. Suggest a reason why this may be so.

26. Explain why radioactivity is hazardous to humans.

27. The first significant application of newly discovered nuclear energy was in the construction of an atomic bomb. Suggest a reason why this was so.

28. Nuclear weapons tests in space, in the atmosphere, and in the ocean are prohibited by international treaty, but underground tests are still permitted. Why are underground tests of nuclear weapons considered to be different from the other tests?

29. Detonations of high explosives such as dynamite and TNT are used for peaceful purposes, in demolition and in construction, for example, as well as in weapons of war. Suggest and describe peaceful uses for detonations of fission or fusion nuclear explosives.

30. As we saw in Question 8, a neutron bomb produces a very small blast when it explodes but instead releases very large numbers of neutrons. Would you classify a neutron bomb as a more humane weapon or a less humane weapon than a uranium bomb of the power that exploded over Hiroshima? Explain.

31. As we saw in Section 9.4, Otto Hahn and Fritz Strassmann carried out certain experiments on uranium late in 1938 in Berlin, and Lise Meitner identified the results of these experiments as newly discovered nuclear fission, a process that could release incredible amounts of energy. In September 1939, Germany invaded Poland and World War II began. Not quite a month before the outbreak of war, and believing that Germany was working toward the development of an atomic bomb, several scientists persuaded Albert Einstein to write a letter to President Roosevelt, as we have seen in Section 9.4, revealing the possibility that such a bomb might be built. Assume that you are a member of the scientific community in 1939, you are aware of the possibility of building bombs of such devastating power, and you are also aware of the [illegible] of the implications they hold for [illegible]. Would you have joined other scientists in urging Einstein to write his letter to Roosevelt, or would you have [illegible] that he not write [illegible]?

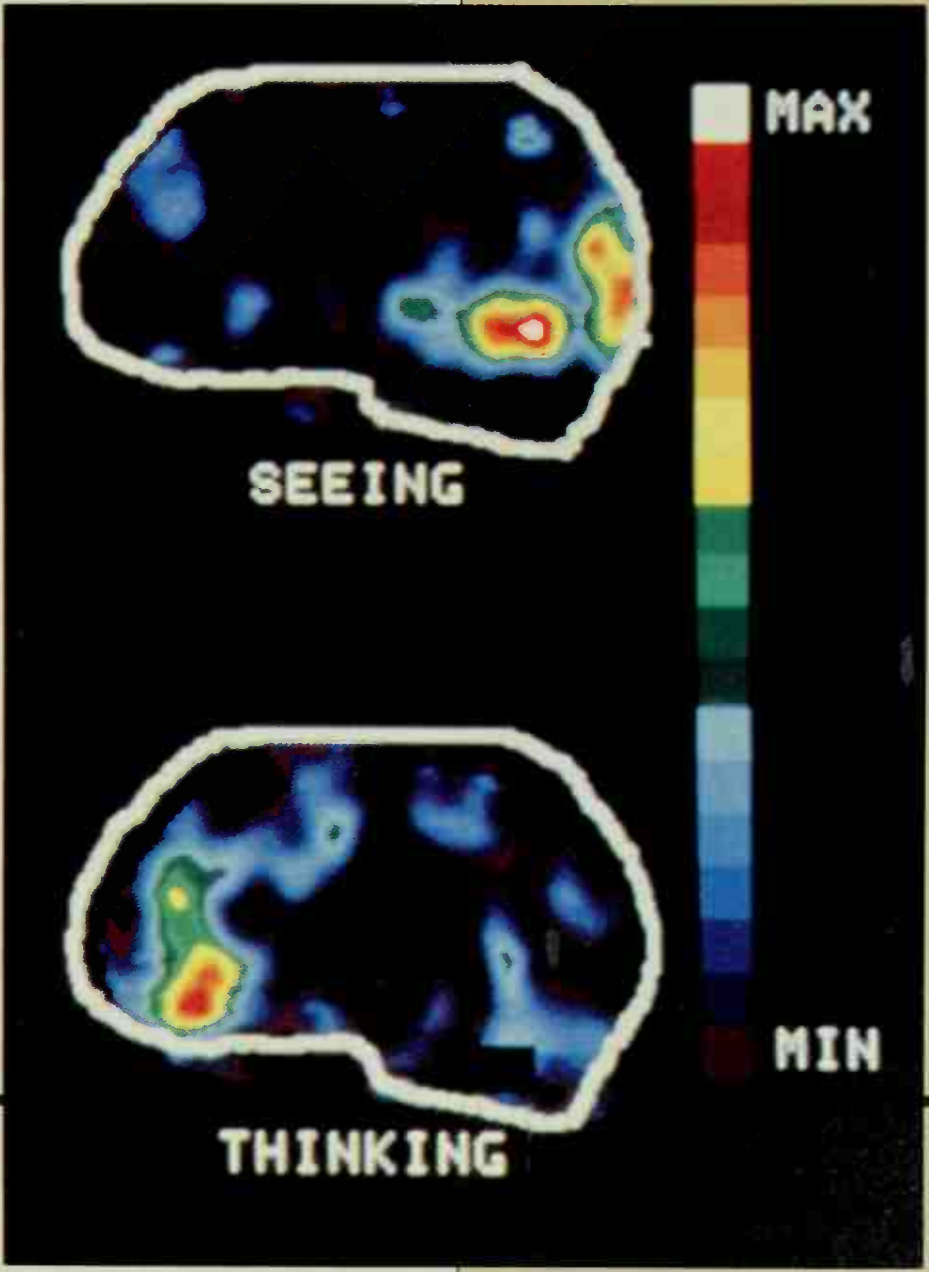
32. Assuming that the nations of the world will continue to maintain military forces and arm themselves with weapons of war, do you think that nuclear weapons ought to be an accepted part of a nation's arsenal of weapons? Do you think that all nations ought to be allowed to [illegible] one, destroy any and all [illegible] certain [illegible] or helping others to build [illegible] nuclear weapons [illegible] that [illegible] Give your reasons for answering as you do.

33. One of the motives for dropping atomic bombs on Japan at the end of World War II was to save the lives of American troops who would otherwise have had to invade the [illegible] of Japan. There is still dispute about whether such an invasion would have been necessary [illegible] that such an invasion might have been [illegible] and that the lives of [illegible] troops would have been lost as a result. Suppose you had been president of the United States in 1945 and that the military [illegible] would save the lives of [illegible] U.S. troops. Knowing what you do now of the effects of the bombs that dropped on Hiroshima and Nagasaki, would you have authorized their use? Suppose that the best estimates were that Japan was [illegible] and that our [illegible] no more than [illegible] U.S. troops [illegible]. Under these conditions, would you have authorized the use of nuclear weapons? [illegible] the [illegible] of the [illegible] of [illegible] between your decision to [illegible] to authorize the use of the atomic bombs? [illegible] why you answered as you did.

Energy, Medicine, and a Nuclear Calendar

5

USING THE SECRETS OF THE NUCLEUS



The mental processes of seeing and thinking, revealed by positron emission tomography.

Enrico Fermi built the first atomic pile and produced the first controlled chain-reaction on December 2, 1942.

Static under Stagg Field: The First Atomic Pile

If the spectacular blast that dwarfed the sun above the barren sands of New Mexico in the summer of 1945 heralded the use of nuclear power for war, then the birth of peaceful nuclear power came more quietly on a cold winter's day in 1942, with a noise no greater than loud static, in a squash court beneath a football stadium in the populous city of Chicago.

It happened like this. The people designing the bomb knew in the early days of World War II that detonation would occur only if a sustained chain reaction could be generated as the critical mass formed. It would be the chain reaction that would cause the explosive, instantaneous fission of all the nuclei. But in 1942 no one had ever seen or produced a sustained chain reaction. No one was quite certain that it would even occur when the critical mass formed. To produce a *controlled* chain reaction, to demonstrate that such a chain reaction could be made to occur without restraint within the bomb itself, the physicist Enrico Fermi designed and built the first *atomic pile* (also known as a *nuclear pile*) beneath Stagg Field, the University of Chicago's unused football stadium. Born in Italy, Fermi won the Nobel Prize in physics in 1938 for his work with radioactivity and for finding a way to slow the speed of neutrons emitted in nuclear reactions, an achievement critical to harnessing nuclear power. With the rise of fascism in Italy, Fermi came to the United States, became a citizen, and continued his work.

The pile that Fermi built in the squash courts below Stagg Field consisted of a cubical lattice of uranium cores and bricks of highly purified graphite, a form of carbon. Rapidly moving neutrons slow down considerably as they pass through graphite and certain other materials, thereby increasing the chance that some of them will be absorbed into a uranium-235 nucleus and produce fission. (Slower-moving neutrons are more often absorbed by these nuclei than are faster ones, which tend to bounce off the nucleus in a process called *neutron scattering*.)

The lattice of uranium and graphite grew upward from an 8-foot-square base until, on December 2, 1942, Fermi decided it was ready for a trial. Located within the lattice was a rod of cadmium, an element that absorbs large quantities of neutrons. The cadmium rod, which prevented any chain reaction

A depiction of the dawn of nuclear power as the first chain-reaction begins beneath Stagg Field, Chicago.

from starting, would be pulled out slowly, a foot at a time, to get the neutrons flowing and the pile running.

Would the test fizzle? Would it all blow up, squash court, stadium, and all, right there in Chicago? No one could be entirely certain. Several other cadmium rods, in addition to the one buried in the pile, were stationed around it, set to be thrust in if needed. One attendant held an axe to a rope suspending one of the rods above the pile, ready to drop it in an emergency. Three others stood above the pile with buckets of a cadmium solution. If all else failed they would douse the pile with cadmium, smothering any runaway reaction.

Just past 10:30 on the morning of December 2, the test began. As the cadmium rod that had been placed within the lattice was withdrawn slowly, radiation detectors around the pile, one of them emitting audible clicks, began responding. With each stage of removal the clicks grew more frequent. As the rod was removed, the level of response rose, in step with the rod. The clicking soon became a continuous static. Finally, at a point predicted by Fermi, the meters began responding out of proportion to the withdrawal of the rod. The neutrons were cascading freely and a controlled chain reaction had begun. After it had proceeded successfully for half an hour the cadmium rod was driven back in and the pile was shut down.

It had worked. A chain reaction had been started, had been allowed to continue for a period, and had been ended. The bomb could be built. What's more, the chain reaction had been controlled. Because the power of the nucleus could be released slowly, moderately, under controlled conditions, it could be used as a source of energy for peace as well as war.

In this chapter we'll see how the slow release of nuclear energy from atomic piles, similar to the one Fermi used, is used for the production of electricity on a commercial scale. Then we'll examine some of the applications of radioactivity in medicine and, still later, we'll see how an unusual property of naturally occurring radioisotopes allows us to determine the age of ancient objects.

5.1 Electricity from Steam, Steam from Heat, Heat from the Nucleus

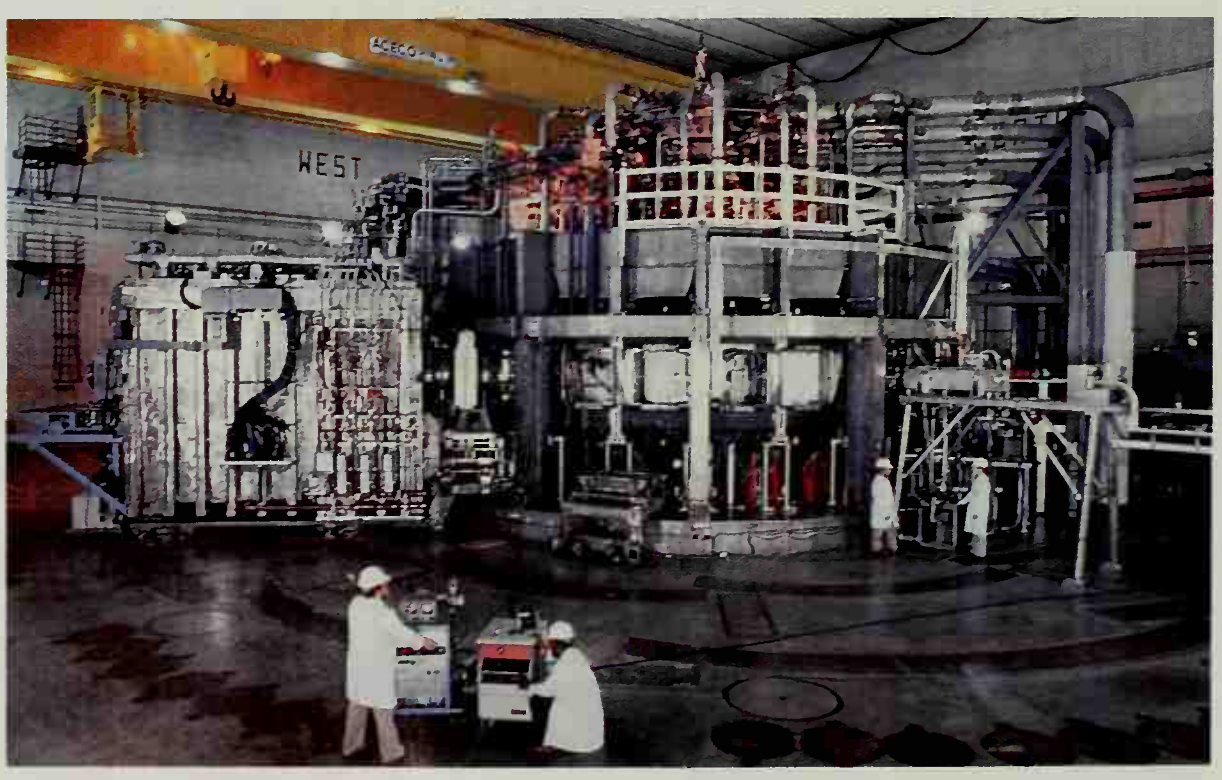
Released more slowly than in the explosions of bombs, the energy of nuclear fission can provide electricity in much the same way as the energy of burning oil, gas, or coal provides it: by furnishing the power that turns the shaft of an electric generator. Any force that can turn a generator's shaft can produce electric power. The action of a human arm can do it; the force of falling water on a water wheel or the force of the wind on a windmill can do it; the power of steam striking the blades of a turbine can do it (Fig. 5.1).

Thus, any fuel that can heat water to boiling and convert it to steam can be used to generate electric power. To the list of more conventional fuels, including oil, coal, and gas, we can now add nuclear fuel, especially as it generates heat in an atomic pile. Ideally, as we saw in Section 4.15, a fusion reaction would be far more efficient at power production than a fission reaction. Moreover, as we'll see later in this chapter, fusion is cleaner than fission. It doesn't produce the large amounts of hazardous, radioactive wastes that fission produces, wastes that can contaminate the immediate environment for tens of thousands of years. In practice, though, there's no known material that can withstand the high temperatures needed to maintain a fusion reaction, so there's no way at present to construct an enclosure for this kind of nuclear furnace. The best hope lies in holding the fusing nuclei within a magnetic field rather than material walls. Nevertheless, a realistic, commercially practical *fusion reactor* lies far in the future.

QUESTION

(a) Name three fuels (other than nuclear fuels) that can be used to generate electricity through the action of steam. (b) Describe a way to generate electric power commercially without the use of steam. ____________________

Test of an experimental nuclear reactor that generates power from nuclear fusion.



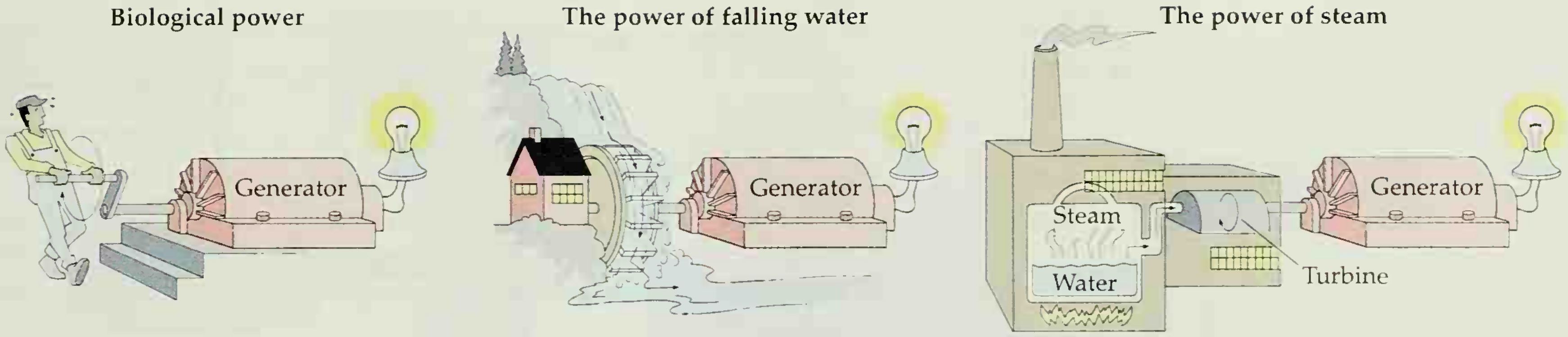


Figure 5.1
Power in the generation of electricity.

5.2 Nuclear Power: The Promise

Much more practical as a source of energy, today at least, are *fission reactors* constructed around atomic piles similar to the one Enrico Fermi built. His pile was designed for research rather than the production of power. The practical, large-scale generation of electricity by nuclear fission dates to December 1951, when the National Reactor Testing Station in Idaho began supplying power to about 50 nearby homes.

In a contemporary nuclear power plant a variation of Fermi's pile serves as the *core* of the reactor. Movable *control rods*, often made of boron or cadmium, slide up and down among the uranium rods to control the rate of heating and energy production. They maintain the neutron flow through the fissionable material at a level high enough to maintain useful energy production, but low enough to prevent overheating. Meanwhile a heat-transfer fluid, often water at very high pressures, circulates through the core to cool it and to carry the generated heat to the steam turbine. Figure 5.2 sums up the operation of a typical nuclear power plant in simplified detail.

Currently, just over a hundred commercial nuclear power plants supply energy at various locations in the United States. About half this number are

A commercial nuclear power plant.

The core of a nuclear reactor.

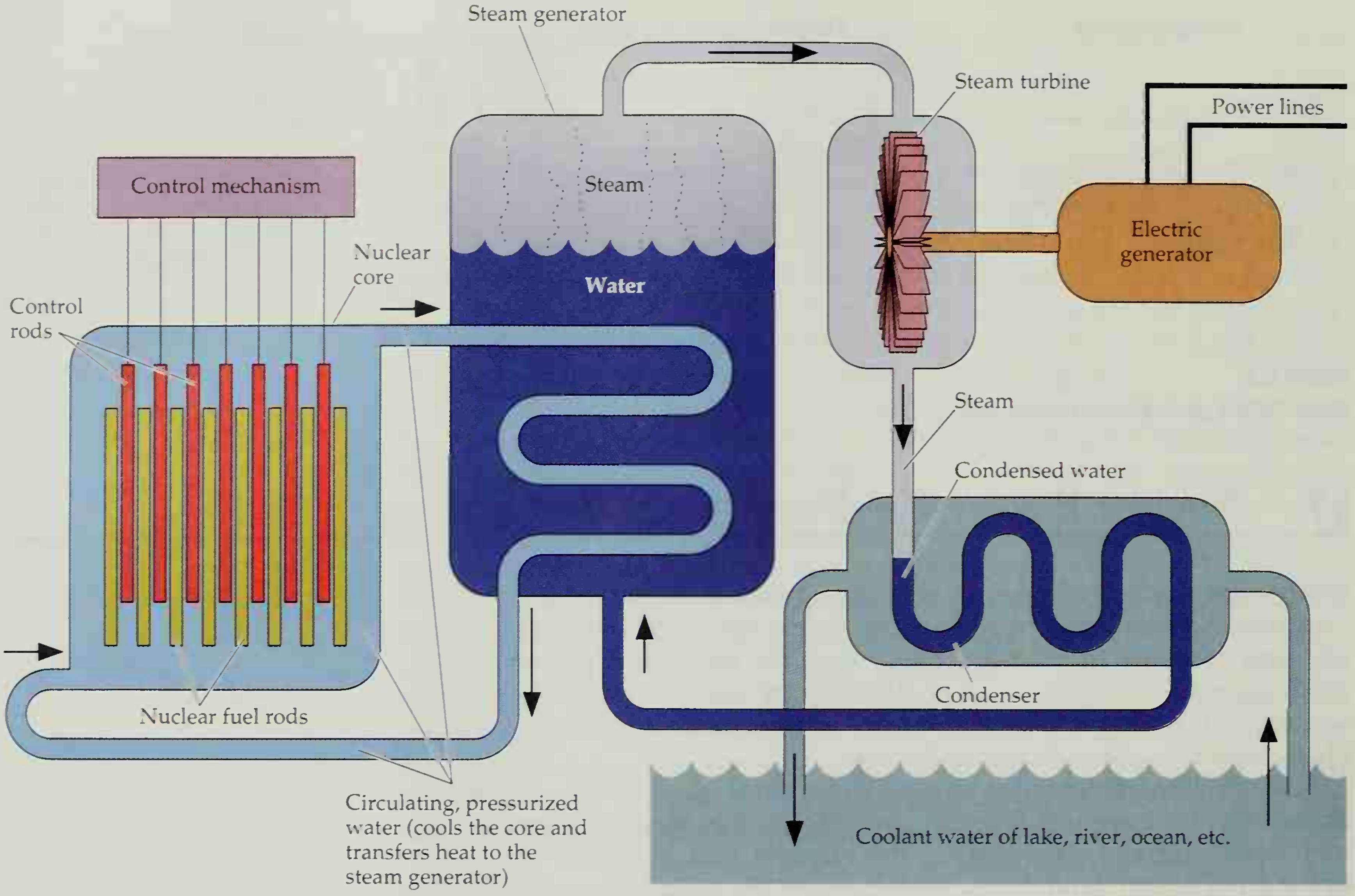


Figure 5.2
Schematic diagram of a nuclear power plant.

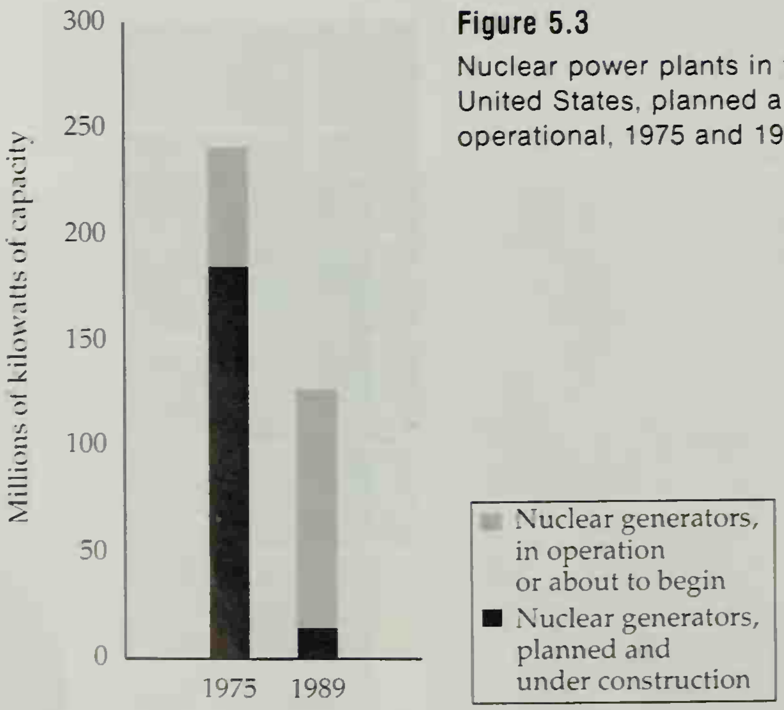


Figure 5.3
Nuclear power plants in the United States, planned and operational, 1975 and 1989.

operating in the Soviet Union and even fewer in France, Great Britain, and Japan. In 1989 nuclear power generated nearly a fifth of all electricity produced commercially in the United States. Only coal, which furnished about 56% of all commercial electricity, surpassed nuclear power.

The initial promise was cheap, plentiful electricity produced by a fuel that would free us from the smoke, smog, and other pollutants of coal, oil, and similar fuels. With the application of a bit of scientific ingenuity, it was thought, our supply of nuclear fuel could last thousands of years.

QUESTION

What approximate percentage or fraction of all commercial electric power was produced in the United States in 1989 by all sources of energy *other than* coal and nuclear energy? ____________________________

5.3 Nuclear Power: The Problems

The initial promise soon gave way to problems and fears that have stunted the growth of commercial nuclear power, as we can see in the following data (Fig. 5.3). In 1975 there were 56 nuclear plants either operating or about to begin, with an additional 180 in various stages of planning or construction (for a grand total of 236 either planned or in existence). By 1989 the number in operation or about to begin had risen to 111 but those on the drawing board dropped to 16 (for a grand total of 127). The total expected capacity of all nuclear plants, either operating or planned, dropped from 236 million kilowatts in 1975 (the same as the number of plants) to 116 in 1989, a decrease of more than 50%. Although the percentage of U.S. electric power actually produced by nuclear plants has risen from about 10% in the mid-1970s to about 20% today, the dream, though far from dead, has grown dim.

Several factors have contributed to the fading of the dream. Among those we consider here are (1) the real and imagined dangers of nuclear power plants themselves, (2) limitations in the available supply of fissionable fuels, (3) hazards involved in the disposal of nuclear waste, and (4) the financial costs of nuclear power.

5.4 Problem 1. Nuclear Power Plants: Real Dangers and Imagined Dangers

Perhaps the most obvious and yet least realistic of all the fears is that a nuclear power plant might blow up in a nuclear fireball. This concern is completely groundless. A nuclear explosion requires the almost instantaneous release of nuclear energy as the fissionable material is compacted into an explosive critical mass. A fission pile, on the other hand, is designed to produce a slow and continual release of energy. Because of the low concentration of U-235 in the nuclear fuel, there just isn't enough U-235 present to form an explosive


Three Mile Island, after the accident of March 28, 1979.


The nuclear power plant at Chernobyl, after the accident of April 16, 1986.

mass of fissionable material. In the absence of such a mass neither a bomb nor a fission pile can produce a nuclear explosion.

Concerns about other kinds of accidents are more realistic. These include, among others, the accidental overheating of the core and the occurrence of nonnuclear fires or explosions that might release radioactive material. In December 1952, almost exactly one year after the first distribution of nuclear-generated electricity to consumers by the Idaho plant (Section 5.2), the first major accident occurred at a nuclear generator. Four control rods were accidentally removed from the core of a pile near Ottawa, Canada. The result was a partial *meltdown*, a situation in which uncontrolled heating leads to the literal melting of the reactor and the destruction of the building that contains it. Although millions of gallons of water within the reactor became contaminated with radioactive material, there were no reported injuries. Five years later a fire in a reactor at Windscale, on the Irish Sea in northwestern England, led to the release of radioactive material into the countryside with the eventual radiation-related deaths of an estimated 39 people.

The most serious accident in the United States occurred on March 28, 1979, in a plant at Three Mile Island, near Harrisburg, Pennsylvania. A combination of equipment failures and human errors led to a loss of coolant. The core overheated to perhaps 2000°C and came very close to a meltdown. The accident resulted in the flooding of the building surrounding the reactor, the *containment building*, with large quantities of radioactive water and the release of a small amount of radioactive gas into the atmosphere.

Worldwide, by far the most spectacular and potentially most damaging accident produced explosions and a fire in the graphite core of a reactor at Chernobyl, in the Soviet Union, on April 16, 1986. Although the exact cause may never be known, mechanical and human errors were probably at fault. The pile may have overheated and burst as the result of a loss of coolant. Large quantities of water were apparently used to quench the reactor, but the reactor itself was probably hot enough to cause the decomposition of the coolant water into a mixture of hydrogen and oxygen. The gaseous mixture presumably exploded, tearing open the roof of the containment building. What is known with certainty is that the accident released considerable radioactive smoke and debris from the reactor. Radioactive particles traveled high into the atmosphere and spread over parts of western Europe and England.

The accident caused two deaths immediately at the plant and an estimated 29 additional fatalities that were attributed directly to the explosion. The danger posed by the radioactive fallout (Chapter 4, Perspective) resulted in the evacuation of more than 135,000 people from the region. Nearby fields of crops had to be destroyed, and even the bark of trees growing as far as 40 miles away had to be scraped free of radioactivity.

Even now, an area of about 1000 square miles around the remains of the plant is still considered too radioactive for the return of permanent communities. Lingering effects of radioactive fallout have produced abnormalities in the thyroid, a gland in the neck that regulates growth and metabolism (Section 5.9), in an estimated 150,000 people, of whom 13,000 are children requiring continuous medical attention. A remarkably brave helicopter pilot who hovered above the burning plant to drop fire-extinguishing materials directly onto the flames died several years afterward of leukemia. Although the long-term effects of the accident are still uncertain, estimates of the total number of deaths expected to result from all aspects of the explosion range from 17,000 to 475,000.

QUESTION

(a) Was the accident at Three Mile Island the result of a *nuclear* explosion of fissionable material? (b) Was the accident at Chernobyl the result of a *nuclear* explosion of fissionable material? Explain your answers.

5.5 Problem 2. Available Supplies of Fissionable Fuels: Is the Breeder Reactor a Solution?

Despite the spectacular nature of the accidents that have already occurred and despite the numbers of people who have been affected or may yet be affected by them, concerns about the actual safety of the nuclear power plants may be overshadowed by the other three factors mentioned in Section 5.3. Even if the perfect fission reactor could be built and could be completely protected against any form of failure or accident, major problems would still exist in the supply of economical, fissionable fuel, in the disposal of nuclear wastes, and in the overall economics of energy production.

Of these three remaining concerns we'll examine first the supply of nuclear fuel. We've already seen that U-235, the most efficient of the fissionable isotopes of uranium, constitutes less than three-quarters of one percent of the naturally occurring uranium ore deposits (Section 4.10). At the current rate of energy production, estimates of the time it would take to exhaust the world's supply of this isotope—at least the supply that can be extracted from the ore at a reasonable cost—range from a maximum of about a century to less than 50 years.

One way to extend the supply of nuclear fuel by a factor of 100 or more is to use a **breeder reactor,** which actually produces more fissionable material than it consumes. Several different types of breeder reactors are technically

A breeder reactor is a nuclear reactor that produces more fissionable fuel than it consumes.

feasible, each using a different type of nuclear fuel and each operating through a different set of nuclear reactions. In one, plutonium-239, manufactured in ways similar to those used in building the first atomic bombs (Section 4.11), serves as the nuclear fuel in the core. Wrapped around the core is a layer of U-238, the common and relatively abundant but ineffective isotope. Neutrons emitted by fission of the Pu-239 (or by some other spontaneous process) strike the U-238 and convert the uranium, through a short segment of a decay chain, to Pu-239, as shown in the following three reactions.

In the first reaction of the sequence, a neutron enters a U-238 nucleus and converts it to the isotopic U-239.

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U}$$

In the next step, the uranium-239 (the product of the first reaction) loses a β particle from its nucleus to produce neptunium-239 (Np-239). With an increase in the atomic number (and therefore the positive charge) of the nucleus, but no change in the number of electrons surrounding the nucleus, the neptunium is produced as a cation. This newly formed Np-239 cation captures an electron from some outside source. As the newly captured electron enters the shells surrounding the nucleus it neutralizes the positive charge of the cation and transforms the Np-239 cation into an electrically neutral Np-239 atom. In the entire process, then, there is no *net* loss of an electron from the nucleus of the U-239 atom into the surrounding electron shells. Although the electron that ends up in the outer shells isn't necessarily the same one that left the nucleus as a β particle, we write the set of equations as if it were.

$${}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np}^{+} + {}^{\ 0}_{-1}e^{-} \rightarrow {}^{239}_{93}\mathrm{Np}$$

Finally, the Np-239 loses a β particle in a similar manner to form Pu-239. The entire process produces energy and at the same time "breeds" fissionable Pu-239 from U-238.

$${}^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu}^{+} + {}^{\ 0}_{-1}e^{-} \rightarrow {}^{239}_{94}\mathrm{Pu}$$

With the conversion of an inefficient isotope such as U-238 into the much more efficient Pu-239 through breeding, the useful supply of fissionable fuels can be made to last thousands of years. Because this type of reactor uses faster moving neutrons than those of the U-235 reactor and also uses liquid sodium as a coolant rather than high-pressure water, it's sometimes called a *liquid metal fast breeder (LMFB) reactor*.

Breeder reactors offer some important advantages in energy production, including a long operating life and low operating expenses. But because of their relatively high initial costs as well as some important technical and political factors, very few now exist throughout the world. Virtually all of them operate on an experimental rather than a commercial scale. One of the major political concerns centers on the ease with which the generated plutonium can be converted into a fission bomb. The widespread use of breeder reactors could extend nuclear weapons to countries that do not now have them and perhaps even to terrorist organizations. Another problem lies in the extraordinarily great health hazard presented by plutonium, which emits α particles as it decays. When the element enters the body it tends to settle in the lungs and other organs and in the bone marrow. The accidental ingestion of even traces of plutonium presents a serious cancer hazard; as little as 1 microgram (1 μg, 10^{-6} g) in the lungs may be enough to induce cancer.

QUESTION

In the conversion of U-238 to Pu-239 in the breeder reactor, another element is produced momentarily from the uranium and decays quickly to plutonium. What is this transient element produced on the path from U-238 to Pu-239? ________________

5.6 Problem 3. The Disposal of Nuclear Wastes: The Persistence of Radioactivity

Solutions to the first two problems of Section 5.3, safety and the supply of fissionable resources, still leave the third and perhaps most troubling problem of all: What is to be done with the radioactive wastes generated by nuclear power plants? The most serious concerns about radioactive material come not so much from fears of an accidental nuclear explosion but rather from its ionizing radiation, from the α and β particles and the γ rays given off by decaying radioisotopes. Later in this chapter we'll examine the nature of this radiation in more detail. We'll see that it can be an invisible, odorless, tasteless, silent killer. But we'll find as well that while this radiation can kill, it can also save lives through applications in medical diagnosis and treatment.

As we saw in Section 4.10, the fission of a U-235 nucleus can occur in many different ways with the production of a great variety of isotopes, almost all of which are radioactive. We've also seen, in Section 4.6, that the spontaneous, radioactive decay of any particular radioisotope (with the loss of a small nuclear particle) can be part of a decay chain of several steps that represent the appearance and decay of still other radioisotopes. It follows, then, that as a nuclear pile operates it generates an enormously large number of radioactive isotopes, each emitting its own hazardous radiation. The combination of all these nuclear by-products of power generation, including residual nuclear fuel whose radioactivity, while still hazardous, has dropped below useful levels, constitutes the waste matter of nuclear power generation. The safe disposal of these radioactive wastes represents the most serious of all the technical problems presented by commercial nuclear power.

Eventually, of course, the radiation dies out and the hazard disappears. As each chain of decay comes to an end in a stable isotope (as we saw in Section 4.6 for the decay of U-238 to Pb-206), every radioisotope that now exists in the universe will become transmuted into a stable, nonradioactive atom. This doesn't mean, though, that one day, very far in the future, radioactivity will vanish from the universe. Natural processes, such as the one that converts plentiful, nonradioactive nitrogen-14 into radiocarbon, which we'll examine in Section 5.14, serve to replenish the supply of some radioisotopes.

Nevertheless, the by-products of nuclear power generation are, indeed, radioactive and some of the radioisotopes among them remain dangerously radioactive for a very long time. Until all radioactive nuclear wastes undergo spontaneous transformations all the way down the chain to the stable nuclei at the end, they present an environmental hazard. The actual amount of time required for the transformation depends on the *half-life* of each radioisotope.

QUESTION

What is the ultimate fate of every radioactive atom now in existence? ______

5.7 More about Problem 3: The Half-Life of a Radioisotope and the Permanent Storage of Nuclear Wastes

The **half-life** of a radioisotope is the time it takes for exactly half of any given quantity of the isotope to decay.

The **half-life** of a radioactive isotope represents the length of time it takes for exactly *half* of any quantity of that isotope to decay. Each isotope decays at its own particular rate and so each has its own, specific half-life. Iodine-131, for example, has a half-life of 8 days. This means that if we start with 100 g of ${}^{131}_{53}I$, only 50 g of I-131 will be left after 8 days; 25 g will remain after another 8 days (a total of 16 days); 12.5 g will be left after another 8 days (a total of 24 days); and so on (Table 5.1). During this time the lost iodine is transformed into other isotopes in its decay chain.

The half-life of C-14 is 5730 years; for U-235 it's 7 × 10^8 years; for Kr-93, one of the many products of U-235 fission (Section 4.11), it's 1.3 seconds. These and other representative half-lives are listed in Table 5.2.

TABLE 5.1 Radioactive Loss of I-131

Total Elapsed Time (days)	Number of Days Since Previous Measurement	Remaining I-131 (g)
0	0	100.0
8	8	50.0
16	8	25.0
24	8	12.5
32	8	6.2
40	8	3.1
48	8	1.6
56	8	0.8
64	8	0.4
72	8	0.2
80	8	0.1

TABLE 5.2 Typical Half-Lives

Radioisotope	Half-Life
Kr-93	1.3 seconds
U-239	23.5 minutes
Tc-99*m*	6 hours
Np-239	2.4 days
I-131	8 days
Ba-140	12.8 days
C-14	5730 years
Pu-239	2.4 × 10^4 years
U-235	7 × 10^8 years
K-40	1.25 × 10^9 years
U-238	4.5 × 10^9 years

If we note two general characteristics of half-lives we can understand a bit more clearly the problems associated with nuclear waste disposal. First, regardless of the actual numerical value of a half-life, we can't consider any particular radioisotope to have vanished (for all practical purposes) until at least 10 half-lives have passed. As we can see from the data in Table 5.3, half (50%) of any specific radioisotope remains after 1 half-life has passed; half of this (25% of the original quantity) remains after a second half-life; and so on. After 10 half-lives just under 0.1% of the original material remains, over 99.9% having decayed into other materials. The first general rule is that, regardless of the length of the half-life, 10 half-lives must pass before the residual radioactivity becomes negligible.

To illustrate the importance of half-lives, let's return for a moment to the discovery of nuclear fission in the laboratory of Otto Hahn (Section 4.9) and to one of the possible fission reactions that may have taken place there.

EXAMPLE (HALF) LIFE GOES ON

Recall from Section 4.9 that after having bombarded uranium with neutrons, Otto Hahn found barium among the products. Assuming that the barium-producing reaction that occurred in his laboratory was the one shown in Figure 4.8

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n$$

and assuming that it took him about a week to carry out the experiment and to analyze the products, do you think he might have found the krypton produced in this reaction, as well as the barium? (Both Ba-140 and Kr-93 are radioisotopes.)

Referring to Table 5.2, we find that the half-life of Ba-140 is 12.8 days, and the half-life of Kr-93 is 1.3 seconds. We'll also refer to Table 5.3, which shows the percentage of a radioistope that remains after successive half-lives have passed.

One week is much less than 1 half-life of Ba-140 (which is 12.8 days), so we shouldn't be surprised that a majority (more than half) of the Ba-140 generated in the neutron bombardment remained in existence and could be detected within a reasonable time for Hahn to have completed his work, perhaps a week. Yet with a half-life of just 1.3 seconds (Table 5.2), more than 99.9% of any Kr-93 formed would have vanished in just 10 × 1.3 seconds, or 13 seconds. (This period corresponds to 10 half-lives of the radioisotope.) It's unlikely, then, that Hahn might have detected any of the Kr-93 that formed in this reaction.

The second important characteristic of radioactivity is that there's no known way to change the rate of the kinds of radioactive decay we have examined in this chapter. The half-lives of these radioisotopes can't be in-

TABLE 5.3 The Disappearance of a Radioisotope

Half-Lives Expired	Percent of Radioisotope Remaining (to the nearest 0.001%)
0	100.
1	50.
2	25.
3	12.500
4	6.250
5	3.125
6	1.562
7	0.781
8	0.391
9	0.195
10	0.098

creased or decreased by temperature, pressure, magnetic fields, or any other known physical phenomenon. Since we can't increase the rate of their decay (so as to convert them quickly to stable or nonradioactive isotopes), large quantities of radioactive nuclear wastes will be with us and with those who come after us for generations almost beyond measure. To protect ourselves and future generations from these hazards, a safe way must be found to store the most highly radioactive and therefore the most dangerous of these wastes so that they remain out of contact with our environment. At present they're being stored temporarily on the grounds of nuclear power plants themselves and at sites used for the production of nuclear weapons.

Through the Nuclear Waste Policy Act of 1982, Congress provided for the permanent storage of spent nuclear fuels and high-level nuclear wastes in repositories that would effectively isolate them from us and our environment. Currently under study is a plan to seal these wastes in glass blocks, pack these blocks in secure, corrosion-resistant containers, and store the containers far inside the earth at remote, dry locations, where they might remain undisturbed for at least 10,000 years. It's important that the containers remain perfectly dry since the high-level radioactivity of their contents keeps them warm. No matter how corrosion-resistant the containers may seem to be by our current standards, contact of the warm containers with moisture over years, decades, centuries, and longer could lead to eventual corrosion and leakage of their radioactive contents into undergound water supplies.

Plans currently call for the burial of the containers in a 115-mile maze of tunnels deep under the earth at Yucca Mountain, Nevada. Development of the site, which should be ready to receive the first of the containers in 2010, may eventually cost as much as $15 billion.

A corroded container symbolizes the problems of disposing of nuclear wastes.

[The 170 tons of radioactive material remaining at the Chernobyl plant (Section 5.4) is now sealed in a cube of steel and concrete some 20 stories high. Even with regular maintenance, this sarcophagus isn't expected to last more than about 25 years before it must be rebuilt.]

QUESTION

Plutonium-239 has a half-life of about 24,000 years. How long will it take for 99.9% of the plutonium wastes of a breeder reactor to decay into other substances? If we assume that there are four generations of humans in each century, how many generations will this period cover? ______________________________

5.8 Problem 4. The Cost of Nuclear Power

Even with concerns about the safety of the nuclear generator and the wastes it produces, the fourth problem—the economic cost of nuclear energy—may be the most significant restraint to the commercial production of electricity from nuclear energy. The cost includes all the expenses of building and maintaining the plant, adhering to safety standards, and disposing of the nuclear wastes. As a very rough estimate, it currently costs about twice as much to supply a family with electricity generated by nuclear power as it does to supply them with an equivalent amount of electricity produced from coal.

5.9 The Power to Kill . . .

With all the problems involved in generating electrical power from nuclear energy, the most valuable use of nuclear reactions in today's society may well lie in their medical applications, in their ability to cure disease and to save lives. So that we can understand more clearly how and why radiation has the power to cure and to prolong lives, we'll first return briefly to the other side of nuclear radiation, the danger that radioactivity poses to living things.

We saw in Chapter 4 that radioisotopes emit ionizing radiation consisting of α particles, β particles, and γ rays. As this ionizing radiation passes through matter it collides with molecules to form ions that can react with still other chemical particles to form new and unusual products. The result of the passage of ionizing radiation through matter, then, is the destruction of molecular forms originally present and the accumulation of other, often undesirable products. Enough damage of this sort in a living system can produce illness and death.

In general, the damage done to living things by ionizing radiation depends on both the radiation's ability to penetrate tissue, its *penetrating power*, and its ability to produce disruptive ionizations within that tissue, its *ionizing power*. Alpha particles, with a relatively large mass (4 amu) and carrying two positive charges, have enough mass and charge to do considerable damage to whatever atoms and molecules they collide with. They have considerable ionizing power. But they're so big that they're easily stopped by frequent collisions with other chemical particles. They have little penetrating power and simply don't travel very far. Yet they do a considerable amount of damage in the short distances they do travel.

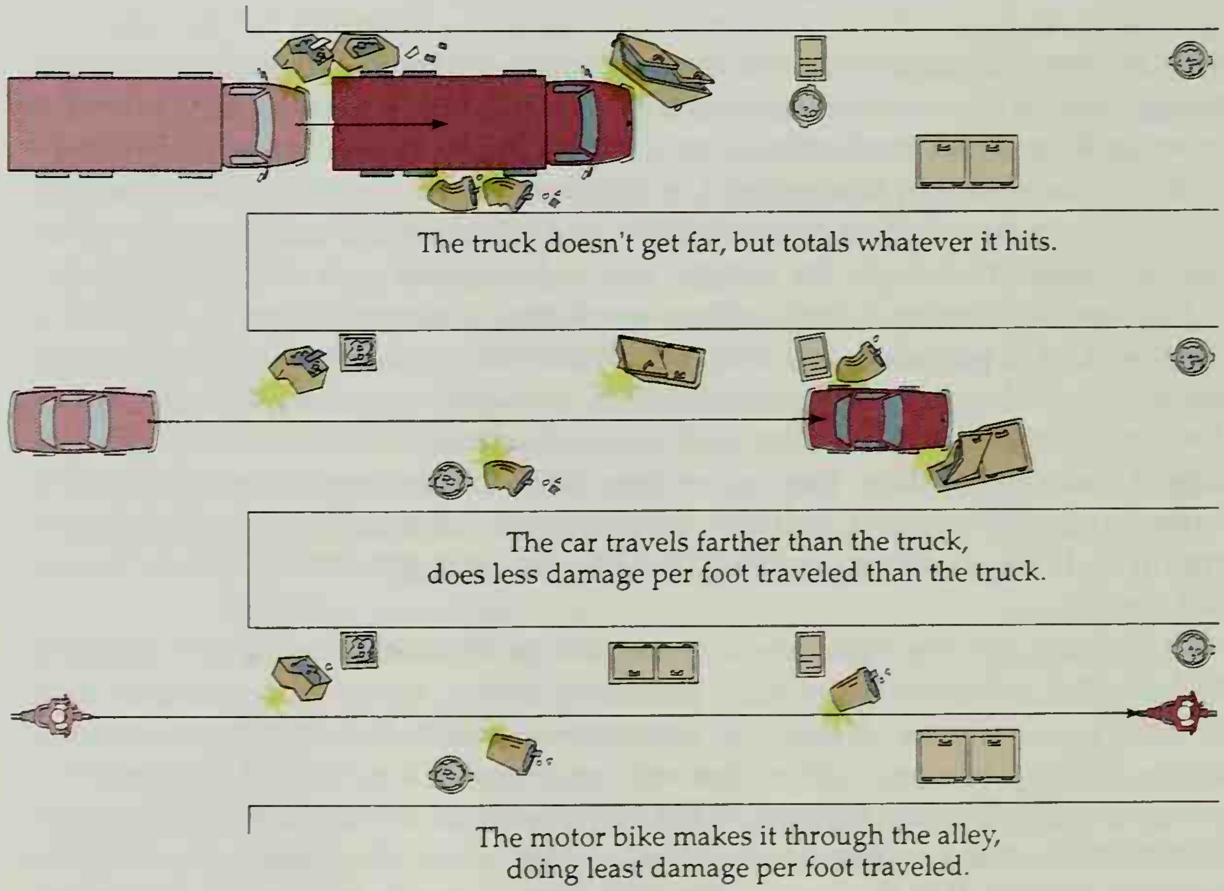
A β particle, with a much smaller mass and carrying a single negative charge, has less ionizing power than an α particle, but being smaller than the α particle, it has less frequent collisions and so it travels farther. Over comparable distances β particles do less damage than α particles. Gamma rays, with neither mass nor charge, have considerably more penetrating power, but with little ionizing power they do less damage than α particles or β particles over comparable distances of travel.

As an analogy, you might think of a narrow alleyway, cluttered with cars parked here and there, garbage bins strewn around, pushcarts blocking the way, and assorted other obstacles on the street and in the gutters. A large, multiwheel tractor-trailer truck (the α particle) trying to bully its way through the alleyway probably wouldn't get very far, but it would do a lot of damage over the short distance it traveled. A small sports car (the β particle) speeding recklessly along might get farther along in the alley with fewer collisions and less overall damage, but it still wouldn't make it all the way through. Someone on a motor bike (the γ ray) would be more likely to get all the way through the clutter to the other end of the alley, with only minor damage (Fig. 5.4). No analogy is perfect, but this one provides a useful comparison of the penetrating power and ionizing power of α particles, β particles, and γ rays.

As ionizing radiation passes through living matter, much like the vehicles in the crowded alleyway, it encounters and collides with a variety of molecules, ranging from simple water molecules to the incredibly elaborate structures of the enzymes of life and the DNA and RNA of cell reproduction and heredity. The chemical processes necessary for life and for successful repro-

Figure 5.4

Ionizing power and penetrating power: an analogy. The truck represents an alpha particle, the car represents a beta particle, and the motorcycle represents a gamma ray.



duction depend on the precise interactions of all of these substances, each with its own characteristic and intricate molecular structure. Large doses of ionizing radiation, with their capacity to transform the finely detailed structures of life into a confusion of new and utterly useless or even harmful molecular forms, can bring the processes to a halt. When this damage is extensive enough to cause illness or death of the living body receiving the radiation, it is called **somatic damage.** The more immediate results of somatic damage range from reduced white cell counts in the blood, through such symptoms as fatigue and nausea, to painful death. Delayed effects appear as damage to bodily organs (the spleen, for example), glands (such as the thyroid), and bone marrow, and through the development of leukemia and other cancers. As with chemical poisons and other things that injure the body, the extent of the damage depends on the nature of the radiation, the size of the dose, and the fitness of the individual.

Somatic damage is injury to a living body, causing illness or death to that body.

Smaller amounts of radiation, too small to produce perceptible damage to the living organism receiving the radiation, can nonetheless disorganize the molecules of heredity in the cells of the reproductive system, those DNA structures that carry genetic information from one generation to the next. Such **genetic damage** can leave an individual animal, for example, in apparently good physical condition but with subtle reproductive damage that causes offspring to be born with physical and/or mental defects or heightened susceptibility to diseases. An important distinction between somatic damage and genetic damage is that somatic damage affects the individual receiving the radiation; genetic damage produces illness and physical and mental defects in generations yet to come.

Genetic damage is damage that is transmitted to future generations.

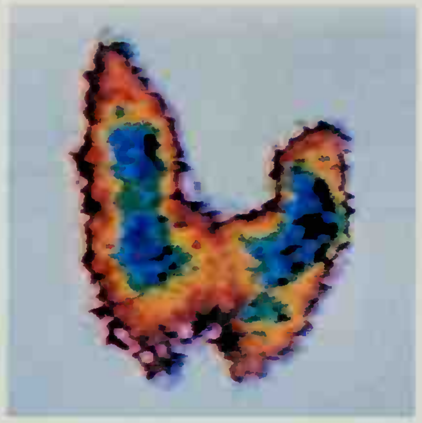
It's worth noting that although genetic damage from radiation has been observed in laboratory animals, there hasn't yet been a clear and unambiguous example of radiation-induced genetic damage in humans, not even in the children of the survivors of the atomic bombs of World War II. While there's no reason to doubt that damage of this sort can occur in humans just as it does in laboratory animals, there may be several good reasons why it has yet to be observed. One of these is that large-scale exposure to artificial or human-generated radiation is still a relatively recent phenomenon, at least on the time scale of human generations. Perhaps not enough time has passed to allow the phenomenon to appear. Moreover, the total number of children born to all the bomb survivors is still relatively small. It may be that, statistically, the number of these offspring is still too small to allow the effects of artificially induced genetic damage to show up clearly against a background of genetic changes that occur normally, as a result of the radiation from natural sources that are always with us. (We'll discuss these briefly at the end of this chapter.) Then again, humans may simply be far more resistant to genetic damage than the kinds of animals that have already been studied. Continuing examinations of children of bomb survivors and of those exposed to radiation as a result of the Chernobyl disaster may reveal a great deal about human susceptibility to genetic damage.

The effects of radiation in a survivor of the atomic explosion at Nagasaki, nearly two years after the blast.

QUESTION

Name and describe two types of biological damage caused by ionizing radiation.

5.10 . . . The Power to Cure



An image of a thyroid gland obtained through the use of radioactive iodine.

Preparing a sample of technetium-99m. A compound containing the radioisotope will be injected into a patient about to receive a diagnostic gamma-ray scan.

Images of a human skeleton obtained from a gamma-ray scan. A compound containing radioactive technetium-99m was the source of the radiation.

We can turn now to the brighter side of radiation—its capacity to heal and to cure. These beneficial effects of radioactivity depend on both the nature of the radiation itself and the chemistry of the element producing it. The radiation emitted by specific isotopes can be used medically in two distinct ways: (1) in diagnosis, to generate visual images of organs and glands, as an aid in detecting tumors for example, and (2) in therapy for treating cancers and other disorders of the body.

As an illustration, the thyroid gland accumulates much of the iodine that enters the body and uses this element in regulating our growth and metabolism. (Adding potassium iodide, KI, to "iodized" table salt helps prevent enlargement of the thyroid, a condition known as *goiter*; see Chapter 16.) Images of the gland, useful in diagnosing metabolic irregularities, can be obtained from the radiation emitted by several different radioisotopes of iodine, usually introduced into the body as NaI. Iodine-131, which emits both β particles and γ rays and has a half-life of eight days, is widely used in these examinations of the thyroid.

Generally, the procedure involves administering a small dose of the radioactive NaI to the patient and, after a brief time to allow the thyroid to accumulate the radioisotope, detecting the radiation coming out of the thyroid and translating its patterns into an image of the gland. Because of the very great sensitivity of the instruments used in detecting and analyzing the radiation, images can be obtained from quantities of radioiodine far too small to cause any harm to the gland or to the rest of the body. In larger amounts the radioisotopes of iodine can produce enough radiation to kill controlled numbers of thyroid cells, thereby repressing the excessive formation of thyroid hormones and alleviating or curing a condition known as *hyperthyroidism*.

Technetium-99*m* ($^{99m}_{43}$Tc) is the radioisotope most widely used in medical diagnosis. The *m* indicates that it is a *metastable* (unstable) isotope that decays with loss of γ rays alone and therefore without any change in its atomic mass or number.

$$^{99m}_{43}\text{Tc} \rightarrow {}^{99}_{43}\text{Tc} + \gamma$$

Incorporated into appropriate chemical compounds, technetium-99*m* can be introduced into the body so that it accumulates in various organs, including the heart, kidneys, liver, and lungs, and in glands such as the thyroid. Since it emits only γ rays, and since these rays penetrate tissue and exit the body as effectively as they enter it, technetium-99*m* is particularly useful in generating diagnostic images. This radioisotope, which has a half-life of six hours, can be used in quantities small enough to avoid noticeable chemical poisoning or radiation damage. It's their ability to leave the body efficiently, with few ionizing collisions, that makes γ rays particularly useful in diagnostic medicine.

[Historically, technetium was the first new element to be produced artificially. Unknown before 1937, the element had been sought for many years to fill one of the gaps in the periodic table (Section 3.6). In 1937 two scientists at the University of California, Berkeley, discovered technetium in a sample of molybdenum that had been bombarded with deuterium. Its name comes from the Greek word *tekhnetos*, meaning "synthetic" or "artificial."]

Radioactivity originating outside the body is also useful in medical therapy. Because cancer cells divide more rapidly than normal cells and are more active metabolically, they are also more susceptible to damage by ionizing radiation. Cancers located deep within the body are sometimes treated with sharply focused beams of γ rays emitted by an external source of cobalt-60. In *cobalt radiation therapy* the cobalt source is swung around the body in a circular arc with the tumor at its center. The tumor, at the beam's focus, receives the γ radiation continually, and therefore in a large cumulative dose; the rays pass only briefly through the surrounding tissues. With this procedure the γ rays kill cancer cells selectively while sparing healthy ones.

A cancer patient receiving radiation therapy.

QUESTION

What property of radioisotopes of iodine makes them particularly useful for diagnosis and therapy of disorders of the thyroid gland? ________________

5.11 Positron Emission Tomography

In addition to providing therapy (by killing off cancerous cells selectively, for example) and yielding structural images of bodily organs, γ rays are also useful for examining the actual operation of an organ through a diagnostic technique known as **positron emission tomography**, or **PET.**

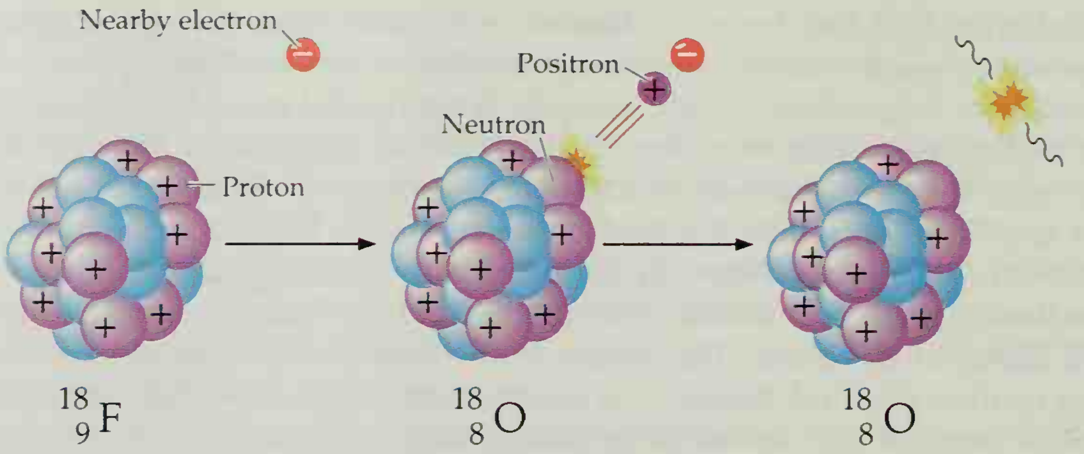
Positron emission tomography, or **PET**, produces images of planes within an organ, generated through the analysis of γ rays emitted by collisions of positrons and electrons.

As we saw in Section 4.8, a positron is a subatomic particle indistinguishable from an electron except for its positive charge. Certain radioisotopes, especially those containing relatively few neutrons, emit positrons, which disappear in a burst of γ radiation when they collide with electrons. (The electrons vanish as well.) Whenever a nucleus emits a positron, one of the protons within the nucleus is transformed into a neutron. To keep track of these nuclear transformations we can think of a proton as a combination of a neutron and a positron. Looking at it in this way, the loss of a positron from the combination (the proton) leaves the neutron behind, with the net conversion of one proton to one neutron.

(Recall that in Section 4.5 we followed β-particle emission by viewing a neutron as a combination of a proton and an electron. Although these combinations may seem to run counter to each other and against common sense, we've already seen in Section 4.8 that the behavior of the subatomic world seldom follows the ordinary logic of the everyday world about us. In any event, β-particle emission *does* convert a neutron to a proton, and positron emission *does* convert a proton to a neutron.)

In PET, a positron-emitting radioisotope—most often carbon-11, nitrogen-13, oxygen-15, or fluorine-18—is incorporated into the molecular structure of a compound normally used by the organ under examination or into a closely related compound that travels along the same biological paths. The compound containing the radioisotope is administered to the patient and travels into the organ. Positrons emitted by the isotope collide with nearby electrons and disappear (along with the electrons) in bursts of energy consisting of two γ rays traveling in opposite directions. Nearby detectors and computers convert these unusual bursts into images of planes or slices of the organ and reveal

Figure 5.5
Positron emission by fluorine-18.



A fluorine-18 nucleus emits a positron, becoming . . . an oxygen-18 nucleus. The ejected positron collides with a nearby electron and . . . vanishes in a burst of two gamma rays.

the molecular activity within it. (*Tomography* comes from the Greek word *tomos*, meaning "slice" or "section.")

In this way PET provides views of the molecular traffic within organs such as the brain and the heart and shows what's going on inside them. As an illustration, PET reveals graphic differences in the brain of a person who is listening, watching, or thinking intensely, trying to remember something, or simply moving around. It also shows the effects of various drugs and medications on an organ. In one of PET's most useful applications, an atom of fluorine-18 is attached to a molecule of *glucose*, the sugar used by the brain as its exclusive nutritional fuel. This tagged glucose enters the brain along with ordinary glucose and emits its positrons, which collide with electrons and emit bursts of γ rays. Analysis of images of the brain obtained in this way allows physicians to follow the path of the glucose as it travels through the brain and to diagnose and treat abnormalities that arise from irregularities in the brain's use of glucose.

Among the advantages of PET are the very short half-lives of the more common positron-emitting isotopes, ranging from 2 minutes for oxygen-15 to 110 minutes for fluorine-18. With isotopes of such short half-lives, the source of ionizing radiation soon disappears from the body. Figure 5.5 illustrates the positron-emitting activity of fluorine-18.

EXAMPLE POSITIVELY POSITRON

Into what element is an atom of O-15 converted when it emits a positron?

Oxygen's atomic number is 8. There must therefore be 8 protons in oxygen's nucleus. Since positron emission converts a proton into a neutron, the atomic number must decrease by 1 unit as the positron leaves the nucleus. Thus oxygen, with its atomic number of 8, is converted into the element whose atomic number is 7, *nitrogen*.

QUESTION

Into what element is an atom of carbon-11 transformed when it emits a positron?

5.12 Detecting Radiation: Seeing the Invisible, Hearing the Silent

Even with its remarkable abilities to produce ions, to destroy tissue, and to kill, as well as to diagnose and to heal, there are nonetheless some important things that radiation doesn't do. It doesn't produce any taste or odor or any other kind of immediate sensation. You can't see it directly and you can't hear it directly. The only way to detect the radiation is through the use of specialized instruments and detection devices, some as simple as a piece of film, others large, complex, and expensive. For example, to monitor the amount of radiation they receive, medical personnel and others who work near radiation often wear *film badges*. These badges respond to radiation much as Becquerel's sealed photographic plate, which produced an image when it shared a desk drawer with radioactive ore. Developing the film reveals the cumulative exposure to radiation.

Other instruments use the ionizing power of the radiation to reveal its presence. One of these, the *Geiger counter*, consists of a gas-filled cylinder connected to a high-voltage battery and to a sounding device and a meter. A gap between the wall of the cylinder and an electrode passing into its center serves to break an electrical circuit connecting the battery to the rest of the counter. In the absence of ionizing radiation this gap keeps the battery from activating the sounding device or the meter. Any ionizing radiation that passes through the cylinder produces a stream of ions in the gas, which temporarily completes the circuit between the cylinder's wall and the central electrode and registers as a click from a speaker. The frequency of the resulting clicks and the meter reading indicate the intensity of the radiation (Fig. 5.6). It was the steady clicking of the Geiger counter that produced the static under Stagg Field as Enrico Fermi's atomic pile began its controlled chain reaction.

A medical worker wearing a film badge. The badge records the accumulated radiation exposure.

A Geiger counter detects radiation directly, as it occurs.

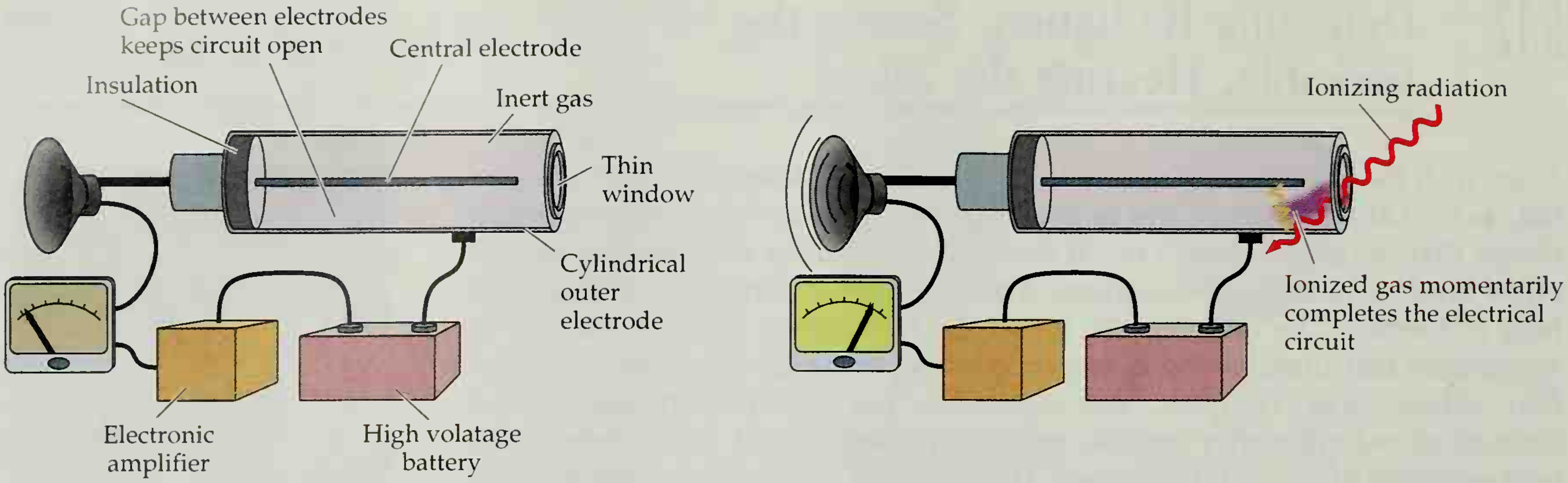


Figure 5.6
The Geiger counter.

Another kind of detector, a *scintillation counter*, uses a material that *fluoresces*, or emits an instantaneous flash of light when the invisible radiation strikes it. Zinc sulfide, ZnS, is a substance of this sort. A light-sensitive detector in the counter registers the intensity of radiation through the amount of light emitted by the fluorescing material.

QUESTION

How could you make a crude but effective radiation detector out of common consumer materials readily available to you? ________________________________

5.13 The Nuclear Calendar: Uranium and the Age of the Earth

With their individual, predictable, and immutable rates of decay, naturally occurring radioisotopes provide an important tool for dating ancient objects, ranging in age from articles formed a few thousand years ago to bodies as old as the earth and the solar system. We can estimate the earth's age from our knowledge of the half-lives of the radioistopes that constitute the decay chain of U-238 (Table 5.2) and from a chemical analysis of the oldest known rocks.

To understand how, suppose that the oldest sample of rock we can find contains exactly equal numbers of atoms of lead-206 (the stable isotope of lead at the end of the U-238 decay series) and of uranium-238. If we assume that all of the lead-206 came from decay of the U-238, then we have evidence that exactly one half-life of the U-238 has passed since the rock was formed. This amounts to 4.5×10^9 years (Table 5.2). If we find a ratio of three atoms of Pb-206 for every atom of U-238, then two half-lives (9.0×10^9 years) have passed, and so on. By measuring the ratio of the atoms of each of these isotopes, and by making several critical assumptions (especially that all the lead atoms were formed from decay of uranium atoms) we can calculate the age of the rock containing the U-238.

EXAMPLE OLD ROCKS

Analysis of a piece of meteorite shows that it contains seven Pb-206 atoms for every atom of U-238. How old is the meteorite?

Since there are seven Pb-206 atoms for every U-238 atom, one-eighth of the total is U-238 and seven-eighths of the total is Pb-206. To calculate the age of the meteorite we make the same sort of assumptions described in this section. We assume that no Pb-206 was present at the formation of the meteorite and that all the Pb-206 now present in the meteorite came from radioactive decay of the U-238. If this is true, then just one-eighth, or 12.5%, of the original U-238 remains in the meteorite. Since

50% of the original radioisotope remains after one half-life,
25% of the original radioisotope remains after two half-lives, and
12.5% of the original radioisotope remains after three half-lives,

three half-lives of the U-238 must have passed since this sample of matter was formed. As the half-life of U-238 is 4.5×10^9 years (Table 5.2), three half-lives are

$$3 \times 4.5 \times 10^9 \text{ years} = 13.5 \times 10^9 \text{ years}$$

If our assumptions are correct, the sample of the meteorite is 13.5×10^9 years old.

This technique, as well as others that are based on different chains of radioactive decay and that require different assumptions, give estimates of the age of the earth's surface that fall in the broad range of 3.5 billion to 4 billion years (3.5×10^9 to 4×10^9 years).

We might expect, at first, that the half-lives of all the other radioisotopes in the chain have to be used in the calculation as well, but this isn't the case at all. The U-238 decays so much more slowly than any of the other isotopes that its half-life alone reveals the age of the rock. To see why, we can use an analogy involving an hourglass with an unusual shape.

Imagine a sand-filled hourglass shaped like the one shown in Figure 5.7. The time it takes for the sand to fall from the top bulb to the bottom is determined exclusively by the width of the first neck. The remaining necks are much wider than the first one, so they don't affect the rate at which the sand falls. With this analogy, both the rate at which the sand falls through the narrowest (and, it happens, the first) constriction and the rate of decay of the U-238, which has by far the longest half-life in the decay chain (and, as it happens, occupies the first position in the chain), determine the time it

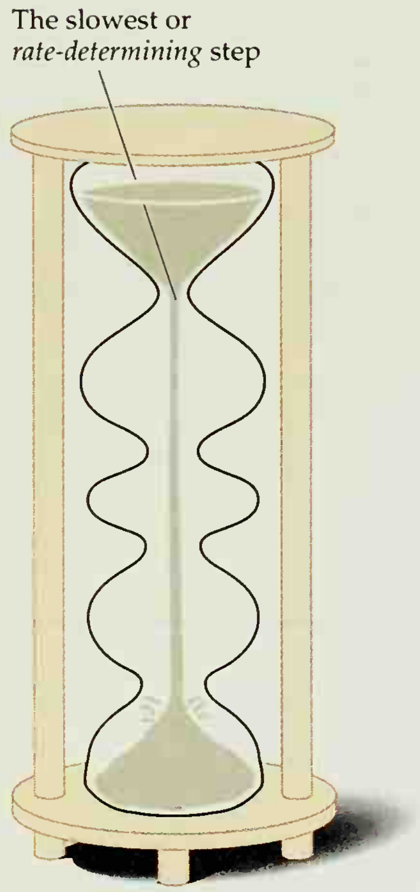


Figure 5.7
An unusual hourglass.

A **rate-determining step** is the single step in a sequence of steps that, by itself alone, determines the rate of the entire, multistep process.

takes for each process to occur. The slowest step of a sequence that proceeds through other, much faster steps as well—the single step that determines the rate of the entire sequence—is called the **rate-determining step** of the overall process.

QUESTION

Would it make any difference in the calculations of this uranium dating process if the decay step with the longest half-life were at the *end* of the sequence rather than at the beginning? Use an hourglass analogy in arriving at your answer.

5.14 The Nuclear Calendar: Carbon and the Shroud of Turin

A variation of this dating technique allows us to determine the age of carbon-containing objects made of materials derived from plants. Unlike uranium-238, which decays without being replenished by any natural phenomenon, the radioactive isotope carbon-14 ($^{14}_{6}C$) is formed continuously by the action of cosmic radiation on the earth's atmosphere. Neutrons generated by the cosmic radiation react with atmospheric nitrogen atoms to produce carbon-14 and a proton:

$$^{1}_{0}n + ^{14}_{7}N \rightarrow ^{14}_{6}C + ^{1}_{1}H$$

With its half-life of 5730 years, this newly formed C-14

- combines with atmospheric oxygen to form $^{14}_{6}CO_2$
- migrates (as part of the carbon dioxide) down to the surface of the earth, and
- becomes incorporated into the cellulose and other carbohydrates of plant life.

In this way the C-14 becomes part of the cotton, paper, and wooden products of society and it enters the bodies of animals, and our own bodies as well, through the food chain. The entire process, from formation of the C-14 in the upper atmosphere to its incorporation into living plants and animals, is relatively rapid compared with its half-life.

All this time, of course, the radiocarbon continues to decay to common nitrogen by loss of a β particle:

$$^{14}_{6}C \rightarrow ^{14}_{7}N + \beta^-$$

With the death of the plant—through its use as food or its conversion into fabric, paper, or wooden objects—the plant's incorporation of atmospheric $^{14}_{6}CO_2$ into its carbohydrates stops. Yet the C-14 already present within it continues its long decay to nitrogen, thereby continually decreasing the ratio of the radioactive C-14 to the stable isotopes of carbon, C-12 and C-13.

The carbon dating technique itself begins with a measurement of the relative amounts of C-12 and C-13 (both of which are stable, naturally occurring isotopes) and the radioactive C-14 still present in the organic material. By comparing these measured ratios with ratios normally present in the atmosphere, it's possible to estimate the amount of time that has passed since the incorporation of ${}^{14}_{6}CO_2$ into the organic matter ended.

Because the decay of C-14 takes very much longer than its conversion into the organic matter of life, and because the atmospheric C-14 seems to be replaced about as fast as it's removed, radiocarbon dating provides good estimates of the age of substances composed of organic materials.

In 1988 this form of dating was applied to the Shroud of Turin, a 14-foot-long piece of linen in the shape of a burial cloth. The shroud first appeared in France sometime between 1350 and 1360 and was later transferred to the Italian city of Turin. Imprinted on it is the distinct image of a man.

Many have believed that the image is that of Jesus and that the shroud is the actual burial cloth of Jesus, which would make the shroud approximately 2000 years old. The image was believed to have been imprinted miraculously on the shroud as it held Jesus's body. Still others held that the image was placed on the cloth, in one way or another, by a human agent and that the cloth is more likely a hoax than an authentic relic.

Since the cloth could be the authentic shroud only if its fibers were formed *no later* than the time of Jesus's death, radiocarbon dating was used to examine its authenticity. The analysis, which was carried out on several portions of the cloth, each about the size of a postage stamp, placed the time of the formation of the carbon-containing material of its linen as probably between 1260 and 1390, but surely later than 1200. The certainty of the radiocarbon dating technique requires that the linen could not have been in existence at the time of Jesus's death, and that it must have been fabricated centuries afterward. The radiocarbon dating thus reveals that, however the image itself may have been formed, the cloth could not have held the body of Jesus.


The image on the Shroud of Turin.

QUESTION

Which of the following can be dated by radiocarbon techniques: (a) a rock b) a leather slipper c) a wooden boat; (d) a mummified body; (e) a silver spoon. Describe your reasoning. ____________________

PERSPECTIVE: Living with Radiation

In beginning our examination of the extraordinary chemistry of ordinary (as well as a few not so ordinary) things, we've started with the atomic nucleus. In Chapter 4 we saw how an unexpected event in a desk drawer in Paris led, half a century later, to the first large-scale use of nuclear energy in the bombs that ended World War II. Here in this chapter we've seen that despite this terrifying beginning, and the spectacular accidents of Three Mile Island and Chernobyl, reactions within the nucleus are now routinely used in many productive ways in the world about us. We've seen, in summary, that although the energy released by nuclear reactions can be used destructively, in weapons of war, it can also be used constructively and beneficially, to produce commercial electric power, for example.

We've also seen that, like the energy that's released by nuclear reactions, the radioactivity accompanying these reactions can be either harmful or beneficial, depending on how we use it. We've seen that ionizing radiation can cause illness and can kill, and yet it can also provide us with the means to diagnose and cure illness and to save lives.

It's also important to recognize, as we close, that other forms of ionizing radiation exist in our world, in addition to the streams of α and β particles and the γ rays of radioactivity we've examined here. In the energy they carry with them, γ rays lie between the more energetic cosmic rays that reach the earth from remote regions of space (Section 5.15) and the less energetic but more familiar X rays of medical and dental examinations. Like γ rays, the ionizing X rays of these examinations are capable of destroying living tissue and, in massive doses, of causing illness and death, much like other forms of ionizing radiation.

As with most of the chemicals of our everyday world, the risk of harm from ionizing radiation depends on several factors, including the conditions of their use and the extent of our contact with them. The actual doses of X radiation used in medical and dental diagnoses, for example, are negligible and are essentially harmless. Yet while the diagnostic benefits of these minute doses of X radiation far outweigh the risks of their use, X rays are not ordinarily used in examining women in the early stages of pregnancy. In these cases, the risk of harming a developing fetus normally outweighs any benefit gained from its exposure to the ionizing radiation.

Even if we should wish to reduce our risk for ionizing radiation to zero by avoiding all forms of ionizing radiation completely, we simply couldn't. Aside from ionizing radiation generated by human activities, such as the use of radioactive substances and X rays in the health professions, we are continuously bathed in a very low level of radiation from natural sources, called **background radiation.** The bricks of our buildings and the rocks and soil under our feet, for example, contain traces of naturally occurring radioistopes. In many localities the radioactive gas radon escapes from the earth under us and enters our homes (Section 4.6). What's more, high-energy cosmic rays, carrying greater energy than γ rays, constantly bombard the surface of the earth and everything on it, including us. We could shield ourselves from these forms of background radiation only by living encased in a thick shell of lead.

Background radiation is the low level of natural radiation to which we are all exposed.

But even if we should choose to live our lives in a lead shell, we would still carry within our very bodies a completely inescapable source of ionizing radiation: the radioisotope potassium-40. As we saw in Table 1.1, potassium is an element essential to life. It's the most abundant cation within our cells and helps regulate the water balance in our bodies. A 60-kg (132-lb) person carries around roughly 200 g of potassium at all times. We could not live without it. Yet just over 0.01% of all the potassium in the universe, including the potassium in our bodies, consists quite naturally of the radioisotope K-40, with a half-life of 1.25×10^9 years (Table 5.2). A simple calculation shows that each of us is carrying about 20 mg of radioactive potassium-40 within our bodies at all times. That, too, contributes to the background radiation.

To put all this into perspective, we must recognize that not only we, but all of our ancestors as well, have lived with this same background radiation,

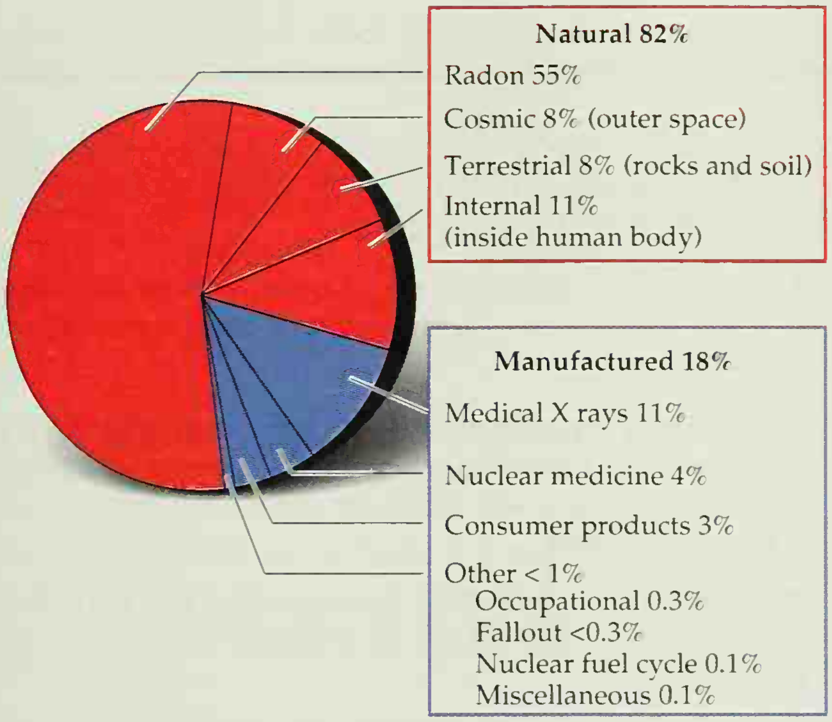


Figure 5.8
Risk to the average person from low-level sources of ionizing radiation. (Adapted from "Health Effects of Low Levels of Ionizing Radiation," Committee on Biological Effects of Ionizing Radiation, BEIR V, National Academy Press, Washington, D.C., 1990, p. 19.)

by and large, for eons of time. But now, in these two chapters, we have learned of *additional* sources of low-level radiation, produced by humans, that have come into our lives in the past century and that have only recently extended our risk of exposure to ionizing radiation beyond the background that has been tolerated by the human race for so long. We can thus ask how great a risk we run from these additional sources of low-level radiation, the products of human activities of the last hundred years.

A study titled "Health Effects of Exposure to Low Levels of Ionizing Radiation," published by the National Research Council and the National Academy of Sciences, organizations of distinguished American scientists and engineers, provides a partial answer to our question. Taking into account such factors as the likelihood of the average, nonsmoking individual's exposure to radiation from various sources, the size of the probable dose, and the kinds of radiation involved and their impact on biological processes, the study assesses (with many acknowledged uncertainties) the contribution of each source to our overall risk of harm. Figure 5.8 presents a pie chart showing each risk as a percentage of our overall risk. It's worth noting that more than four-fifths of our risk of harm, by the study's estimate, comes from natural sources, primarily from radon gas. In addition to these sources of exposure, smokers run an added risk of lung cancer from the ionizing radiation of polonium-210, a radioisotope that occurs naturally in tobacco. It seems clear that, with the possible exception of smokers, the greatest risk of harm from ionizing radiation comes from natural sources.

In the next few chapters we'll leave the nucleus and the energy of nuclear reactions and move outward to the surrounding shells of electrons and to the forms of energy they provide. We'll continue our examination of the chemistry of our everyday world, and especially the chemistry that provides us with energy, by examining how the electrons of these outermost atomic electron shells, the valence shells, furnish the electrical energy of batteries and how they provide the energy of fuels such as gasoline and kerosene.

EXERCISES

FOR REVIEW

1. Complete this statement with the words and terms that follow. Each is used once.

Peaceful uses of nuclear reactions include the generation of ________, medical ________, and ________. Currently the most practical form of nuclear power plant is the ________, in which heat produced by an ________ creates steam, which turns a turbine attached to an electrical generator. Although most nuclear power plants use a uranium fuel which is enriched in the more highly fissionable isotope ________, a ________ converts the more common, but less efficient isotope ________ into fissionable ________ as it simultaneously generates power. Someday electrical power may be produced by an environmentally cleaner ________, in which small nuclei, such as hydrogen isotopes, combine to form larger nuclei, such as helium atoms.

Medically, ________ is valuable in the diagnosis and control of hyperthyroidism; ________ is used widely as a source of diagnostic γ rays.

Since the ________ of radioisotopes are well known and are constants, unaffected by physical or chemical conditions, naturally occurring radioisotopes are useful in determining the age of ancient materials. The dating of objects made of wood, paper and linen, for example, is often accomplished by analysis of their ________ content.

atomic pile
breeder reactor
carbon-14
diagnosis and therapy
electrical power
fission reactor
fusion reactor
half-lives
iodine-131
plutonium-239
radioisotopic dating
technetium-99*m*
uranium-235
uranium-238

2. Identify, describe, or explain each of the following:

a. background radiation
b. film badge
c. Geiger counter
d. LMFB reactor
e. meltdown
f. PET
g. positron
h. scintillation counter

3. In what way was Enrico Fermi's nuclear pile at Stagg Field important to building the first atomic bomb? In what way was it important to the development of nuclear-powered electric generating plants?

4. Describe the steps involved in the conversion of the heat produced in a nuclear pile into electricity by a commercial power plant.

5. Describe how a source of energy *other than heat* is used to generate electric power on a commercial scale.

6. What is the principal advantage of nuclear *fusion* over nuclear *fission* for generating power? What is the principal obstacle yet to be overcome in building a fusion reactor?

7. List four factors that have slowed the expected growth of nuclear power as a source of commercial electricity.

8. Explain why a nuclear explosion cannot occur in a commercial fission reactor. What kinds of accidents can occur? What happens during a *meltdown*?

9. Of the accidents at Seascale, England, Three Mile Island, Pennsylvania, and Chernobyl, Russia, which released the greatest amount of radioactive fallout?

10. Write the three sequential nuclear reactions that convert U-238 into Pu-239 in a breeder reactor.

11. Describe two hazards associated with a breeder reactor that converts uranium to plutonium.

12. Why is it important that high-level nuclear wastes be stored in an area that is completely dry?

13. What was the first new element to be produced by artificial means? How does its name reflect its origin?

14. Describe how ionizing radiation can be used to cure or control hyperthyroidism.

15. How does the emission of a positron affect the atomic number of an atom? How does it affect the mass number of an atom?

16. What form of radiation is detected by the instruments used in PET?

17. Describe how ionizing radiation can cause (a) somatic damage and (b) genetic damage.

18. Name four sources of background radiation that might affect someone standing outside in a rocky field. Name one source of background radiation to which someone standing in a well-sealed

room with walls of thick lead and someone buried deep within a mine would be exposed.

19. List α rays, β rays, and γ rays in order of increasing ability to pass through a thick wooden wall. List them in order of increasing ability to generate ions over equivalent paths of travel within that wooden wall.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

20. Using the data in Table 5.2, calculate how long it would take for 1 kg of Tc-99*m* to be reduced to just under 1 g of Tc-99*m* by the process of radioactive decay.

21. Ten grams of krypton-93 were prepared through the use of nuclear reactions. A measurement taken after a certain period had passed showed that radioactive decay left a total of 0.625 g of this radioisotope. How long a period had elapsed between the formation of the 10 g of krypton-93 and the measurement?

22. You have a balance that will weigh masses down to 0.1 g, but gives a reading of zero for anything less than that. Using that balance, you have just measured out 100.0 g of each of the radioisotopes in Table 5.2. What weight of each of these isotopes will be left (using the same balance) after 20 years have passed?

23. Section 4.11 informs us that U-235 can undergo the following mode of fission:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{137}_{52}\mathrm{Te} + {}^{97}_{40}\mathrm{Zr} + 2\,{}^{1}_{0}\mathrm{n}$$

Suppose that as Otto Hahn bombarded uranium with neutrons, some of the fission had followed this route. Suppose further that Hahn had taken about 4 days to analyze the products of this study. Do you think he might have found any tellurium-137? Do you think he might have found any zirconium-97? (Te-137 has a half-life of 4 seconds; Zr-97 has a half-life of 16.8 hours.)

24. You have just examined a wooden utensil recovered from an ancient archeological site and have found that the ratio of C-14 to C-13 is less than 0.1% of the ratio of C-14 to C-13 in a branch just cut from a nearby tree. What, if anything, can you conclude about the age of the wooden utensil? What assumptions do you make in arriving at your answer?

25. In determining the age of the earth by measuring the ratio of lead-206 atoms to uranium-238 atoms in the earth's crust, we made the assumption that all of the lead-206 in the rock samples came from the radioactive decay of uranium-238. How would our calculations of the earth's age be affected if some of the lead-206 atoms were formed at the same instant the uranium-238 atoms were formed? Suppose, that is, that at least some of the lead-206 atoms that we found along with the uranium *did not* come from radioactive decay of the U-238 but were formed along with the U-238. Would the earth be older or younger than our calculations would show? Describe your reasoning.

26. You have 10 g of a mixture made up of exactly 5 g of I-131 and 5 g of K-40 and you also have a radiation detector that is able to detect radiation down to a level of 0.10% of the current level of radiation given off by the sample. How long do you estimate it will take for the level of radiation of the 10-g sample to drop to (a) 75% of its current level? (b) half of its current level? (c) 0.10% of its current level?

THINK, SPECULATE, REFLECT, AND PONDER

27. What was the function of the graphite in Fermi's pile? What was the function of the cadmium?

28. How did Enrico Fermi's studies of nuclear reactions contribute to the use of atomic energy for the production of commercial power?

29. Why do health professionals working in radiology departments of hospitals wear film badges on their coats?

30. Describe the operation of each of the following radiation detection devices: (a) a Geiger counter; b) a scintillation counter; c) a film badge. How would you use each to estimate the *quantity* of ionizing radiation that is present? Which one of these detectors do you think is the best for determining the amount of accumulated radiation exposure a person receives over a long period, a week, for example? Describe your reasoning.

31. What properties should a radioisotope have if it is to be administered internally in a medical diagnostic procedure?

32. You are the administrator of a major research institute. One of your research scientists presents a plan to build an instrument much like that used for cobalt radiation therapy, except that this new instrument would use an α emitter rather than a γ emitter for the treatment of deep-seated tumors. What would your response be? Would you (a) promote or (b) fire the research scientist who proposed the idea? Why?

33. Of α radiation, β radiation, and γ radiation, which is most damaging to living things when it is emitted by a nearby, external source? Explain your answer. Of the three, which is most dangerous to a living thing when it is emitted by a radioisotope located within the body? Explain your answer.

34. Describe the similarities and the differences in the use of γ radiation to (a) determine the shape and size of an internal organ and to detect the presence of tumors in it; b) to determine how well the organ is performing its biological functions, such as metabolizing a particular nutrient; c) to kill a cancerous tumor in the organ.

35. Suggest *three* possible reasons why genetic damage by ionizing radiation has not yet been observed in humans.

36. Suppose there were to be a vote soon in your state to ban *all* forms of production of ionizing radiation by human activities, such as in the production of electricity by nuclear power plants, the production of radioisotopes for medical use, and the use of X rays in medical and dental examinations. Would you vote for or against the proposal? Explain your answer.

37. Which one of the four factors that have slowed the growth of commercial nuclear power do you think provides the most important argument against further development of commercial nuclear power? Which one carries the least weight in arguments against further development?

38. Suppose a commercial electric utility wanted to build a nuclear power plant a few miles from where you live and your county or municipal government held a referendum to determine whether to permit the construction and operation of the plant. This would give you the opportunity to cast a vote in favor of the plant or against it. What factor(s) would sway you toward voting *for* the construction and operation of the nuclear power plant? What factor(s) would sway you toward voting *against* the plant?

39. Is there any way to detect an actual difference between the electricity that is generated by a nuclear power plant and the electricity generated by a plant run with oil? If your answer is *yes*, how would you go about detecting the difference? If your answer is *no*, how would you go about convincing someone (who believes otherwise) that you are right?

40. Do you think that the continued production of electricity by nuclear plants justifies the accumulation of high-level nuclear wastes? Explain.

41. If you had a choice between connecting your home or apartment to electrical power provide by a plant that burns imported petroleum or a plant powered by nuclear reactions, which would you choose? Why?

42. Among the various proposals suggested for the disposal of high-level nuclear wastes is the possibility of sealing them in drums and transporting them by rocket to the moon, to remain on its surface forever. What would be the advantages of such a plan? What would be its drawbacks? Would you support a plan of this sort? Explain your answer.

43. It's possible to convert the energy of steam into electricity, and it's possible to reverse the process by using electricity to produce steam from water. It's possible to convert the energy of falling water into electricity and it's possible to reverse the process by using electricity to pump water from a lower level to a higher level. It's possible to convert the energy of the wind into electricity with a windmill connected to a generator, and it's possible to reverse the process by using a fan to convert electricity into a stream of moving air. It's possible to convert the energy of fissioning atoms into electricity. Do you think it might be possible to reverse the process and use electricity to produce fusion? Describe your reasoning.

44. Suppose that the isotopic analysis of the Shroud of Turin had dated its origin to a few years earlier than the birth of Jesus. What conclusion could we have drawn from this result?

Oxidation and Reduction

6

THE ELECTRICITY OF CHEMISTRY

Electricity in the form of lightning.

Galvanized Tacks, Drugstore Iodine, and Household Bleach

In the preceding chapters we've emphasized the chemistry of the atomic nucleus. In this chapter we'll extend our study outward from the nucleus to the shells of electrons surrounding it. A simple but intriguing demonstration starts us off. Cover the bottom of a glass with a layer of small, galvanized tacks, the kind you can get in any hardware store. (*Galvanized* tacks, garbage cans, and other metal products are covered by a thin layer of zinc to protect them from corrosion.) Now add some tincture of iodine to the glass, the kind drugstores sell as antiseptic solutions. Use just enough of the iodine solution so that it doesn't quite cover every bit of the topmost tacks. It's better to use a bit too little of the tincture of iodine than too much.

The iodine solution covering the tacks now has the very dark, purple-violet color of elemental iodine itself. But if you let the glass stand for about half an hour you'll see the liquid fade slowly to a very pale yellow, or lose its color completely. The actual time it takes for the color to fade depends on several factors, including the temperature. In warm weather the color disappears more rapidly. Swirling the glass gently can speed up the decolorization.

So that you can see clearly what happens next, carefully pour the solution itself into another glass, leaving the tacks behind. Now add a few drops of liquid household bleach to the pale solution. Immediately the very dark purple violet of the iodine returns. If the color appears to form clumps, producing a lumpy appearance within the liquid, add a few drops of vinegar. The vinegar causes the clumps to dissolve, producing a dark solution that looks very much like the iodine you used originally. Figure 6.1 sums up this entire procedure.

What you've just seen results from the sort of chemistry we'll cover in this chapter. The loss of color from the iodine solution and the regeneration of the original color both take place as electrons are transferred from atoms of one element to atoms of another. Specifically, the purple-violet elemental iodine (I_2) of the tincture of iodine reacts with the zinc coating on the tacks and is converted to the colorless iodide anion (I^-) as the zinc atoms (Zn) are

1. The equipment: household bleach, galvanized tacks, tincture of iodine, and vinegar.
2. Add the iodine solution to the tacks, nearly covering them.
3. The color of the iodine fades as time passes.

4. Adding a few drops of bleach to the faded solution . . .
5. . . . restores the original color.
6. Adding a little vinegar produces a clear, intensely colored solution.

Figure 6.1
Color changes with galvanized tacks, iodine, and household bleach.

transformed into zinc cations (Zn^{2+}). With the disappearance of the purple-violet I_2 from the solution, the color fades as well. The liquid bleach that you add to restore the color contains elemental chlorine (Cl_2), which reacts with the I^-, reconverting it to the original purple-violet I_2. The color returns. (The reason for the formation of the solid material when you add the bleach, and its disappearance when you add the vinegar will become clear in Chapter 10.)

We'll examine in more detail *how* and *why* these changes take place—why the zinc atoms on the galvanized tacks cause the deeply colored iodine molecules to be transformed into colorless iodide ions, and why the chlorine of the household bleach reconverts the iodide to iodine and restores the color—after we've examined some of the chemistry that takes place when electrons move from one chemical particle to another. It's this same kind of chemistry that runs one of our most common, everyday consumer products, the electric battery.

6.1 Beyond the Nucleus

In this chapter we'll examine some of the ways we can harness the movement of electrons between chemical particles. We've already seen an example of a transfer of this sort in the migration of an electron from the valence shell of a sodium atom to the valence shell of a chlorine atom, with the formation of a sodium cation and a chloride anion in the process (Section 3.8). We'll examine other, similar transfers of electrons among various atoms and ions. We'll learn how we describe quantitatively the tendency or potential for such an electron transfer to take place, how we use the flow of electrons among atoms and ions to store and to extract electric currents from batteries, and how we use some of the chemistry involved in all this to manufacture products important to society.

6.2 Inside the Flashlight Battery

Almost anywhere we go we can find batteries to provide light from our flashlights and sound from our portable radios and CD and tape players, to fire off the flash attachments to our cameras, to operate our digital clocks and watches, to run our toys and games, and to start our cars. These portable storehouses of electricity are available in a variety of forms for a variety of uses. They can be found as the relatively inexpensive, common flashlight battery, known variously as the standard, classic, or heavy-duty cell (or, more technically, as the carbon–zinc dry cell), or as the more expensive and longer lasting or more specialized alkaline, lithium, mercury, or silver oxide batteries, or as rechargeable batteries, such as the lead–acid batteries that start our cars and the nickel–cadmium batteries that run our rechargeable power tools.

The inside of an ordinary flashlight battery—a standard, classic, or heavy-duty carbon–zinc dry cell—looks much like Figure 6.2. The outside of the battery itself is a cylindrical zinc cup, sheathed in a protective paper cover. This cup is filled with a moist, black paste of ammonium chloride (NH_4Cl), zinc chloride ($ZnCl_2$), and manganese dioxide (MnO_2). Sticking down into the center of this mass is a porous rod of carbon. A metal cap covers the top of the rod and forms one of the battery's contacts. (The bottom of the zinc shell is the other contact.) Plenty of insulation protects the carbon rod and its metal cap from direct mechanical and electrical contact with the shell.

Although the carbon–zinc battery is one of our simpler consumer products, the chemistry that goes on inside that wet, black paste is much too complex to be described in detail here. We can say something, though, about how these batteries provide us with electrical power when we put them into a flashlight, for example. When we turn the flashlight on we complete a *circuit*, a path followed by electrons, that allows the electrons to leave the zinc casing of the battery, travel to the bulb over a portion of the circuit that's built into the flashlight itself, travel through the bulb (causing it to light up), and then back along the remainder of the circuit to the batteries, which they enter through the small, round contact on the top of the metal cap. From that contact they move through the carbon rod attached to it and into the body of the battery. There they take part in the chemical reactions that occur inside the

Figure 6.2
A flashlight battery.

Alkaline, lithium, mercury, and rechargeable nickel cadmium batteries.

black paste. What we've just described is an **electric current,** a flow of electrons along a particular path or **circuit.**

An electric current is a flow of electrons. A **circuit** is the path the electrons follow.

As the electrons leave the zinc casing of the battery, the zinc atoms that lose the electrons become transformed into zinc cations, Zn^{2+}. It's the flow of these electrons, from the metal casing of the battery through the electrical circuits of our appliances and back into the core of the battery, that provides the power to our radios, flashlights, clocks, and the like. (The metal casings of alkaline, mercury, lithium, and other kinds of batteries also provide the electrons these batteries release. Like the carbon–zinc battery, though, the chemistry that goes on inside these batteries is too complex to be covered here.)

QUESTION

As electrons depart from the zinc casing they leave behind positively charged zinc cations that cause the zinc casing to acquire an overall positive electrical charge. Is the zinc casing the battery's anode or cathode? (For help, see Section 1.3.) ______

6.3 Two Potatoes, a Clock, and a Cell Named Daniell

The release of electrons and the conversion of metals into their cations occur in other electrical devices as well as in batteries. Although none of the other devices is as common as the flashlight battery, several operate through simpler chemical reactions. Examining how they produce electricity reveals a good deal about how all batteries generate electricity.


Figure 6.3
A clock run by a chemical reaction.

One of these creations is a cleverly designed digital clock that runs from the power provided by two potatoes, or so it seems. The clock itself is attached to two wires, each ending in a different metal plate: one copper, the other zinc. Pushing each of these plates into its own potato and joining the two potatoes to each other by a third wire (also with ends of copper and zinc) starts the clock running as though it were connected to a commercial battery (Fig. 6.3).

Using potatoes isn't critical here. Moist soil will do, as will an ordinary soft drink, or even salt water. Actually, anything that acts as an electrolyte (Section 1.1) will run the clock. The secret lies not in the potatoes or in any specific electrolyte, but in the chemical identity of the embedded metals themselves. Together with the electrolyte, these zinc and copper strips make up an **electrochemical cell** (a cell or battery that uses chemical reactions to produce electricity) similar to the one invented in 1836 by John Frederic Daniell, an English physical scientist who had been appointed the first professor of chemistry at King's College, London, in 1831.

An **electrochemical cell** is a cell or battery that produces electricity from chemical reactions.

We can build one form of his *Daniell cell* easily with two beakers, one containing a solution of zinc sulfate, $ZnSO_4$, and a strip of zinc that dips into the liquid; the other holding a solution of copper sulfate, $CuSO_4$, and a copper strip.

(The sulfate group, SO_4^{2-}, is an anion consisting of four oxygen atoms covalently bonded to a single sulfur atom and bearing, as an entire group, a charge of 2−. In $ZnSO_4$ the two negative charges of the SO_4^{2-} anion balance the two positive charges of the Zn^{2+} cation of $ZnSO_4$; in $CuSO_4$ they balance the two positive charges of the Cu^{2+} cation.)

The two solutions are joined by a *salt bridge* that allows ions to move physically from one beaker to the other. This bridge need be no more than a strip of cloth soaked in a solution of sodium chloride, with its ends dipping into the two solutions (Fig. 6.4). The sodium chloride serves as an electrolyte, allowing an electric current to flow between the beakers just as the electrolyte allowed current to flow between the two wires of the electric light demonstration in Section 1.1. An electrochemical cell of this sort, made up of a strip of copper metal dipping into a solution of copper sulfate and a strip of zinc dipping into a solution of zinc sulfate, with the two solutions joined by a salt bridge, is known as a Daniell cell in honor of its inventor.

Figure 6.4

A form of the Daniell cell. The sodium chloride of the salt bridge acts as an electrolyte and allows ions to flow between the two beakers, generating almost 1.1 volts.

Connecting a voltmeter to the two metal electrodes of the cell completes the electrical circuit and gives a reading of very nearly 1.1 volts. The response of a voltmeter gives us proof that the cell is producing an electric current. (We'll have more to say about just what this reading indicates in later sections.) Similarly, the combination of the zinc strips and the copper strips of the two-potato clock, connected by the electrolyte consisting of the water and the ions within the potatoes, generates a current that runs the clock (Fig. 6.3).

Although it's more cumbersome than our modern batteries, the Daniell cell is just as much a battery as any of the small sources of electrical power we fit into our flashlights, radios, and tape players. Understanding how it works sheds light on how our more modern batteries work.

QUESTION

Could you operate a "two-potato" clock from zinc and copper strips that dip into solutions of table salt in distilled water? Could you run one from zinc and copper strips in solutions of table sugar in distilled water? Explain your answers. ________

6.4 The Blue Disappears, and So Does the Zinc

The simplest and most direct way of learning how the Daniell cell operates is by using the scientific method (Section 1.4) and asking a simple, straightforward question: "What happens to the cell as it produces the current?" To answer the question we simply build a Daniell cell, connect the zinc and copper strips to each other, and watch the cell over time. At first the zinc and the copper remain clean and bright and the copper sulfate solution shows the intense blue color of its Cu^{2+} ions. Slowly, over hours or days, depending on how we construct the cell and the conditions of its operation, the deep blue color of the copper sulfate solution fades and the copper plate darkens. In the other part of the cell the zinc strip develops pits, erodes, and eventually disappears, especially if it's very thin.

These same changes show up much more quickly and dramatically if we simply place a strip of clean zinc directly into a blue copper sulfate solution.

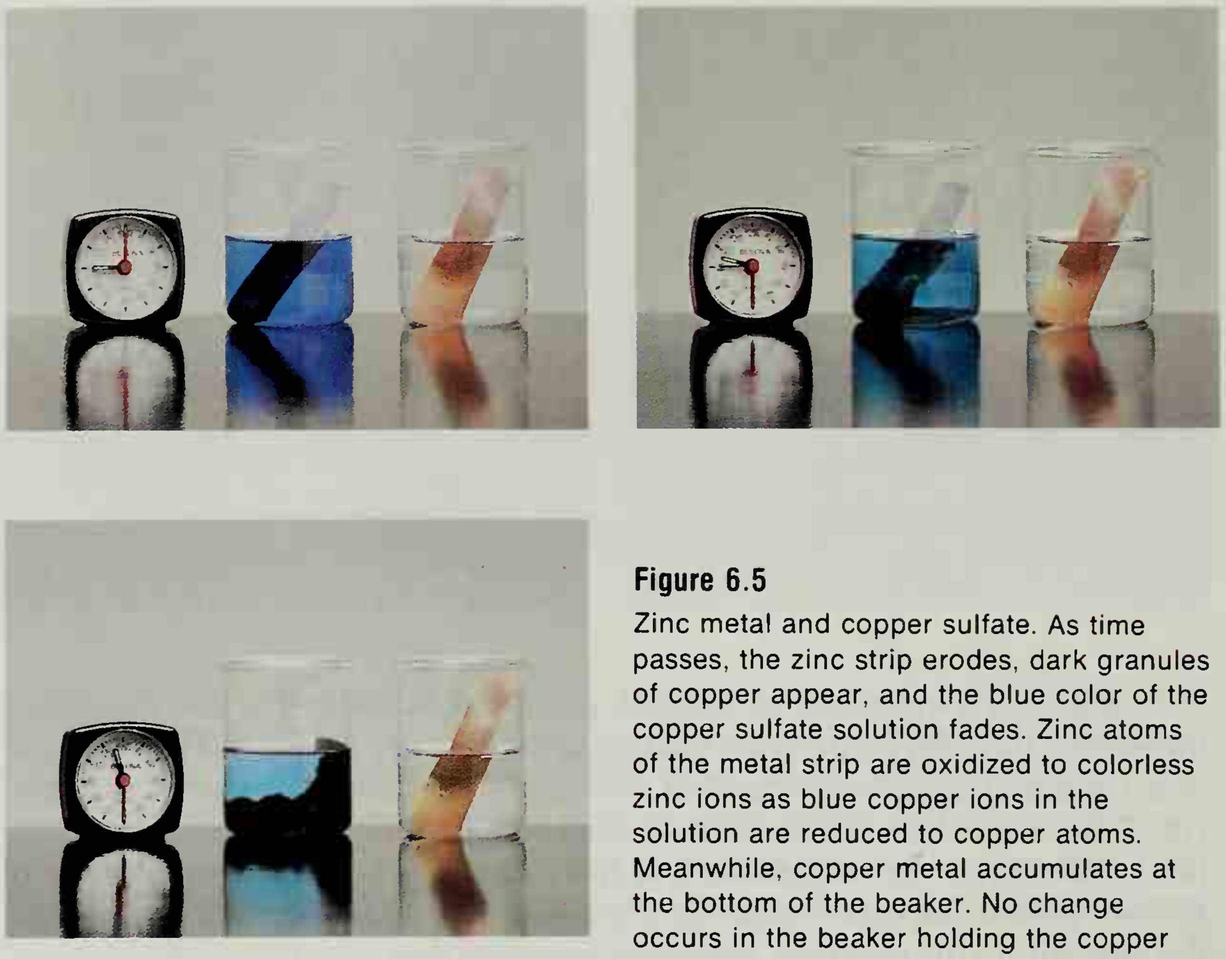


Figure 6.5

Zinc metal and copper sulfate. As time passes, the zinc strip erodes, dark granules of copper appear, and the blue color of the copper sulfate solution fades. Zinc atoms of the metal strip are oxidized to colorless zinc ions as blue copper ions in the solution are reduced to copper atoms. Meanwhile, copper metal accumulates at the bottom of the beaker. No change occurs in the beaker holding the copper strip immersed in a solution of zinc sulfate.

Almost immediately the strip darkens. With time it crumbles into the solution as the blue color of the copper sulfate fades. While all this is going on, the dark coating on the zinc strip thickens and flakes off as fine rust-colored or black granules of copper metal (Fig. 6.5).

Continuing with our use of the scientific method, we can ask what happens if we place a strip of clean *copper* directly into a *zinc sulfate* solution. The answer we obtain is that nothing at all happens.

QUESTION

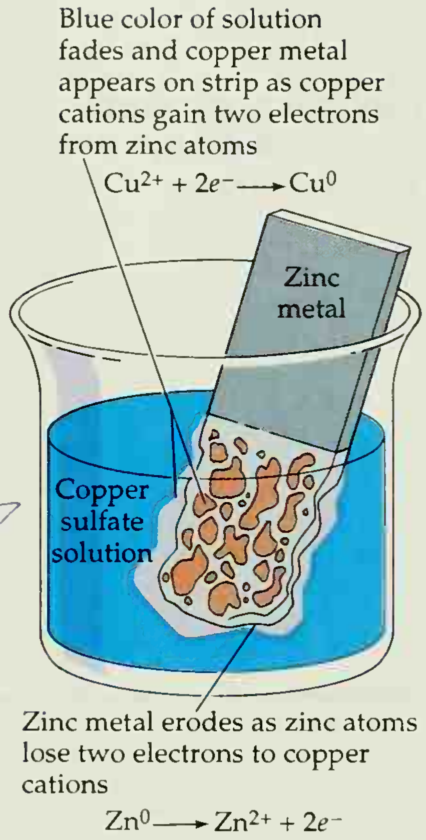
We can infer that copper ions in water have a blue color by noting that a solution of copper sulfate in water, which contains copper ions and sulfate ions, is blue, and that a solution of zinc sulfate in water, which contains zinc ions and sulfate ions, is colorless. Why does this observation lead us to infer that the copper ions of the copper sulfate solution produce the blue color? ____________________

6.5 Our Investigation Bears Fruit: Redox

The simplest explanation for all these observations is that the zinc atoms of the strip of zinc metal, which certainly isn't soluble in water, lose two electrons each and become zinc ions (Zn^{2+}), which *are* soluble in water. That's why the zinc strip erodes. It's converted into zinc ions, which dissolve in the water. In addition, each of the blue copper ions (Cu^{2+}), which are also soluble in water, gains the two electrons lost by each zinc atom. In this way the copper ions become transformed into particles of copper metal, which is *not* soluble in water (Fig. 6.6). The copper metal appears as the rust-colored or black solid granules that form as the blue copper ions of the solution are converted into copper atoms of the granules. The blue color disappears because the copper ions themselves, the source of the color, disappear. Our observation that nothing happens when we place a copper strip into a zinc sulfate solution adds weight to our conclusion. Electrons flow from the zinc atoms to the copper ions, not from the copper atoms to the zinc ions.

The entire process, then, occurs as each zinc *atom* loses two electrons to a copper *ion*. As a result, the zinc atom, which we now write as Zn^0 to emphasize that it bears no net electrical charge, is transformed into a zinc cation. The copper cation is transformed into a copper atom, which we now write as Cu^0 for the same reason.

Zn^0 +	Cu^{2+} →	Zn^{2+} +	Cu^0
atoms that form the zinc strip; each of these loses two electrons to a copper ion	blue ions in solution; each of these gains two electrons from a zinc atom	colorless ions in solution	atoms that form the rust-colored or black granules


Blue color of solution fades and copper metal appears on strip as copper cations gain two electrons from zinc atoms

$Cu^{2+} + 2e^- \longrightarrow Cu^0$

Zinc metal erodes as zinc atoms lose two electrons to copper cations

$Zn^0 \longrightarrow Zn^{2+} + 2e^-$

Figure 6.6
Zinc metal in copper sulfate solution.

The overall reaction, the transfer of one or more electrons from one atom or molecule to another, is known as a **redox reaction,** which we examine in the next section. The redox reaction of the Daniell cell is an example of an **electrochemical reaction,** a chemical reaction that can produce a flow of electrons from one location to another, or a reaction that's caused by such a flow. In this particular redox reaction the sulfate anions remain unchanged. They do not take part in any way.

A **redox reaction** is a reaction that takes place with a transfer of one or more electrons from one chemical species to another. An **electrochemical reaction** is a reaction that can produce a flow of electrons from one location to another or that is caused by such a flow.

QUESTION

Suppose that as the zinc metal is converted into zinc ions in this reaction, and dissolves in the solution, *all* the copper ions in solution are converted to copper metal. What new compound, a combination of a cation and a balancing anion, would then exist in the colorless solution? ______________________________

6.6 Redox, a Combination of Reduction and Oxidation

The term *redox* itself comes from a combination of the two words "*red*uction" and "*ox*idation." The word **reduction** has many meanings in both the English language generally and in the science of chemistry in particular. But when we're dealing specifically with reactions involving the transfer of electrons, *reduction* refers to the *gain* of electrons by a chemical particle. In this sense the blue Cu^{2+} ions of the solution are being *reduced* as they gain the two electrons lost from the zinc metal.

Reduction of the Cu^{2+} ion: $Cu^{2+} + 2e^- \rightarrow Cu^0$

Oxidation is the loss of electrons. **Reduction** is the gain of electrons.

Oxidation has several meanings, too. In a broad and general sense, the word "oxidation" indicates the gain of oxygen by any substance. In electrochemical reactions, though, **oxidation** refers specifically to the *loss* of electrons by a chemical particle. In the reaction of copper ions with zinc atoms, the zinc atoms lose two electrons to the copper ions and are oxidized.

Oxidation of the zinc atom: $Zn^0 \rightarrow Zn^{2+} + 2e^-$

Oxidation, then, is the loss of electrons; reduction is the gain of electrons. As a result, whenever any chemical species loses an electron and undergoes oxidation the electrical charge it bears becomes more positive (or less negative). Conversely, as any chemical species gains an electron and undergoes reduction its electrical charge becomes more negative (or less positive). For an easy way to remember what happens to electrons in oxidations and reductions, just think of an OIL RIG. You'll know instantly that *O*xidation *I*s *L*oss, *R*eduction *I*s *G*ain (of electrons).

Electrons, of course, can't be taken from or lost into thin air. Each electron acquired by any ion, atom, or molecule *must* be lost by something else. The converse is also true. Electrons lost from anything *must* be gained by something else. What this amounts to is that nothing can be reduced unless something else is oxidized and nothing can be oxidized unless something else is reduced. The electrons gained by the copper ions as they are reduced come from the zinc atoms as they are oxidized. Since the copper ions are the agents that remove the electrons from the Zn^0 and cause it to be oxidized, the copper ions constitute the **oxidizing agent** in this reaction. Similarly the zinc atoms, the agents that cause the copper ions to acquire electrons and become reduced to Cu^0, act as the **reducing agent**. It comes to this: The substance being reduced is the oxidizing agent, and the substance being oxidized is the reducing agent.

An **oxidizing agent** acquires electrons from something else and causes it to be oxidized; a **reducing agent** releases electrons to something else and causes it to be reduced.

To emphasize that reductions and oxidations must occur together, hand-in-hand, the overall reaction

$$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$$

and others like it are called *redox reactions*. Note that we can consider a redox reaction to be the sum of a reduction reaction and an oxidation reaction that combine to produce the overall redox reaction. The two electrons that appear on both sides of the arrows, among both the reactants and the products, cancel each other and can be eliminated in writing the redox reaction itself.

Reduction: $Cu^{2+} + \cancel{2e}^- \rightarrow Cu^0$

Oxidation: $Zn^0 \rightarrow Zn^{2+} + \cancel{2e}^-$

SUM (redox): $Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$

In this sense a redox reaction is simply a combination of a reduction reaction and an oxidation reaction that occur simultaneously.

Since each of the individual oxidation and reduction reactions makes up *half* of the overall redox reaction of an electrochemical cell, each one is known as a **half-cell reaction.** The redox reaction, then, is a combination of two half-cell reactions, a *reduction half-cell* and an *oxidation half-cell.*

Each of the oxidation and reduction reactions that combine to form a redox reaction is a **half-cell reaction**.

QUESTION

As we saw in Chapter 3, elemental sodium and elemental chlorine react with each other to form sodium chloride. Although chlorine normally exists as diatomic molecules (Cl_2), we can write the reaction of sodium atoms with chlorine atoms as

$$Na^0 + Cl^0 \rightarrow Na^+Cl^-$$

In this reaction as written, what is being oxidized and what is being reduced? What is the oxidizing agent and what is the reducing agent? Write the individual half-cell reactions that combine to form the redox reaction. You may wish to review the discussion of the reaction in Chapter 3. ______________________

6.7 The Electrochemical Cell: A Summary

To summarize, we've chosen the Daniell cell as a specific example of an electrolytic cell. It generates electricity as the zinc atoms of the zinc strip lose their electrons and become oxidized to zinc ions. These ions enter the solution and, over time, the zinc strip erodes to nothing. As the metal strip is eroding, the solution it stands in becomes enriched with a surplus of zinc cations.

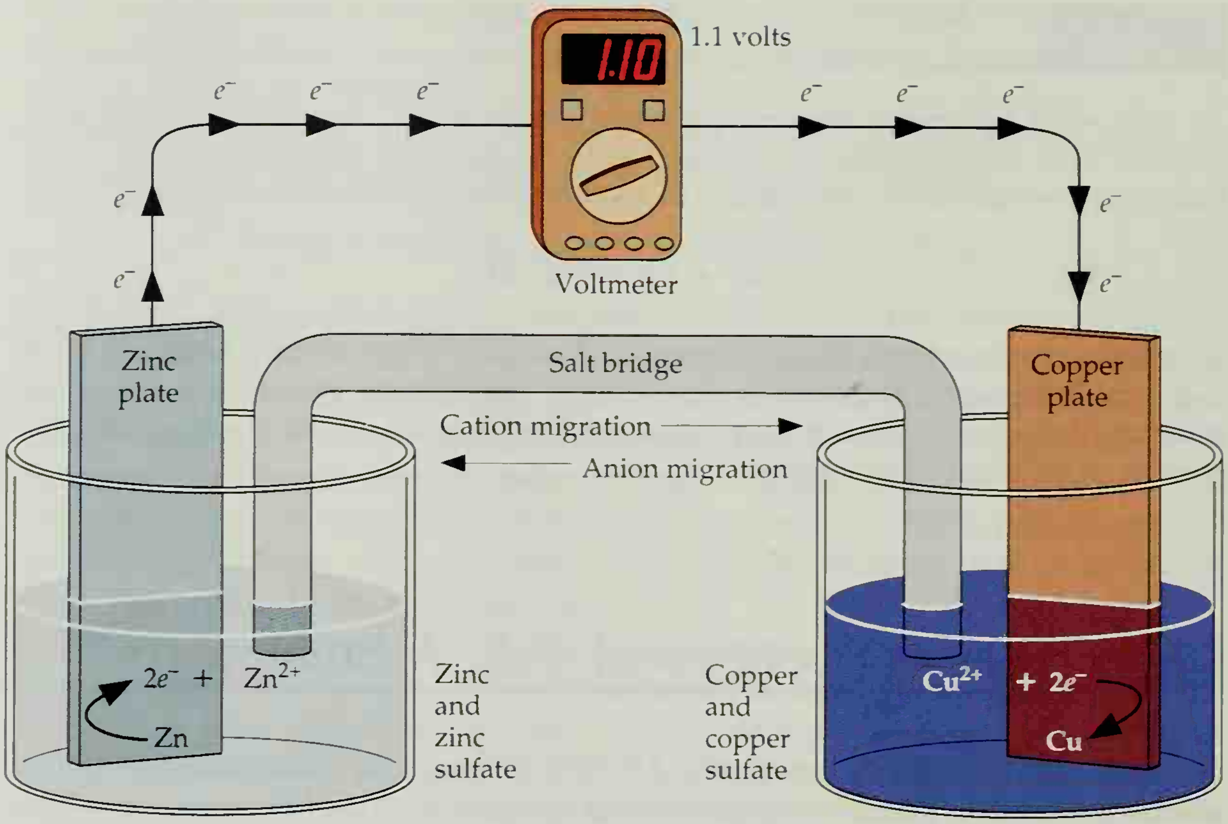
The electrons released by the zinc atoms travel up, along the wire of the electrical circuit, to the voltmeter, where they register 1.1 volts; then they move along the other wire, down to the copper strip. Once they are in the portion of the copper strip that's in contact with the solution, the electrons combine with the copper ions of the solution and reduce them to copper metal, which deposits on the strip as rusty or black solids. With this loss of copper cations, the copper sulfate solution develops a deficiency of cations.

With a surplus of cations developing in the zinc sulfate solution and a deficit of cations developing in the copper sulfate solution, there has to be a way to reestablish an electrical balance. That's where the salt bridge comes in. It allows cations to travel over it, away from the surplus of positive charge in the zinc sulfate solution and toward the deficit of positive charge in the copper sulfate solution. This charge imbalance is also corrected by the travel of anions through the salt bridge in the opposite direction. With either or both of these migrations occurring, the movement of ions through the salt bridge maintains electrical neutrality in both solutions. The cell continues to produce an electrical current as long as there are any zinc atoms left to be oxidized and copper ions left to be reduced (Fig. 6.7).

QUESTION

We prepared the salt bridge of our demonstration Daniell cell by soaking a strip of cloth in a sodium chloride solution. As the cell begins to operate would you expect the sodium and chloride ions of the bridge to move? If your answer is *yes*, in which direction would the sodium ions move and in which direction would the chloride ions move? If your answer is *no*, explain why not. ______________________

Figure 6.7
Chemical and electrical changes in the Daniell cell.



6.8 Electrical Voltage: Putting Pressure on an Electron

The **volt** is a unit of electrical potential, the pressure that moves electrons from one point to another.

As long as we stick to strips of zinc and copper, regardless of their size or shape, we'll get the same reading from the meter, a little under 1.1 volts. Understanding just what this voltage reading represents is a key to understanding how electrolytic cells and other kinds of batteries operate. The **volt** is a unit of electrical potential, the tendency of electrons to move from one point on the circuit to another. The greater the voltage, the greater the pressure that moves the electron through the circuit. It's a bit like water pressure. The greater the water pressure in a pipe the greater the force behind the water, moving it along from point to point inside the pipe. The greater the voltage, the greater the force that moves an electron along from point to point within the circuit.

Alessandro Volta, the scientist for whom the volt is named.

The word *volt* honors Alessandro Volta, an Italian physicist who published a description of the world's first electrical battery, the *Volta pile,* in 1800. His pile consisted of a series of disks made of silver, paper moistened with a salt solution, and zinc. This trio was repeated over and over to form a tall pile. (In later versions, copper successfully replaced the silver.) As with the Daniell cell, the voltage delivered by the Volta pile does not depend on the size or shape of the disks.

While the volt is a unit of electrical potential, the **ampere** measures the rate of flow of the current in much the same way as a unit like gallons/minute measures the rate of flow of water. As amperage increases, there's an increase in the number of electrons traveling through a circuit during any particular period. André Marie Ampère, the French physicist for whom the unit is named, was a contemporary of Volta and, like the Italian physicist, is remembered for his pioneering work in electricity and magnetism.

The **amp** or **ampere** is a unit of electrical current, or the rate of flow of electrons.

Under normal conditions it takes a combination of a high voltage and a high amperage, such as occurs in a lightning bolt or inside a television set, to pose a hazard to humans. The voltage of ordinary consumer batteries, though, is too low to do us any harm. An automobile battery, for example, can deliver a current measuring in the hundreds of amperes, but at such a low potential, 12 volts, that it simply can't cause us serious injury under ordinary conditions.

(A high voltage that delivers an insignificant number of amperes is equally harmless to people. The spark you produce as you walk across a carpet on a dry day and touch a light switch or another person carries thousands of volts, but its infinitesimal current can't hurt humans. The spark's high voltage, nonetheless, can do considerable damage to sensitive electrical and magnetic equipment. It can, for example, change or destroy data stored in computers and on magnetic disks and tape.)

QUESTION

By increasing the areas of the zinc and copper plates in the Daniell cell we can increase the amperage of the current flowing through the circuit without affecting the voltage we measure with the voltmeter. How does increasing the size of the zinc and copper plates affect the electrical pressure that moves the electrons along? How does increasing the size of the plates affect the rate of flow of the electrons through the circuit?

6.9 Standard Reduction Potentials

Since it's the zinc strip that disappears and the dark, finely divided copper metal that appears as the color of the copper ions fades, we have concluded that the zinc atoms are being oxidized and the copper cations are being reduced. The electrons that pass through the meter with a force or electrical potential of 1.1 volts must be moving *from* the zinc strip *to* the copper strip rather than in the reverse direction.

To take our conclusion one step further, there must be a greater electrical potential for electrons to leave zinc atoms than there is for electrons to leave copper atoms. Similarly, the Cu^{2+} cations must have a greater potential for acquiring two electrons than do the Zn^{2+} cations. We've observed indirectly, then, that the copper cations, which acquire electrons spontaneously in the cell, have a greater electrical potential for reduction, or a greater **reduction potential,** than the zinc cations. Similarly, the zinc atoms, which lose electrons spontaneously to the copper cations, have a greater electrical potential for oxidation, a greater **oxidation potential,** than the copper atoms. We measure these potentials for the gain and loss of electrons as electrical voltages.

A **reduction potential** is the voltage produced by or required for the addition of electrons to an atom or ion. An **oxidation potential** is the voltage produced by or required for the removal of electrons from an atom or ion.

Although we can't isolate an individual oxidation or reduction reaction from the redox combination, we can nevertheless measure the electrochemical potential of any one of these individual half-cell reactions relative to a universally accepted standard reaction, the reduction of two hydrogen ions to a hydrogen molecule:

reduction of hydrogen ions: $2H^+ + 2e^- \rightarrow H_2$
standard reduction reaction

In this reduction of hydrogen ions, the addition of an electron to each of two protons produces two hydrogen atoms, which combine through the sharing of their two electrons to form a diatomic hydrogen molecule, H_2 (Fig. 6.8 and Section 3.13). If we now define the electrochemical potential of this particular reduction (arbitrarily) as exactly zero volts, we can measure all other half-cell potentials with respect to it. These measurements, standardized at 25°C and at specific concentrations of the ions, produce a series of **standard reduction potentials** (Table 6.1) that are universally applicable. The numerical values of Table 6.1 express the electrical pressure for the gain or loss of electrons from the chemical particles shown in the table, all in units of volts. The

The **standard reduction potential** of a substance is the value of its reduction potential as compared with the reduction of the hydrogen ion, which is defined as zero volts.

TABLE 6.1 Standard Reduction Potentials (25°C)

Half-Cell Reaction	Potential (volts)
$Li^+ + e \longrightarrow Li$	−3.04
$K^+ + e^- \longrightarrow K$	−2.93
$Cs^+ + e^- \longrightarrow Cs$	−2.92
$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.87
$Na^+ + e^- \longrightarrow Na$	−2.71
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.38
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	−0.83
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$PbSO_4 + 2H^+ + 2e^- \longrightarrow Pb + H_2SO_4$	−0.36
$Ni^{2+} + 2e \longrightarrow Ni$	−0.26
$2H^+ + 2e^- \longrightarrow H_2$	0
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54
$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.07
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
$PbO_2 + H_2SO_4 + 2H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69
$F_2 + 2e^- \longrightarrow 2F^-$	+2.87

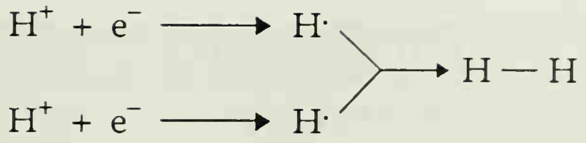


Figure 6.8
Reduction of two hydrogen ions to a hydrogen molecule.

potential for the standard reduction reaction, the reduction of hydrogen ions to a hydrogen molecule, is simply defined as zero volts.

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(defined as zero volts)}$$

As long as reaction temperatures and the concentrations of ions in solution are equivalent in all cases, reductions with positive standard reduction potentials occur more readily than the reduction of two protons to H_2; those with negative potentials occur less readily than the standard reduction. To carry this a step further, the more positive the standard reduction potential, the greater the driving force for the ion, atom, or molecule to acquire electrons and for the reduction to occur. Similarly, the less positive (or more negative) the standard reduction potential, the smaller the driving force for the reactant to acquire an electron and to be reduced.

In view of this, any chemical with a large, positive standard reduction potential has a strong tendency to acquire electrons from some other substance (that's capable of releasing electrons) and to oxidize it. As a result, a chemical with the large, positive standard reduction potential is itself a strong oxidizing agent, readily capable of oxidizing (removing electrons from) many other substances. To summarize, *the more positive the standard reduction potential of a chemical, the greater its tendency to behave as an oxidizing agent* (Section 6.6).

QUESTION

Which element, atom, molecule, or ion in Table 6.1 is the strongest oxidizing agent? ______________________________

6.10 Fluorine, a Powerful Oxidizing Agent

Fluorine shows a large reduction potential, +2.87 volts, and so it's very easily reduced itself and it's very effective at oxidizing other substances. Indeed, fluorine is one of the most powerful oxidizing agents known.

reduction of fluorine: $$F_2 + 2e^- \rightarrow 2F^- \qquad (+2.87 \text{ volts})$$

Elemental fluorine itself, F_2, is an extremely reactive gas that combines explosively with hydrogen gas. The product, HF or hydrogen fluoride, forms highly corrosive hydrofluoric acid when it's dissolved in water. Hydrofluoric acid is capable of etching glass.

H_2	$+$	F_2	$\rightarrow$	$2HF$
one diatomic hydrogen molecule		one diatomic fluorine molecule		two molecules of hydrogen fluoride

Other fluorine compounds are more common and more useful to us as consumers. Stannous fluoride (SnF_2, a compound of tin and fluorine), for example, is added to some toothpastes to harden the enamel of teeth and prevent cavities. Fluorine atoms are also incorporated into the molecules of Teflon, a polymer (Chapter 20) used in coating frying pans and other utensils so that food doesn't stick to them. (Combining fluorine with other elements to form compounds often converts this extremely reactive and dangerous element into substances that are far less reactive and occasionally quite useful to us in our everyday world. We saw other examples of differences between the hazards of elements and the practical uses of their compounds, and the reverse, in Section 3.3.)

QUESTION

What is the *weakest* oxidizing agent in Table 6.1? ______________

6.11 Oxidation Potentials

The reverse of each of the reductions in Table 6.1 is an oxidation. Reversing any of the reduction half-cells, then, gives us an oxidation half-cell. With this reversal we must also change the algebraic sign of the standard reduction potential to convert it to a standard oxidation potential. To find an oxidation potential, then, we simply reverse the direction of the corresponding reduction reaction—the one that gives us the oxidation half-cell we're looking for—and we reverse the algebraic sign of its standard reduction potential. For example, the +2.87 volts for the reduction of molecular fluorine becomes −2.87 volts for the standard oxidation potential of the fluoride anion.

oxidation of fluoride ion: $2F^- \rightarrow F_2 + 2e^-$ (−2.87 volts)

In parallel to standard reduction potential, this relatively large, negative number indicates that there's very little tendency for a fluoride anion to release its acquired electron and to be oxidized to F_2. The fluoride anion is such an extremely weak reducing agent that it's not normally considered to be a reducing agent at all. After all, once a powerful oxidizing agent acquires an electron from another substance, it's hardly likely to give up that acquired electron easily, so it can't be much of a reducing agent once it has secured the electron.

Notice that the reduction or oxidation potential doesn't depend on the number of atoms, molecules, or electrons involved in the reaction. The potential is the same for the oxidation of a single fluoride ion to a fluorine atom as it is for the oxidation of two fluoride ions to a diatomic fluorine molecule:

oxidation of fluoride ion: $F^- \rightarrow F^0 + e^-$ (−2.87 volts)

QUESTION

What is the most powerful *reducing* agent in Table 6.1? Explain your answer.

____

6.12 Why Batteries Work

Batteries work because electrons flow spontaneously from reducing agents to oxidizing agents. When we plug a battery into a flashlight, portable radio, CD or tape player, or flashgun, we provide a circuit for the electrons to follow as they move from the battery's reducing agent to its oxidizing agent. In flowing through that circuit the electrons provide the electrical current that runs the device. What's required is a redox reaction that takes place spontaneously within the battery and causes it to send its electrons out from the oxidation half-cell, through the electrical circuit, and into the reduction half-cell. The significance of the table of standard reduction potentials (coupled with the oxidation potentials we can derive from them) is that it tells us whether any particular redox reaction occurs spontaneously, and it also allows us to calculate the resulting voltage of the electrochemical cell.

To learn whether any particular redox reaction will occur spontaneously, simply add the voltages of its two component half-cells, the reduction half-cell and the oxidation half-cell. If the resulting redox voltage is positive the redox reaction that is the sum of the two half-cell reactions *can* occur spontaneously with the release of energy. (Remember that we obtain the sign of the oxidation half-cell by reversing the sign of its corresponding reduction half-cell.) The numerical value we calculate for the redox voltage is the voltage we can expect to obtain from the electrochemical cell or the battery.

If the sum is *negative,* the redox reaction *cannot* occur spontaneously and no current will flow. Nevertheless, we can cause a reaction with a negative redox potential to take place by adding energy to the cell from an external source, as we'll see in Section 6.16. As we do, though, the electrochemical cell no longer *produces* energy; rather, it *consumes* energy.

EXAMPLE DANIELL'S POTENTIAL

Show that the Daniell cell generates electricity spontaneously and calculate the voltage it produces.

For the Daniell cell, we add the electrochemical potentials for the reduction of Cu^{2+} and the oxidation of Zn^0 to get

reduction:	$Cu^{2+} + 2e^- \rightarrow Cu^0$	(+0.34 volts)
oxidation:	$Zn^0 \rightarrow Zn^{2+} + 2e^-$	(+0.76 volts)
SUM (redox):	$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$	(+1.10 volts)

Change Sign when oxidized

Since the sum is positive we can expect the Daniell cell to produce a current (as we know it does). The electrical potential the cell will deliver if we build it to exact specifications of ion concentrations, temperature, and so forth, is 1.10 volts, which is just about the reading we got from the voltmeter.

EXAMPLE SPONTANEOUS REACTIONS

Will the following reaction take place spontaneously?

$$Zn^0 + I_2 \rightarrow Zn^{2+} + 2I^-$$

Here we add the half-cells for the oxidation of Zn^0 and the reduction of I_2 to get the redox reaction and the redox potential.

oxidation: $Zn^0 \rightarrow Zn^{2+} + 2e^-$ (+0.76 volts)

reduction: $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 volts)

SUM (redox): $Zn^0 + I_2 \rightarrow Zn^{2+} + 2I^-$ (+1.30 volts)

Since the redox voltage is positive, we can conclude that this reaction will, indeed, take place spontaneously.

EXAMPLE REDOX REDONE

Will the following reaction take place spontaneously?

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

In this case, the half-cell reactions and the combined redox reaction are

oxidation: $2I^- \rightarrow I_2 + 2e^-$ (−0.54 volts)

reduction: $Cl_2 + 2e^- \rightarrow 2Cl^-$ (+1.36 volts)

SUM (redox): $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$ (+0.82 volts)

Yes, this redox reaction takes place spontaneously.

EXAMPLE ONE MORE TIME

Will sodium cations and chloride anions react with each other to form sodium metal and chlorine gas?

In this case, we're asking whether the following redox reaction occurs spontaneously:

$$2Na^+ + 2Cl^- \rightarrow 2Na^0 + Cl_2$$

Once again we add an oxidation potential and a reduction potential to get a redox potential. (Notice that although it's necessary to double all the chemical species in the reduction reaction so that the number of electrons matches the number used in the oxidation, the reduction voltage remains unchanged.)

oxidation:	$2Cl^- \rightarrow Cl_2 + 2e^-$	(-1.36 volts)
reduction:	$2Na^+ + 2e^- \rightarrow 2Na^0$	(-2.71 volts)
SUM (redox):	$2Na^+ + 2Cl^- \rightarrow 2Na^0 + Cl_2$	(-4.07 volts)

The answer is no. This time the redox potential is negative. The negative redox potential tells us that sodium cations and chloride anions won't react spontaneously to form sodium metal and chlorine gas. And it's a good thing they don't. If they did, all the table salt in our kitchens and restaurants would be churning away right now, with sodium cations and chloride anions interacting with each other, producing very dangerous sodium metal and poisonous chlorine gas (Section 3.2).

QUESTION

Will the reaction

$$Fe + I_2 \rightarrow Fe^{2+} + 2I^-$$

take place spontaneously? Justify your answer by calculating the redox potential of the reaction. [You can check your answer by finding out whether the "steel wool" of scouring pads, which consists of interwoven strands of a metal containing a high percentage of iron, decolorizes tincture of iodine, much as was described earlier for a similar reaction of galvanized tacks with tincture of iodine (chapter-opening demonstration). You'll know whether you're right in about half an hour at normal room temperature.]

6.13 Galvanized Tacks, Drugstore Iodine, and Household Bleach Revisited

The middle two examples of the previous section answer the questions of *how* and *why* galvanized tacks cause the disappearance of the color of tincture of iodine and liquid household bleach brings it back, questions that were asked in the chapter-opening demonstration. As for *how*, they show us that the decolorization of iodine by galvanized nails and the regeneration of the purple-violet color of the iodine by household bleach take place by redox reactions. In reducing the iodine molecules to iodide ions, the zinc metal acts as a reducing agent and transfers its electrons to iodine molecules. The purple-violet iodine molecules are reduced to colorless iodide ions. In restoring the color, the solution of bleach, which contains a reserve of chlorine molecules, oxidizes the colorless iodide ions back to purple-violet iodine molecules. As for *why*, the redox potential of each of these reactions is positive. Each one proceeds spontaneously by the transfer of electrons from a reducing agent to an oxidizing agent.

QUESTION

Which, if any, of the following metals will decolorize tincture of iodine: (a) nickel, (b) copper, (c) silver, (d) magnesium, (e) calcium? ______________________

6.14 Energy Vs. Rate

We've seen that the sum of the two half-cell voltages—the redox potential—represents the measured voltage of the entire cell. Standard reduction potentials not only provide the voltages of batteries, whether real or proposed, but they also tell us something about the energies of chemical reactions. Sodium and chlorine, for example, react explosively when they come into contact with each other under ordinary conditions. The sum of the oxidation potential of sodium and the reduction potential of chlorine is over 4 volts, a sizable value compared with the voltages generated by the Daniell cell (1.10 volts), by a common flashlight battery (1.5 volts), or by one of the cells of the lead–acid storage battery (about 2 volts, as we'll see shortly). We should note, though, that the vigor of the reaction between sodium and chlorine, or between any other substances for that matter, depends not only on the *amount* of energy released, which is indicated by the electrochemical potential, but also on the *rate* at which the energy is liberated. Some reactions that release plenty of energy take place so slowly that not only are they *not* explosive, they're too slow even to be observed under ordinary conditions. That isn't the case with sodium and chlorine.

QUESTION

Using the half-cell reactions of Table 6.1, write the redox reaction that would release the greatest amount of energy. That is, write the redox reaction that produces the greatest redox voltage. ______________________

6.15 Ideal Batteries and Real Batteries

At the other end of the table from fluorine lies lithium. With its reduction potential of −3.04 volts, the lithium cation shows very little tendency to pick up an electron and be reduced. On the other hand, reversing the half-cell reaction and changing the algebraic sign of the potential to +3.04 volts reveals that lithium metal has a very strong tendency to lose an electron and to be oxidized to the lithium cation.

$$Li^0 \rightarrow Li^+ + e^- \qquad (+3.04 \text{ volts})$$

Lithium metal, then, is a powerful reducing agent. In its redox reaction with fluorine, lithium produces a potential of +5.91 volts.

EXAMPLE HIGH VOLTAGE

Show that the redox reaction of lithium and fluorine produces a potential of +5.91 volts.

For the redox reaction we have

oxidation: $2Li^0 \rightarrow 2Li^+ + 2e^-$ (+3.04 volts)

reduction: $F_2 + 2e^- \rightarrow 2F^-$ (+2.87 volts)

SUM (redox): $2\,Li + F_2 \rightarrow 2Li^+ + 2F^-$ (+5.91 volts)

Although the cell's high voltage might make it an ideal battery for many uses, we've already seen that fluorine gas is far too reactive and far too hazardous to be used in any consumer products (Section 6.10). Of course we're not restricted to half-cell combinations of the highest possible potentials in our search for practical, commercial batteries. We can get potentials far greater than 6 volts from batteries made of reasonably safe, convenient, economical materials simply by connecting several of them in series, with the positive terminal of one connected to the negative terminal of another, as we do when we place two common 1.5-volt flashlight batteries head-to-tail in flashlights. For a two-battery flashlight this alignment gives a total, combined voltage of about 3.0 volts, the sum of the voltages of each individual battery.

Another of the more common, popular, practical, commercial batteries is the alkaline battery, built much like the carbon–zinc battery but containing potassium hydroxide in addition to the other substances described in Section 6.2. Like the carbon–zinc battery, the alkaline battery delivers about 1.5 volts, but over a much longer lifetime. Other more specialized batteries include the lightweight lithium battery, in which lithium rather than zinc is oxidized and which provides over 3 volts; the mercury battery, which delivers a very constant 1.3 volts from a redox reaction of zinc and an oxide of mercury, HgO; and the small and long-lived silver oxide battery, which provides about 1.5 volts from a reaction of zinc and silver oxide, Ag_2O. The rechargeable nickel–cadmium battery, consisting principally of cadmium and an oxide of nickel and the rechargeable lead–acid battery, which we'll examine in the next section, round out the list of the most widely used commercial batteries.

QUESTION

Would you expect the Daniell cell itself to be a commercial success for portable applications? Explain. ____________________

6.16 Chemistry That Starts Cars

Figure 6.9
Construction of the lead–acid storage battery.

The anode of a battery is the part that provides the electrons flowing through the external circuit. The **cathode** is the part of the battery that receives the returning electrons.

We turn now to a battery that's more practical than the Daniell cell and that produces electricity by a simpler set of chemical reactions than do the batteries of the preceding section. It's the lead–acid battery that starts our cars (Fig. 6.9). The battery is relatively inexpensive, can be discharged and recharged repeatedly, lasts from about three to five years (depending on its construction and use), and is small enough and light enough to be installed in cars and trucks.

Inside this battery two sets of plates stand immersed in a solution of sulfuric acid and water. One set, made of a spongy form of metallic lead, serves as the *anode;* the *cathode* consists of plates of lead dioxide, PbO_2. (The **anode** is the part of the cell from which electrons leave as they travel through the circuit. The **cathode** is the part of the battery that receives the returning electrons.) When you start a car, the battery jolts the engine into action by a combination of oxidation of the lead metal of the anode and reduction of the lead dioxide of the cathode.

In the oxidation half-cell the spongy lead reacts with sulfuric acid, producing lead sulfate and releasing two protons and two electrons in the process. Neither the sulfate anion (SO_4^{2-}) nor the protons (H^+) undergo any change in their oxidation state throughout this half-cell reaction. Only the lead is oxidized, from an oxidation state of zero (Pb^0) to an oxidation state of 2+ (Pb^{2+}). It's the lead atoms that lose the two electrons:

oxidation: $$Pb^0 + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e^- \qquad (+0.36 \text{ volts})$$

In the reduction half-cell the lead dioxide reacts with sulfuric acid and two protons to form lead sulfate and water. Once again it's the lead, this time the Pb^{4+} ions of the lead sulfate, that undergoes a change in oxidation state. These lead ions pick up two electrons and are reduced from an oxidation state of 4+ (in the PbO_2) to 2+ (in the $PbSO_4$):

reduction: $$PbO_2 + H_2SO_4 + 2H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O \qquad (+1.68 \text{ volts})$$

Adding both half-cells produces the redox reaction that takes place when you turn the ignition key; adding the two half-cell voltages gives the electrical potential of the cell as it discharges:

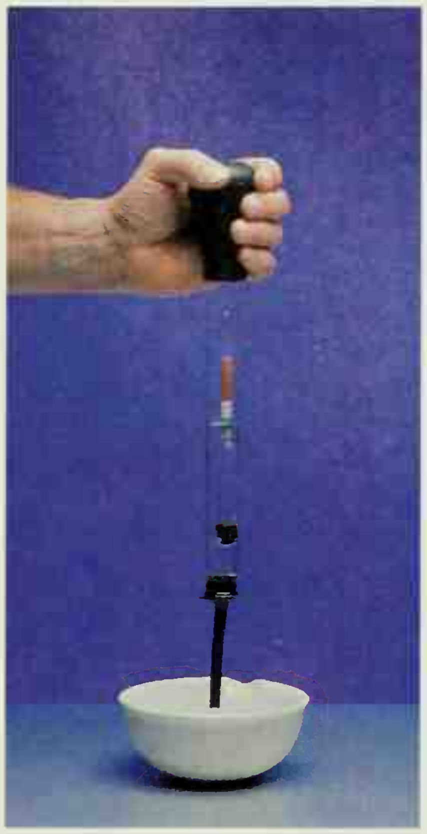
discharge: $$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$ (+2.04 volts, which we can round off to +2 volts for convenience)

The lead–acid battery discharges and provides energy whenever there is a demand that's not met by the car's alternator or generator, such as when you start the car or run the radio or tape deck with the engine off, or if you park and forget to turn the lights off. That bit of forgetfulness is often enough to drain all the electrochemical energy out of the battery, leaving it dead, unable to provide enough current to start the car again.

(Although both an alternator and a generator produce electricity, the alternator produces an alternating current, much like house current but at a considerably lower voltage; the generator produces a direct current, the kind we get from batteries. One or the other is attached to the engine to furnish electricity while the engine is running.)

The lead–acid battery offers one great advantage over the common flashlight battery: It can be recharged. As long as the engine is running, whether you're driving the car or simply letting it idle at a stoplight or in neutral, the electric current produced by the generator or the alternator restores the electrochemical energy of the battery by reversing the redox reaction. The current enters the battery and reconverts the lead sulfate and water into sulfuric acid, spongy lead metal, and lead dioxide.

charge: $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$ (−2.04 volts, which we again round off to −2 volts)


Using a hydrometer.

The negative potential of the redox reaction tells us that a battery won't recharge itself spontaneously. (Common sense tells us the same thing.) To carry out this redox reaction electrical energy must be put into the battery, as we saw in Section 6.12.

Notice that the electrical potential produced by the discharge redox reaction is 2 volts. The case of the standard 12-volt automobile battery actually encloses six of these 2-volt cells in series, head-to-tail as in a flashlight.

Notice also that in the chemical reaction taking place during discharge, water replaces the sulfuric acid in the solution that bathes the plates. Since water is much less dense than sulfuric acid, the density of the fluid inside the battery drops as current is drawn from the battery and rises as the battery is recharged. Because of this, the density of the fluid in the battery serves as a good indicator of the battery's condition. A simple *hydrometer*, an instrument that measures the density of fluids, can be used to test the condition of auto batteries, at least those with removable caps on their cells. After some of the fluid of a cell is drawn up into the hydrometer the position of a float indicates the fluid's density. If the float shows that the density of the fluid in all six cells is low, the battery needs to be recharged. On the other hand, one cell with a density far out of line with the other five often indicates that the cell is defective and isn't being recharged fully as the engine runs.

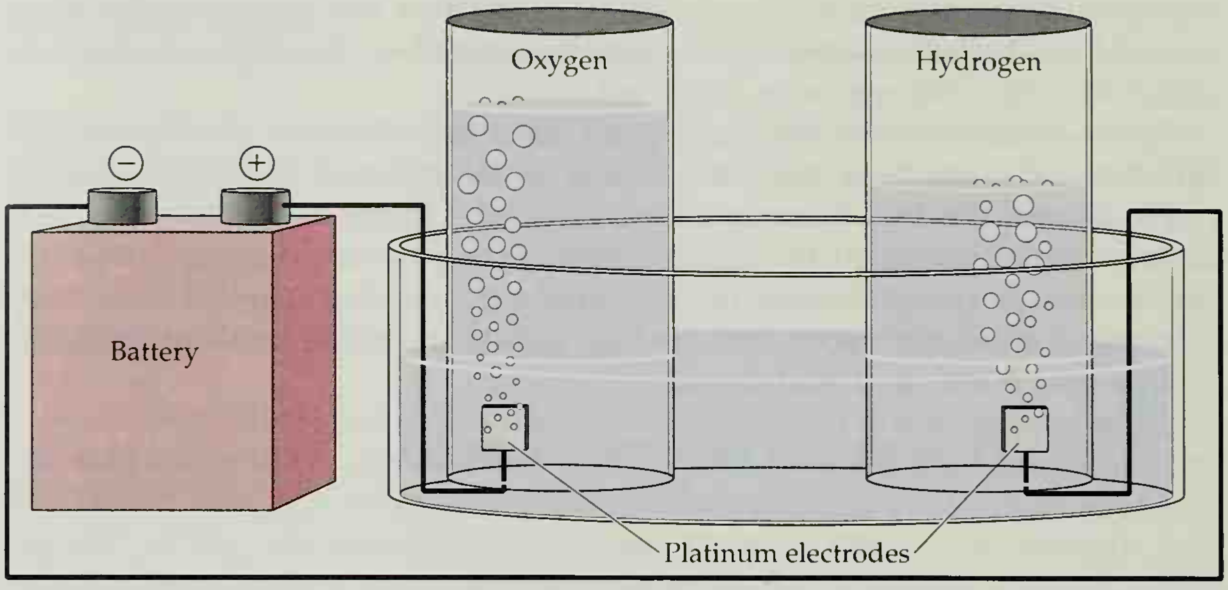
QUESTION

What change takes place in the density of the battery fluid as the battery is recharged by the generator or alternator? Explain you answer. ____________________

6.17 Niagara Falls Fights Typhoid

With one exception, all the reactions we've seen in this chapter produce an electric current or a voltage by means of a chemical change occurring in a battery. In that single exception, the recharging of a lead–acid storage battery, electrical energy supplied to the battery *produces* a chemical change within it. Lead sulfate and water are transformed into lead, lead dioxide, and sulfuric acid.

Figure 6.10
The electrolysis of water.



Electrolysis is the decomposition of a substance by means of electricity.

Electrical energy can also be used to generate a variety of other chemical changes that don't occur spontaneously, including the **electrolysis** of water into hydrogen and oxygen. The suffix *-lysis* implies a cleavage, rupture, or decomposition; with electrolysis a substance is decomposed into its component parts by means of electricity. In 1800 William Nicholson, an English writer, lecturer, and experimenter in what was then known as "natural philosophy," read Volta's newly published description of his Volta pile (Section 6.8) and built one of his own. He attached two platinum wires and used them to pass an electric current from the pile through a container of water. The resulting electrolysis of the water produced bubbles of what proved to be hydrogen gas at one wire and oxygen at the other, always in a constant ratio of two volumes of hydrogen to one of oxygen (Fig. 6.10). The consistency of this ratio provided early evidence that a water molecule contains twice as many hydrogen atoms as oxygen atoms.

$$2\ H_2O \xrightarrow{\text{electrolysis}} 2\ H_2 + O_2$$

$2\ H_2O$		$2\ H_2$	+	O_2
two molecules of water		two molecules of hydrogen, each containing two hydrogen atoms		one molecule of oxygen, containing two oxygen atoms

Today electrolysis represents a valuable process in the chemical industry, useful for generating a variety of commercially important chemicals. The electrolysis of a solution of sodium chloride in water, for example, produces chlorine gas at the anode (from oxidation of the chloride ions in the solution) and hydrogen at the cathode.

At the cathode a net reduction of water's protons to H_2 leaves the hydroxide anion, OH^-, in the remaining solution. The combination of this anion with Na^+ left over from the oxidation of the chloride anions results in the formation of NaOH, *sodium hydroxide*, within the remaining solution.

$$Na^+ + OH^- \longrightarrow \underset{\text{sodium hydroxide}}{NaOH}$$

Sodium hydroxide is an important industrial chemical, useful in the production of a variety of commercial products. As a direct consumer chemical itself, though, its application is limited to use as highly caustic *lye* for opening clogged sinks and drains. It is an extremely corrosive and hazardous substance that must be used with great care.

Electrolysis on a commercial scale consumes enormous quantities of electricity and can be carried out economically only in regions where electric power is cheap and plentiful. In one of these locations, Niagara Falls, the power of falling water is harnessed to provide the needed energy. The chlorine produced in the electrolysis reaction is a valuable industrial raw material for manufacturing a large number of consumer products ranging from simple, rugged plastic plumbing fixtures to pharmaceuticals with intricate and complex molecular structures.

As a strong oxidizing agent, chlorine provides an important tool for safeguarding the public health. Its oxidizing power makes it deadly to bacteria, including those that cause typhoid fever. The large-scale chlorination of public water supplies, of swimming pools, and of sewage, made possible by the commercial production of inexpensive chlorine, has played a major role in eliminating epidemics of typhoid fever and other public health threats in developed nations. (Chlorine gas is deadly to humans, too. It was one of the poison gases used in the trench warfare of World War I.)

QUESTION

What three chemicals are produced through the electrolysis of sodium chloride solutions? What three chemicals do you think would be produced by the electrolysis of a solution of sodium bromide? ____________________

6.18 Corrosion and Rust: The Other Side of Redox

Up to this point we've examined some of the more useful aspects of oxidation and reduction chemistry: storing and obtaining electrical energy from batteries, and producing useful chemicals by electrolysis. There's another, undesirable side of redox though: **corrosion.** Although we normally think of corrosion as affecting metals, it's defined more generally as the erosion and distintegration of any material as the result of chemical reactions. The term **rust** applies more often to the corrosion of iron that produces various scaly, reddish-brown oxides of iron, combinations of iron and oxygen of various chemical formulas.

Corrosion is the erosion and disintegration of a material resulting from chemical reactions. **Rust** is the corrosion of iron to form various reddish-brown oxides of iron.

Corrosion of various kinds does billions of dollars of damage each year in the United States. The redox reaction of metals, of which rusting is only one example, is accelerated by moisture, the presence of acids or bases, and various pollutants of the air and water. Because of the variety and complexity of the chemical reactions that lead to corrosion, we'll consider here only a few that affect us most directly. One results from the direct oxidation of metals that are exposed to air and water. (Here we're using *oxidation* in a more conventional sense, the combination of something with oxygen.)

The direct oxidation of metals in the presence of air or water results from a series of redox reactions involving a combination of the metal itself, oxygen, and water. Iron, for example, rusts more rapidly in humid air than in dry air. These reactions result in the formation of *metal oxides*, chemical combinations of the metal and oxygen. Perhaps surprisingly, the formation of these oxides can either accelerate the corrosion or retard it, depending on the nature of the metal and the oxide it forms. Iron rusts rapidly because its oxides are granular and flaky. Once formed, they fall or rub off the metal easily and expose fresh surfaces to additional corrosion. Aluminum, too, reacts quickly with oxygen to form *aluminum oxide*, Al_2O_3. This aluminum oxide, unlike the oxides of iron, forms a thin, tough, protective coating on aluminum that retards further oxidation. Thus, although aluminum metal *oxidizes* easily, it is highly resistant to *corrosion*.

Galvanizing is a process that provides a protective zinc coating to metals.

The largest commercial use for metallic zinc isn't in manufacturing batteries, but rather in **galvanizing** other metals, especially iron and steel products, to provide them with a thin surface film of zinc metal that protects them from corrosion (chapter-opening demonstration). The galvanizing is carried out by dipping the metal into hot, molten zinc, by spraying the molten zinc onto the metal's surface, or by reducing zinc cations directly on the metal surface through an electrochemical redox reaction. The zinc protects iron products by reacting with components of the atmosphere to form a protective film, much as aluminum does, and also through its greater ease of oxidation than the iron it's protecting. If the coating of zinc should crack in spots so that the iron's surface becomes exposed to the atmosphere, the zinc metal corrodes before the iron does. In essence, the zinc is used as a sacrificial metal to protect the more valuable iron.

Of course, some metals are simply inherently resistant to any form of corrosion. Gold's high resistance to oxidation (and other forms of corrosion as well), coupled with its ability to conduct electricity well, make it useful as a coating for electrical connections. Since the ability of the gold coating to conduct a current is high to begin with and doesn't deteriorate through corrosion, many of the more expensive units of stereo and other electronic equipment, for example, use gold-coated parts and connectors.

Galvanic or **bimetallic** corrosion results from the contact of two different metals separated by a thin layer of electrolyte.

Another form of corrosion results from the contact of two different metals separated by a thin layer of electrolyte. Because it results from the generation of an electric current between the two metal parts, it's sometimes called **galvanic** or **bimetallic** corrosion. This type of corrosion occurs when two different metals, with different reduction potentials, are in close contact and are separated by an electrolyte. It results in corrosion from the same sort of redox reaction we saw in the Daniell cell. Anyone who has teeth containing metallic fillings and has inadvertently bitten a piece of metal foil has felt the jolt of the electric current generated in galvanic corrosion. This kind of corrosion is most severe in metallic objects, such as boating equipment, that are in constant contact with salt water.

QUESTION

What is *galvanized* metal? Describe two ways galvanizing helps keep iron from rusting. ______________________________

PERSPECTIVE: Electrochemical Reactions for the Cars of Yesterday . . . and Tomorrow?

One of our themes in this survey of the extraordinary chemistry of ordinary things concerns our use of energy. In this chapter we've investigated how we use the transfer of electrons between chemical particles to produce energy from one of the most ordinary of our everyday things, the common battery. Another theme we touch on in this book is the application of chemistry to the needs of society. These two themes come together here as we ask whether we can use the energy delivered by an electrochemical cell as an alternative to the gasoline and diesel fuel that run our cars, trucks, and buses.

Not long ago, a large part of the Middle East was devastated by a war fought, in part, because of a threat to the supplies of imported petroleum that furnish much of our gasoline and related fuels. We ask in this section whether we can use the chemistry of oxidation and reduction reactions to diminish or even eliminate completely our reliance on these petroleum-based fuels. Can we run our cars on electric batteries? Years ago, the answer was yes. Today the answer is neither certain nor simple.

To understand why, let's first look at its principal competition, the gasoline engine. The original four-stroke internal combustion engine, the kind that runs on gasoline, was built in 1876. With the many improvements that have been made over the years, we now use this same engine in today's cars. (We'll describe the operation of the internal combustion engine and the chemistry of gasoline in Chapter 8.) In 1900, though, this gasoline-powered internal-combustion engine ran only a very small minority of the automobiles then in existence. At the beginning of the 20th century steam-powered cars and cars that ran on electric batteries dominated the marketplace, sharing the road almost equally. Combined, they outsold cars with gasoline engines by better than three to one. Yet of about 3,500,000 cars on the road by 1917, only 17 years later, all but some 50,000 ran on the same sort of gasoline engines we use today. Steam-powered cars had all but disappeared and the electric car was dying rapidly. The electric cars in existence today are no more than experimental cars, or have only specialty uses, such as golf course carts.

The causes of the death of the electric car were varied and complex. They included improvements continuously made to both the internal combustion engine and its associated transmission, as well as disadvantages inherent in the electric car that turned buyers toward the steadily improving gasoline-powered engine. Among these were the limited driving range and low speed of the electric car and the great weight and the long recharge time of its batteries. Other factors were at work, too, such as subtleties of consumer and producer psychology of those years.

Can today's technology revitalize the electric car? Perhaps, but even with today's advanced batteries, gasoline provides, pound for pound, roughly 600 times the power of a charged battery. Expense is another factor. It's estimated that today a commercially feasible, electric minivan run by the most advanced batteries would cost some $6000 more than a conventional, gasoline-powered model. Yet we may soon find that the societal costs of continuing our reliance on petroluem-based fuels outweigh the financial costs and perceived inconvenience of an electric car. Automobiles powered by electricity would not pollute the atmosphere as our current versions do, and over a period of years their lower costs of operation and maintenance could make them more economical to own than gasoline-powered cars. Add to that a potential decrease in our reliance on imports of oil.

So there's still another question to be answered, in addition to whether the electric car *can* be reborn. Do we *want* it to be reborn? Recharging an electric battery takes many hours, probably overnight. Replacing a run-down battery with one that's fully charged, at a roadside "battery station," could be a cumbersome process, with little of the speed or convenience of refilling a gas tank. Driving ranges would be only a bit over a hundred miles. Top speeds would be much less than the internal combustion engine allows. The car might be limited to short trips within a city.

There's yet another, indirect, problem that would have to be faced. If rechargeable batteries replaced gasoline tanks on our roads, where would we get all the additional, commercially generated electric power to recharge all those batteries each day? Electric power is, after all, just another form of energy. Would we have to import even more oil to generate the additional electric power, or would we turn to nuclear power?

The choice might eventually come down to one between cleaner air and, possibly, a greater independence from imported oil on the one hand, and increased nuisance, inconvenience, and perhaps expense on the other. Would it be worth it?

Of course, there may be still another way to use electricity, indirectly, to run our cars. We may be able to operate them on hydrogen produced by the electrolysis of water (Section 6.17). Using water and electricity to generate hydrogen through electrolysis would furnish a fuel that burns to produce little more than water vapor and energy. The electrolysis might be carried out at central locations, where electricity is cheap and plentiful, and the generated hydrogen transported throughout the country much as gasoline is today.

Elemental hydrogen is a highly flammable gas, though, and its use in cars would require sophisticated fuel transportation and refueling technology. Moreover, with its boiling point of about −253°C, some way would have to be found to keep it liquified within the car's fuel tank, or absorbed into a solid somewhat as water is held by a sponge. Nonetheless, hydrogen-powered cars could give us the ultimate "clean" or nonpolluting engine.

$2H_2$	$+$	O_2	$\rightarrow$	$2H_2O$	$+$	energy
two molecules of hydrogen	and	one molecule of oxygen	combine to produce	two molecules of water	and	energy

Certainly much work must go into the development of cars like these if they are to be commercially successful. Experimental cars that run on batteries, on hydrogen, and on yet other sources of energy, even sunlight, are currently being built and tested. Still, the future of the automobile may lie in electrochemical reactions of one kind or another. Considering the history of the automobile, if the car of the future were to run on batteries it could well turn out to be the car of the past.

We'll turn now, in the next few chapters, to a discussion of the electrons that are shared between atoms as covalent bonds. We'll see how these shared electrons hold atoms together in molecules of specific sizes and shapes, how they form the basis of *organic chemistry*, which is the chemistry of carbon compounds, and how they provide us with energy through the combustion of gasoline, natural gas, and other fossil fuels.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

A ______ reaction is one involving two ______ reactions, one of them an oxidation, the other a reduction. When a substance is oxidized it ______; when a substance is reduced it ______. The energy of the gain or loss of electrons is described in terms of an electrical unit, the volt, and is shown in a table of experimentally measured ______. If the sum of the potential of the oxidation half-cell and the reduction half-cell is ______, the redox reaction they form will occur spontaneously, with the release of energy. If the sum of the voltages is ______, the redox reaction will not occur spontaneously and so energy must be added to the mixture (or to the substance) if a reaction is to occur.

An early version of an ______ was the ______, which used the oxidation of metallic ______ and the reduction of ______ ions to generate an electrical voltage. A more modern version is the ______, which uses a redox reaction consisting of the oxidation of ______ and the reduction of ______ to generate the electrical current needed to start an automobile engine. Electrical energy is returned to the battery as an electrical current produced by the car's generator or alternator converts ______, the product of the energy-liberating redox reaction, back into lead and lead dioxide.

copper
Daniell cell
electrochemical cell
gains electrons
half-cell
lead
lead–acid storage battery
lead dioxide
lead sulfate
loses electrons
negative
positive
redox
standard reduction potentials
zinc

2. Define, describe, or explain each of the following:

a. anode
b. cathode
c. electric current
d. electrical circuit
e. electrochemical reaction
f. electrolysis
g. oxidation potential
h. oxidizing agent
i. reducing agent
j. salt bridge

3. What element is used to coat "galvanized" metal products?

4. What happens when the anode and cathode of an electrolytic cell are connected to each other?

5. What's the common term we use for the commercial electrolytic cells we use to provide power to our portable flashlights and radios?

6. (a) What metal makes up the outer casing of a common or heavy-duty flashlight battery? (b) What is the function of that metal? (c) What element makes up the porous rod that forms the inner core of the battery? (d) What is that rod's function? (e) What three compounds, other than water, make up the bulk of the battery's interior?

7. What is the function of the three compounds that make up your answer to Question 6e?

8. What substance does an "alkaline" battery contain in addition to the three compounds referred to in Question 6e?

9. Do electrons move from oxidizing agents to reducing agents or from reducing agents to oxidizing agents?

10. What determines whether such a movement of electrons will actually take place and whether the redox reaction it represents can occur spontaneously?

11. How can you cause a reaction with a negative redox potential to occur?

12. You are given a table of standard reduction potentials. (a) How do you determine the *reduction* potential of a reduction half-cell? (b) How do you determine the *oxidation* potential of an oxidation half-cell? (c) How do you determine the redox potential of a redox reaction?

13. What reaction is used as the reference point for all standard reduction potentials?

14. Which one of the following has the greatest tendency to acquire an electron? Which has the greatest tendency to lose an electron? (a) Zn^0, (b) Cl^-, (c) Br_2, (d) Cs^+, (e) a mixture of $PbSO_4$ and H_2O, (f) H^+, (g) H_2O, (h) Cl_2.

15. Why is a substance that is very easily *reduced* considered to be a good *oxidizing* agent?

16. Name and write the chemical formulas of all the products produced on electrolysis of (a) pure water, (b) a solution of sodium chloride in water, (c) a solution of potassium chloride in water.

17. Potassium is a hazardous metal that reacts rapidly and explosively with water. In contact with water potassium produces potassium hydroxide (KOH) and hydrogen gas, which ignites as a result of the heat generated in the reaction. (a) In view of this (and referring to the table of standard reduction potentials), can water act as an oxidizing agent? (b) Can water can also act as a reducing agent? (c) Name two halogens that water is capable of reducing.

18. What determines whether a substance that, like water, can act as either an oxidizing agent or a reducing agent does, in fact, act as an oxidizing agent or a reducing agent?

19. What is the effective oxidizing agent in liquid household bleach? Explain your answer.

20. Give one reason why a redox reaction with a positive redox potential may not appear to take place.

21. (a) What is the difference between the *oxidation* of a metal that's caused by components of the atmosphere and the *corrosion* of a metal that's caused by components of the atmosphere? (b) Give an example of oxidation of this kind that *accelerates* corrosion. (c) Give an example of oxidation of this kind that *protects against* corrosion.

22. Why are parts of high-quality electronic equipment sometimes coated with gold? What properties of gold make it useful in this application?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

23. What voltage would you obtain from a Daniell cell made of copper and silver sheets and solutions of their cations?

24. What, if anything, would you expect to observe if you put

a. a strip of zinc metal into a solution of copper sulfate
b. a strip of magnesium metal into a solution of copper sulfate
c. a strip of copper metal into a solution of zinc sulfate
d. a strip of copper metal into a solution of magnesium sulfate
e. a strip of silver metal into a solution of copper sulfate
f. a strip of copper metal into a solution of silver sulfate

25. The lead–acid automobile battery consists of plates of spongy lead and plates of lead dioxide. As the battery discharges, the lead and the lead dioxide are converted to lead sulfate. Would a similar battery consisting of plates of spongy lead and plates of *lead sulfate* provide any current? If your answer is yes, what voltage would you expect? If your answer is no, explain why it would not work. Repeat this question for a battery consisting of plates of lead dioxide and lead sulfate.

26. How do we manage to get 12 volts from a car battery when the redox voltage of the electrochemical reaction taking place within it is only 2 volts?

27. Suppose we modify the table of standard reduction potentials and define the reduction of F_2 to fluoride ions as our standard, replacing the reduction of hydrogen ions to H_2, which is the current standard. If we now define the reduction potential for fluorine as zero (arbitrarily, just as the reduction potential of hydrogen ions to H_2 was originally defined arbitrarily as zero).

a. How would this change all the other values in the table?
b. What would be the new reduction potential for hydrogen ions?
c. How would this change affect the *measured* value for the voltage of the Daniell cell?
d. How would this change affect the *calculated* value for the voltage of the Daniell cell?
e. Would we still be able to use the new table to

determine whether a redox reaction can occur spontaneously?

f. If your answer to part e was yes, explain how we would now use our modified table.

g. If your answer to part e was no, explain why we would not be able to use our modified table for this purpose.

h. Does it matter which reduction reaction we choose as our standard? Explain.

i. Why do you think the reduction of hydrogen ions was chosen as the standard?

THINK, SPECULATE, REFLECT, AND PONDER

28. The more expensive, "heavy-duty," "longer-lasting," or "longer-life" carbon–zinc batteries have cups made of thicker zinc than the less expensive, "standard" carbon–zinc batteries. Why? How does a thicker shell of zinc help extend the operating life of a battery?

29. Is it possible to construct a battery that consists of only one, single half-cell? Explain.

30. Household bleach is normally used to *remove* colored stains from fabrics. Yet when we decolorize a solution of tincture of iodine with galvanized tacks, as we did at the opening of this chapter, adding household bleach *produced* a color in the nearly colorless solution. Explain why this happened.

31. Liquid household bleaches are good oxidizing agents. If you add a few drops of a liquid bleach to a clear, colorless solution of KBr in water, the solution turns orange-brown. What do you conclude from this observation? (Note: The products of the *reduction* of the liquid household bleach are colorless.)

32. Buffalo, New York, is a major center for the production of chlorine. Suggest a reason for this.

33. If we carry out the electrolysis of pure water, the reaction proceeds very slowly and produces oxygen at the positive terminal. If we add table salt to the water, the electrolysis proceeds much faster and produces chlorine at the positive terminal. Explain both of these phenomena and show that they are related to each other.

34. What does a table of standard reduction potentials tell us about the likelihood of an explosion when we mix two substances together? Explain.

35. A freshly constructed Daniell cell made of copper metal, copper sulfate, zinc metal, and zinc sulfate generates a voltage of about 1.1 volts. What voltage is produced by the same cell after it has been operating long enough to discharge completely the blue color of the copper sulfate solution and turn it completely colorless? Describe your reasoning.

36. Would a Daniell cell work equally well if the salt bridge were replaced by an ordinary copper wire of the type used with household electrical appliances? Explain your answer.

37. If a lead–acid battery is completely discharged, the fluid in all cells will show a uniform and very low density when tested with a hydrometer. Since sulfuric acid has a higher density than water, could the battery be recharged simply by removing the low-density, dilute sulfuric acid solution of the discharged battery and replacing it with higher-density, more concentrated sulfuric acid? Explain.

38. At least two factors determine how long the electrochemical cell can keep the two-potato clock running. One is the amount of zinc metal embedded in the potato. (The more zinc in contact with the potato, the longer there's a supply of zinc atoms for the oxidation half-cell.) What is another factor?

39. The Daniell cell uses metal plates of copper and zinc, and it operates through a redox reaction involving the oxidation of zinc atoms to zinc cations and the reduction of copper cations to copper atoms. The two-potato clock also uses metal plates of copper and zinc. The redox reaction that runs the clock uses an oxidation half-cell in which zinc atoms are oxidized to zinc cations. But there are virtually no copper ions present in a potato to take part in a reduction half-cell. Considering what you know about raw potatoes, as well at the table of standard reduction potentials, what do you think is being reduced as the two-potato clock operates?

40. Summarize your response to someone who tells you that the successful operation of a two-potato clock from wires plugged into two potatoes proves that potatoes provide you with healthful energy, since they are obviously capable of providing the clock with power.

41. Give an example of corrosion taken from a demonstration described in this chapter.

42. Give two reasons why electric cars eventually gave way to cars powered by the internal combustion engine.

43. What do you believe is the greatest superiority of an electric car compared with a gasoline-powered car? What do you believe is the greatest superiority of a gasoline-powered car compared with an electric car?

44. Would you be in favor of a federal regulation requiring that all cars now on the road be replaced by electric cars, over a reasonable period? Explain.

45. Submarines run on battery-powered engines when they are submerged and on diesel engines (a variation of an internal combustion engine) when they are on the surface. Why don't they run on battery-powered engines all the time?

46. A battery using a redox reaction that converts lithium metal to lithium cations and fluorine gas to fluoride anions would provide about 5.9 volts. Why is a battery of this composition unlikely to become a widely used consumer product?

47. You are the owner of a small firm that produces all kinds of electric batteries. You wish to develop a new battery that uses a redox reaction (with a positive redox potential) never before used in a commercial battery. What are some of the factors you have to consider in deciding whether to manufacture this new battery?

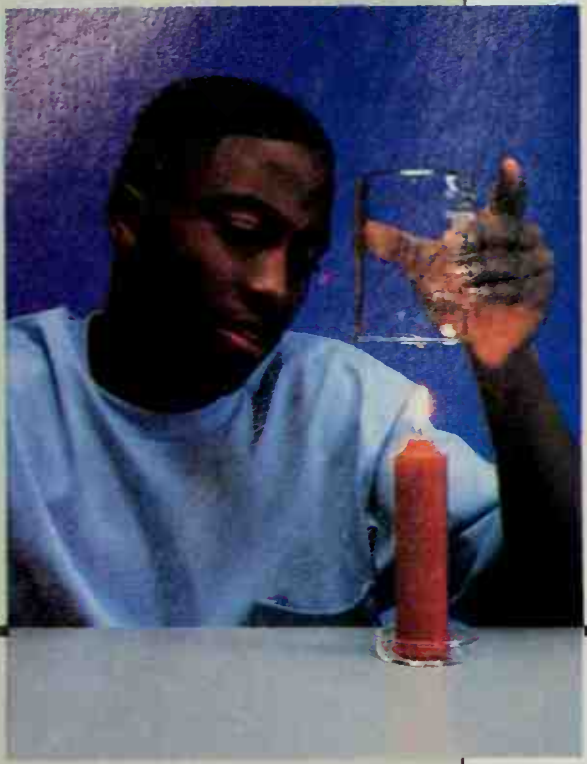
48. Some chemists claim that *all* chemical reactions are redox reactions. In the simple *ionization* of water, what is being oxidized according to this view? What is being reduced? Refer to Section 3.15.

An Introduction to Organic Chemistry

7

THE POWER OF HYDROCARBONS

The burning hydrocarbons of the candles produce light and heat.



A Candle Burning in a Beaker: Energy from Hydrocarbons

As important as the nuclear and electrochemical reactions of the previous chapters are, they provide us with only a small fraction of the energy we use to run the ordinary, everyday things of our lives. We get most of our energy by burning things. We burn gasoline and diesel fuel to run our cars, trucks, and buses. We burn jet fuel for our airplanes. We burn wood, coal, heating oil, and kerosene to heat ourselves. We burn natural gas for heating and cooking.

Much of what we burn, including gasoline, diesel fuel, jet fuel, heating oil, kerosene, and natural gas, belongs to the class of chemicals we call *hydrocarbons*. In this chapter and the next we'll examine these hydrocarbons as representatives of a branch of chemistry known as *organic chemistry*. We'll survey their structures and names and learn how we obtain these compounds from petroleum, how we use their energy to transport us across the earth, and how we modify their molecular structures to make them more useful to us. We'll examine as well some of problems we face as their combustion products pollute the earth's atmosphere and threaten to change our global climate through a phenomenon called the *greenhouse effect*. First, though, we can examine the effects of some of the chemical reactions we're going to discuss by the simple act of lighting a candle and inserting it into a cool, inverted laboratory beaker.

> **WARNING: Don't try what follows with an ordinary drinking glass.** The heat of the flame could cause the glass to crack or shatter. Common laboratory glassware is made of a special glass that expands and contracts very little during heating and cooling, so it's unlikely to break as the flame heats it.

If you light an ordinary household candle, which is composed of hydrocarbons, and insert it into a dry beaker at the temperature of a cool room (Fig. 7.1), you'll soon see the image of the flame grow less distinct as the glass surrounding it becomes fogged. Then the flame itself grows small and dim and, if the candle is far enough inside the beaker, the flame goes out. If you remove the candle and run your finger around the inside of the fogged

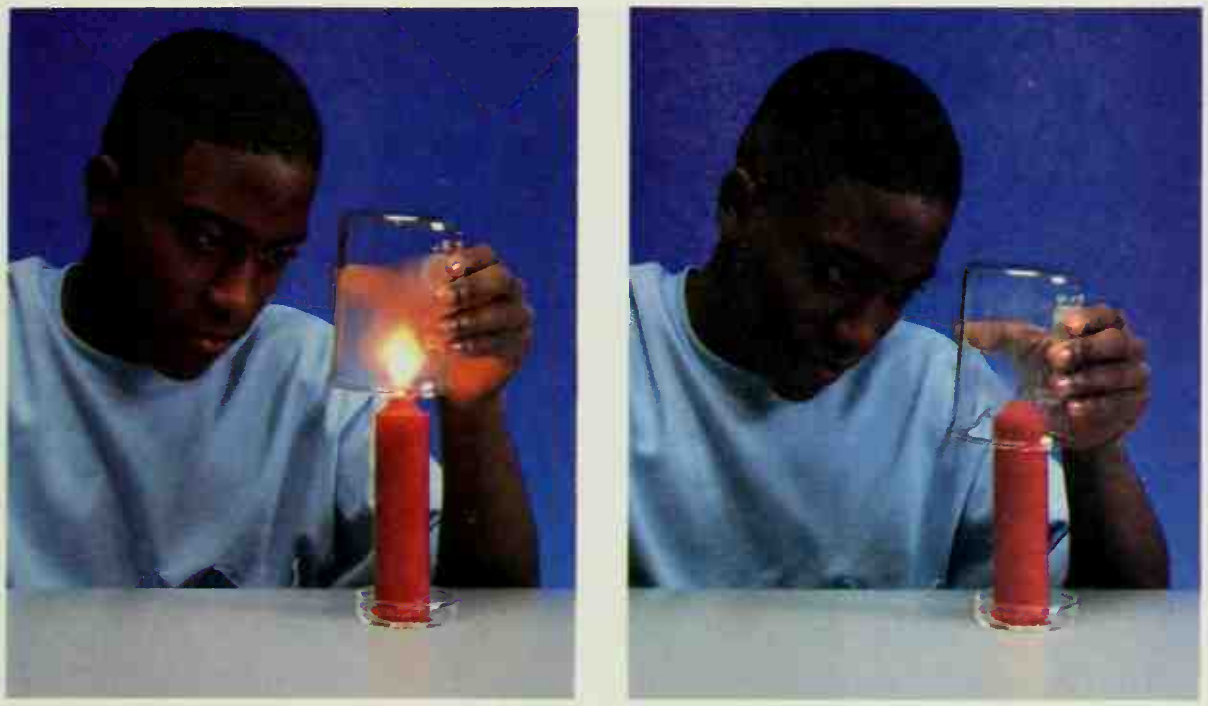


Figure 7.1
Observing the chemistry of a burning candle.
As you lower a beaker over a candle flame, you first see evidence of the water that is formed on combustion of the hydrocarbons. Then, as the oxygen in the beaker is replaced by carbon dioxide, the flame dies.

portion of the beaker, after it cools, you'll find that the fogged band inside the beaker is wet.

This chapter and the next are about the chemistry that caused all this. Our examination of the chemistry of the ordinary things of our daily lives moves outward now from the atomic nuclei and the valence electrons of the previous chapters to the shared electrons of covalent bonds and the molecules they hold intact. We move here from harnessing the energy of nuclear and electrochemical reactions to using the energy released by the combustion of hydrocarbons.

Since the compounds we'll examine, hydrocarbons, introduce us to the branch of chemistry known as organic chemistry, and since the term *organic* is itself applied in various ways in our society—we have "organic" foods, fertilizers, pesticides, gardens, fabrics, vitamins, and so on—and is sometimes poorly defined, we'll start by clarifying what we mean here by "organic."

QUESTION

What is one way we use the energy released by a burning candle? ____________

7.1 What's Organic about Organic Chemistry?

All life depends on water and on the compounds of carbon. Water furnishes the fluids of life, and carbon, in covalent combination with other carbon atoms and with atoms of hydrogen, oxygen, nitrogen, sulfur, and phosphorus as well, provides the molecules of life. Carbon compounds occur in all living things; no life exists without them. It is in these covalent compounds of carbon that we find the basis for all life.

Organic chemistry is the chemistry of carbon compounds.

The chemistry of carbon compounds is **organic chemistry**, a term bequeathed to us by the earliest chemists. Until about 150 years ago, at the dawn of modern chemistry, organic matter—substances obtained from things that are alive or were once alive—served as the only source of these compounds. *Ethyl alcohol*, for example, an organic compound whose intoxicating effects have been known from antiquity, has long been obtained from the fermentation of grains, which gives it the alternative name *grain alcohol*. Soap, another organic substance, has been made for centuries from fats (also organic) rendered from the bodies of slaughtered animals. Organic dyes and drugs of all sorts have been extracted for centuries from great varieties of plants. The red-orange dye *henna*, used in coloring hair and leather, comes from the lawsonia shrub; *quinine*, the first effective treatment for malaria, was originally isolated from the bark of South American trees. If you had lived as late as the first third of the 19th century and you had wanted one of these compounds, or any other compound of carbon, you would have had to isolate it from organic matter. There were simply no other sources.

Friedrich Wöhler synthesized urea in his laboratory in 1828. With this synthesis he ended the reign of the "vital force" theory of the formation of organic compounds.

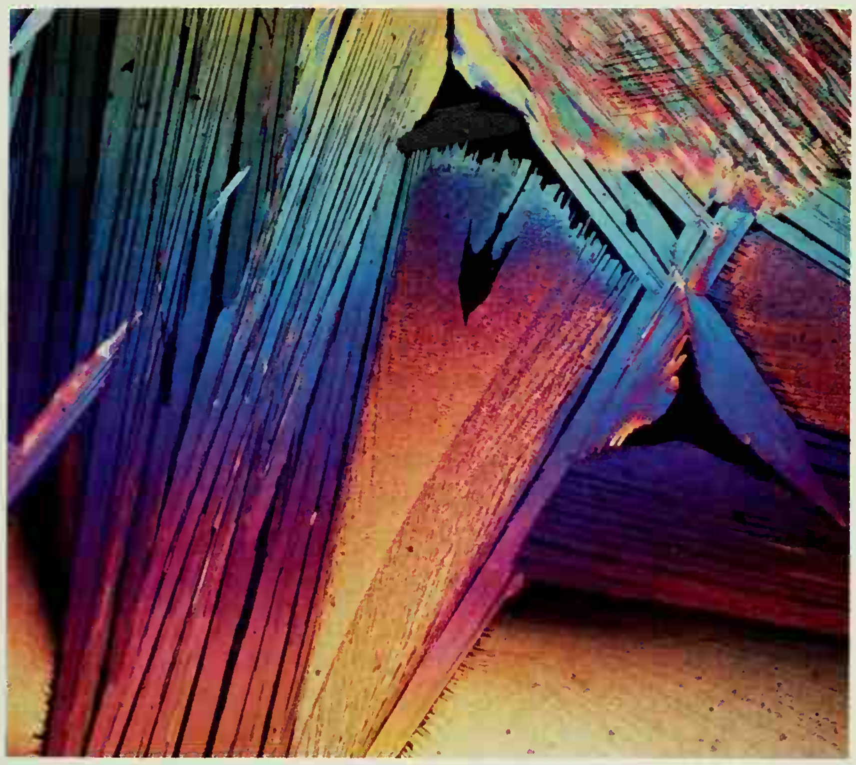
The "organic" mystique was so powerful in those years that it engendered a belief in a "vital force," which was supposedly possessed by all living things and was thought to be uniquely capable of producing the carbon compounds they contain. *Urea* illustrates the idea nicely. It is through urea, with its molecular formula CH_4N_2O, that almost all mammals excrete the unused nitrogen of proteins in their foods. Urea makes up 2 to 5% of human urine. First isolated in 1773, urea was considered "organic" in the sense that urea (so it was believed) could be generated only through the action of the mysterious vital force that exists only within living bodies, and not at all in the sterile glassware of the chemist's laboratory. Substances like the urea that come from living things were supposedly different in a very mysterious sense from those obtained from nonliving sources—water, for example—which were called "inorganic."

In 1828 the German chemist Friedrich Wöhler changed all this. His preparation of urea from ammonia (NH_3) and cyanic acid (HNCO), carried out in the apparatus of his chemical laboratory, proved that the idea of a "vital force" was irrelevant to the development of chemistry. The urea of Wöhler's laboratory was shown to be identical in every way with the urea formed in the bodies of mammals. Indeed, since Wöhler's work no difference has ever been demonstrated between the structure, properties, or behavior of a pure substance isolated from a living or once living thing and that very same pure substance prepared in a chemist's laboratory.

Inorganic compounds are compounds that do not contain carbon. **Inorganic chemistry** is the chemistry of compounds that do not contain carbon.

Since Wöhler's time, the term *organic* has lost its mysterious aura and has become simply the category of all compounds of carbon. The meaning of *inorganic* has changed too. Today, with only a very few exceptions, **inorganic compounds** are those that do *not* contain carbon and **inorganic chemistry** is the chemistry of these compounds. Ironically Wöhler, the chemist who changed the meaning of "organic" with his brilliant synthesis of urea, was himself an inorganic chemist. It was Wöhler who first isolated the elements aluminum, boron, and silicon.

Today, "organic" is once again acquiring meanings that suggest the operation of mysterious vital forces, as in "organic" foods, "organic" gardening, and "organic" vitamins. Chemically, however, Wöhler's work and the ideas that evolved from it remain unchallenged. Organic chemistry is neither more nor less than the chemistry of carbon compounds.



Crystals of urea.

Foods labeled and advertised as "organic."

QUESTION

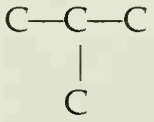
Describe briefly the significance of Wöhler's laboratory synthesis of urea. Was the urea prepared in Wöhler's laboratory different in any way from the urea formed in the bodies of mammals? Would you expect vitamin C prepared in a chemist's laboratory to be different in any way from vitamin C isolated from orange juice? Explain your answer.

7.2 Methane: A Hydrocarbon

Because a carbon atom contains four valence electrons it can form covalent bonds with as many as four other atoms at the same time. Carbon is therefore *tetravalent*. Carbon atoms themselves form strong bonds to hydrogen, oxygen, nitrogen, sulfur, and the halogens, as well as to other carbon atoms. What's more, when four or more carbon atoms bond to each other in a single molecule, the carbon atoms can all lie in a single, unbroken or *unbranched* chain, with each bonded to two others (except for the end carbons), or the carbon atoms can form a *branched* sequence, much as a twig can branch out. The unbranched sequence of carbons is sometimes called a *linear* or *straight-chain* sequence.

C—C—C—C

four carbons in an unbranched, linear or straight-chain sequence



$$\begin{array}{c}\text{C—C—C}\\ | \\ \text{C}\end{array}$$

four carbons in a branched sequence

With carbon's ability to

1. bond to as many as four other atoms simultaneously,
2. form strong bonds to atoms of several other elements, and
3. form molecules containing many and varied branches, as well as molecules composed of long, unbranched strings of carbons,

organic compounds present a complexity of structures and properties as varied as life itself. Perhaps 10 million organic compounds are now known, each with its unique molecular structure, name, and chemical and physical properties.

Families of compounds are composed of compounds of similar structure and similar properties.

Hydrocarbons are compounds composed exclusively of hydrogen and carbon.

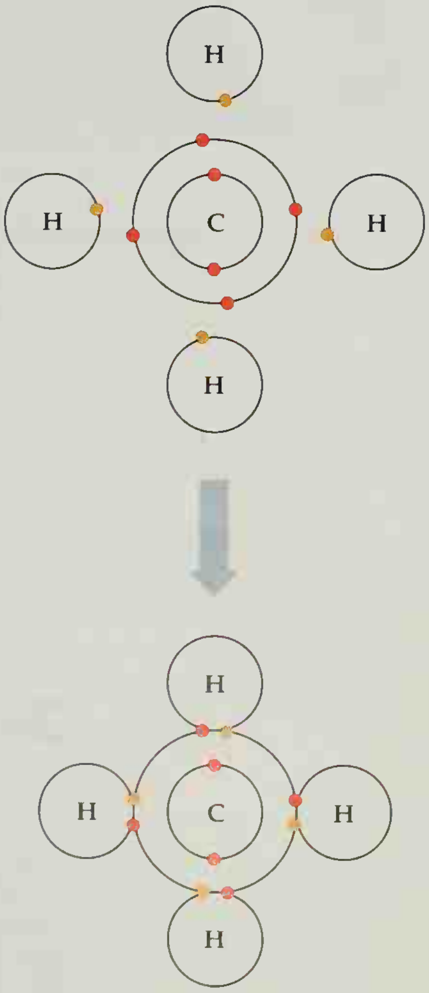
Stereochemistry refers to the arrangement of atoms in space.

A **tetrahedral carbon** is a carbon atom that lies at the center of a tetrahedron and that forms covalent bonds to the four atoms lying at the apexes or corners of the tetrahedron.

To bring a sense of order to this enormous number and almost incomprehensible variety of carbon compounds, chemists have organized them into **families** of compounds of similar molecular structures and similar properties. One of the largest of these is the family of **hydrocarbons,** composed exclusively of compounds containing just two elements, hydrogen and carbon. The very simplest of the hydrocarbons, with just one carbon atom per molecule and with the lowest molecular weight (Section 3.13) of all organic compounds (16 amu), is *methane*, CH_4.

Four shared electron pairs bond the four hydrogens of methane to its carbon atom (Fig. 7.2). In **stereochemistry,** which refers to *the arrangement of atoms in space*, methane is *tetrahedral*. That is, drawing straight lines from each hydrogen to its three neighboring hydrogens forms a tetrahedron, a geometric figure composed of four equilateral triangles joined along their edges. The carbon atom lies at the tetrahedron's center and the four hydrogens at its apexes or corners, with four covalent bonds pointing outward from the central carbon atom to the four corners (Fig. 7.3). Since the geometry of the four bonds extending from the central carbon fixes the stereochemistry of the molecule, we can visualize the carbon of methane, with its valence electrons, covalent bonds, and substituents all forming a tetrahedron, as a **tetrahedral carbon.**

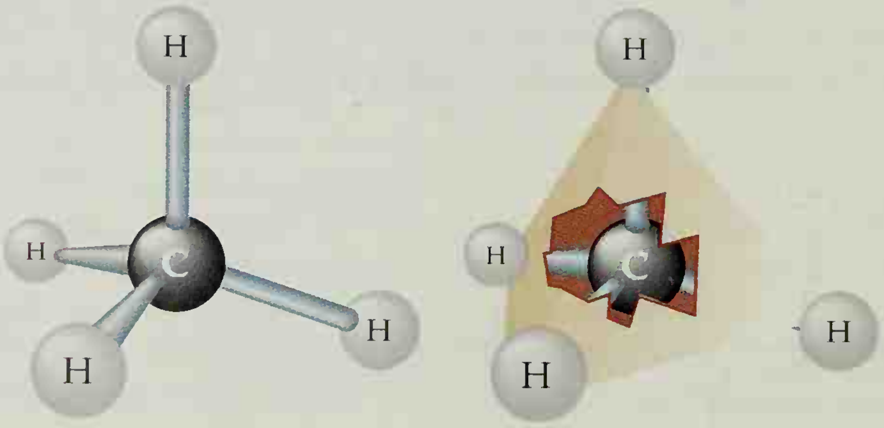
Figure 7.2
Methane, CH_4.



QUESTION

Carbon tetrachloride, CCl_4, was used for many years in fire extinguishers. Draw a diagram similar to Figure 7.2 to show the bonding in carbon tetrachloride. Show only valence electrons. ______

Figure 7.3
Methane and the tetrahedral carbon.



(Carbon tetrachloride was once used in fire extinguishers because it effectively excludes atmospheric oxygen from the fire, thus smothering the fire, and it is not itself flammable. Its use was discontinued for several reasons. Long exposure to carbon tetrachloride vapors can damage vital organs and has also produced cancer in laboratory animals. Moreover, at the very high temperatures produced by some fires, carbon tetrachloride can react with atmospheric oxygen to generate *phosgene*, a deadly gas that was used as a poison gas in World War I. Many commercial fire extinguishers now contain carbon dioxide, CO_2, which is as effective as carbon tetrachloride but without its harmful effects.)

7.3 From Methane to Decane: The Alkanes

Methane is not only the simplest of all the hydrocarbons; it's also the first and simplest member of a family of compounds known as the *alkanes*, which exists as a subset within the larger hydrocarbon family. We begin our examination of this alkane family by removing a hydrogen atom from a tetrahedral methane molecule to yield a *methyl* **free radical,** which is often shortened to the simpler *methyl radical* (Fig. 7.4). The distinguishing characteristic of a free radical is that it contains an unpaired electron.

A **radical** or a **free radical** is a chemical species that has an unpaired electron.

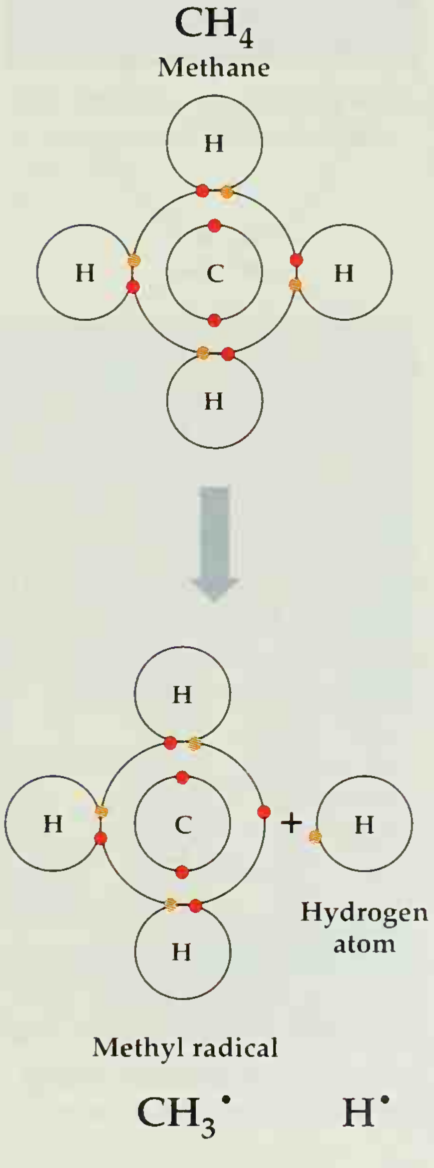
A detailed experimental study of atomic structures reveals that valence electrons tend to couple up in pairs. Sometimes, though, electrons remain unpaired, as though they were aloof. Any atom or group of bonded atoms that contains an unpaired electron is a free radical and reacts in ways different from atoms or groups containing only paired electrons. In the *methyl* free radical, the group of atoms that contains the unpaired electron is CH_3. This is the covalent structure that remains after methane has lost a hydrogen atom.

A hydrogen atom with its single electron is a free radical and so is a halogen atom, with six valence electrons paired into three sets of two electrons each and a seventh unpaired electron (Fig. 7.5). Free radicals such as these are usually highly reactive and often react so as to pair up their odd electrons with another electron, from another chemical species. The drive toward the pairing of electrons is a major force leading to the formation of covalent bonds. It results in the formation of diatomic molecules of hydrogen and the halogens and of other elements as well (Fig. 7.6).

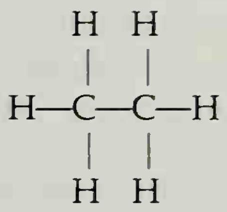
Like other radicals, the methyl radical is also highly reactive. Two of these radicals encountering each other join together to pair their odd electrons into a covalent bond and thereby form a new organic compound, the alkane *ethane* (C_2H_6), which is the second member of the alkane family. To emphasize the carbon–carbon covalent bond shown in Figure 7.7, we'll write the molecular structure of ethane as $CH_3—CH_3$. With the two odd electrons of the two methyl radicals paired up, there are no free radicals in ethane. Here and in other molecules in which the CH_3's are covalently bonded to other atoms, we call the CH_3's *methyl groups;* their carbons are *methyl carbons* and their hydrogens are *methyl hydrogens.*

Note that the molecular formula of ethane, C_2H_6, simply shows us that each of its molecules is made up of two carbon atoms and six hydrogen atoms. The molecular structure, though, shows explicitly the organization of the atoms within the molecule. The *full* or *expanded* structure shows all the covalent bonds; the *condensed* structure omits the carbon–hydrogen bonds. It's

Figure 7.4
Methane and the methyl free radical.



important to remember that even though we may write the structure of ethane as CH_3—CH_3, the covalent bond that's shown links the two carbon atoms of the methyl groups to each other.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

full or expanded structure of ethane

H_3C—CH_3

one way of writing the condensed structure, showing the C—C bond

CH_3—CH_3

a more common way of writing the condensed structure of ethane

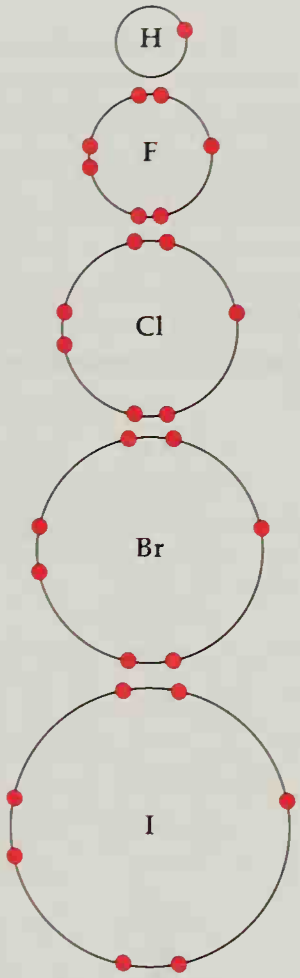


Figure 7.5
Valence shells of hydrogen and the halogens. Each atom is a free radical.

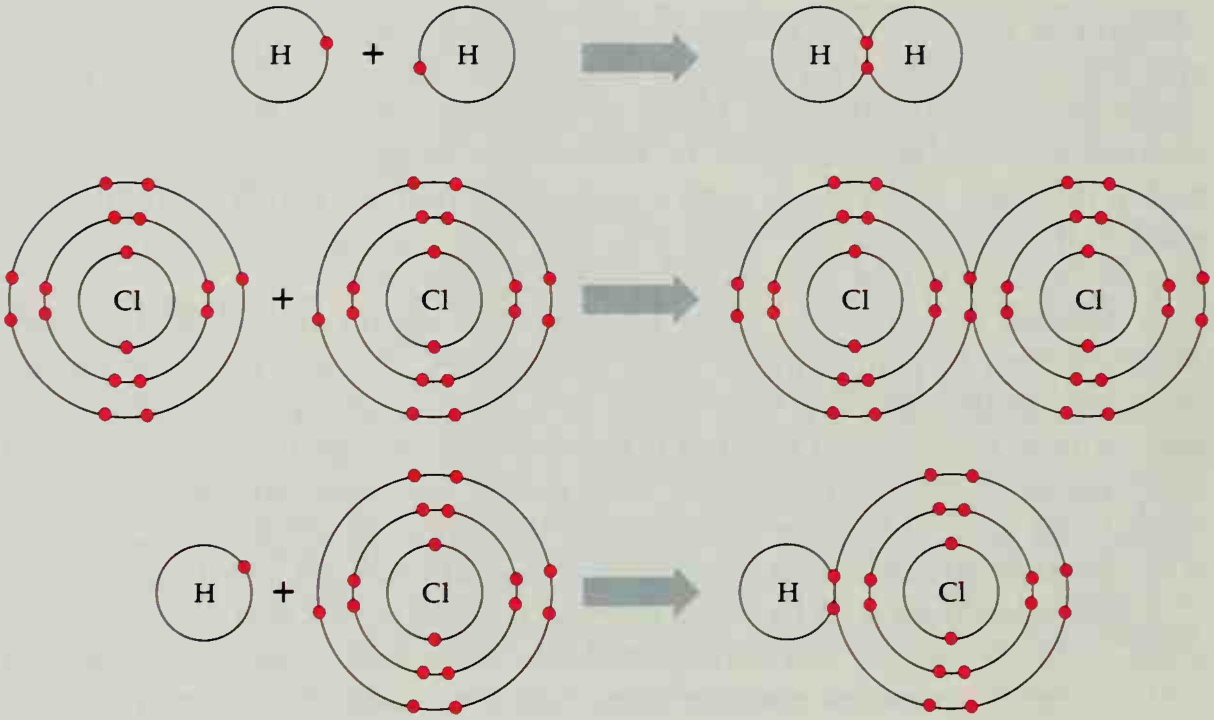


Figure 7.6
Formation of diatomic molecules of H_2, Cl_2, and HCl through the pairing of electrons.

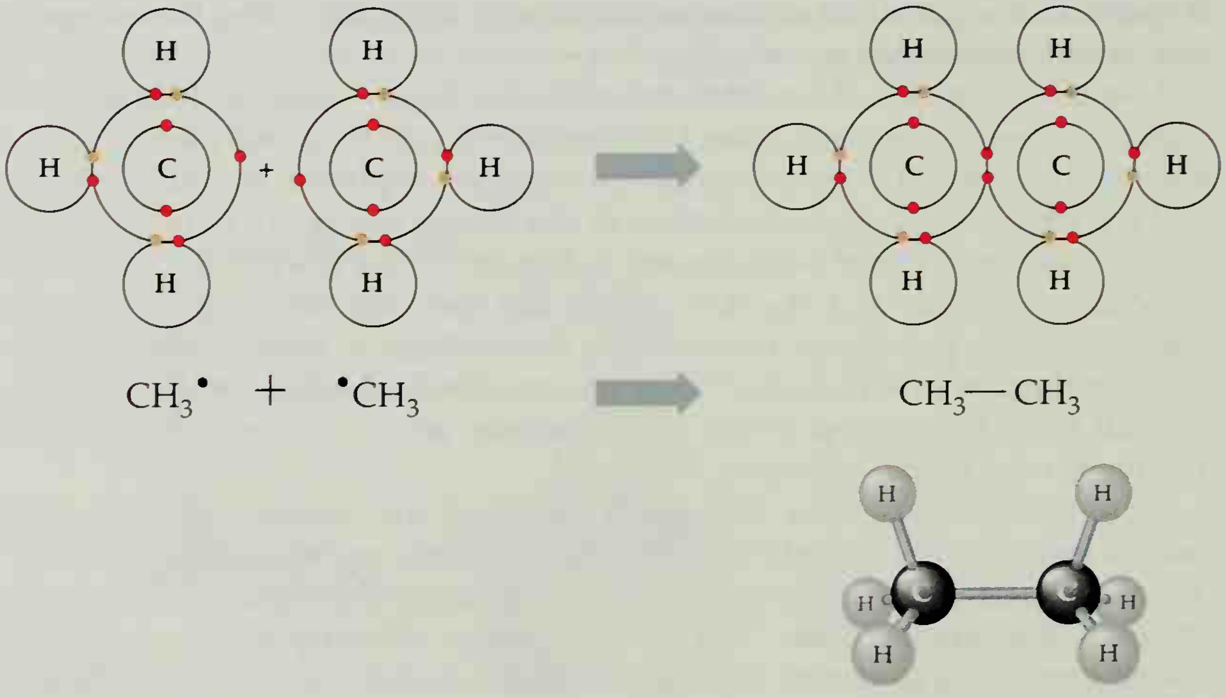


Figure 7.7
The combination of the methyl free radicals to form ethane.

Propane, C_3H_8 or $CH_3—CH_2—CH_3$, is the third member of the alkane family (Fig. 7.8). Notice that adding CH_2 (which simply represents one carbon atom and two hydrogen atoms) to the molecular formula of methane (CH_4) gives C_2H_6, the molecular formula of ethane, and adding CH_2 to ethane's molecular formula (C_2H_6) gives the molecular formula of propane, C_3H_8. Continuing this addition of CH_2 gives the molecular formulas of the entire alkane family, the first 10 members of which appear in Table 7.1.

The molecular formula of each member of the **alkane** series can be obtained from the *general formula* for alkanes, C_nH_{2n+2}, in which n represents the number of carbons in the alkane molecule. To get to the molecular formula of any particular alkane, simply write the numerical value of n as the subscript for the carbon, then double n and add 2 to get hydrogen's subscript. This general formula, in fact, defines the subset of hydrocarbons that we call the alkanes.

Alkanes as a class are compounds of very low toxicity. They are colorless and odorless. Methane, ethane, and propane, the lowest-molecular-weight members of the family, are all gases under ordinary conditions of pressure and temperature. They ignite easily when mixed with air and either burn or explode, depending on their concentrations in the air. Methane itself is the major component of the natural gas used for cooking and heating in some areas. Mixtures of about 5 to 15% methane in air are highly explosive; they are the dangerous *firedamp* that often forms in coal mines. Because methane and other alkanes are odorless, a small leak of natural gas itself, from a gas range for example, could remain undetected long enough to produce a flammable or explosive atmosphere in a building. Even without ignition the leak could prove deadly since the escaping gas, if it remained undetected, could displace the air in an occupied house and asphyxiate the occupants. To prevent such catastrophes, a small amount of an intensely odorous gas, usually an organic compound of sulfur called a *mercaptan*, is added to natural gas to give the gas a pungent odor and to ensure the early detection of any leak.

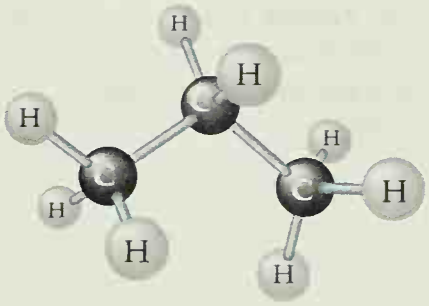
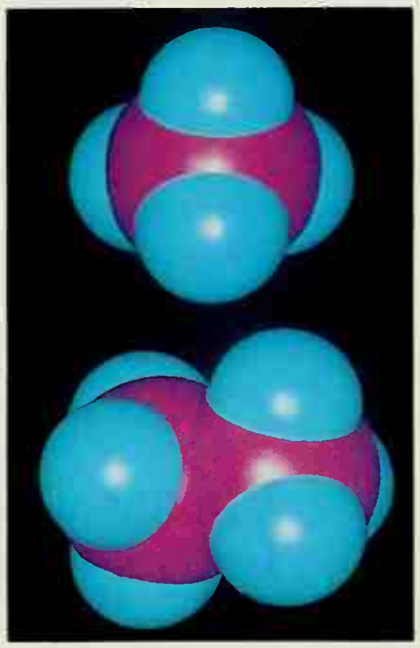


Figure 7.8
Propane.



Representations of molecules of methane, CH_4, and ethane, $CH_3—CH_3$.

TABLE 7-1 The First 10 Alkanes

Name	Molecular Formula
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$

Gasoline, a mixture of hydrocarbons. Their combustion provides the energy that moves our cars.

An **alkane** is a hydrocarbon whose molecular formula fits the general formula C_nH_{2n+2}.

Ethane has little direct application to consumer products, but propane is useful as the commercial fuel, LP gas (which we'll encounter again in Section 7.9). Several of the higher-molecular-weight alkanes, beginning with pentane, are liquids and are major components of gasoline (Chapter 8), while even larger alkanes are waxy solids at room temperature. *Eicosane*, for example, is a 20-carbon alkane that melts at 37°C. The candle wax of the demonstration that began this chapter consists of still larger alkane molecules.

Because of their very low toxicity the higher alkanes are useful as medical lubricants. Both mineral oil, an intestinal lubricant used as a laxative, and petroleum jelly are mixtures rich in alkanes.

QUESTION

Both the methyl free radical and the chlorine atom contain an unpaired electron. When two methyl free radicals combine they form ethane, $CH_3—CH_3$. When two chlorine atoms combine, they form a diatomic chlorine molecule, Cl_2. Write the condensed structure of the molecule that's formed when a methyl free radical combines with a chlorine atom. ______________________

7.4 Chemical Etymology: How Methane Got Its Name, etc.

Etymology is the study of origins of words; *chemical etymology* gives us a glimpse into the history of chemistry through the origins of chemical words. As implied in the 10 names in Table 7.1, all alkanes end in the suffix *-ane*. The root *meth-* of *methane* reflects this particular alkane's connection to *methyl alcohol*, also known as *methanol*, $CH_3—OH$. In 1661, the English natural philosopher Robert Boyle discovered methyl alcohol among the products formed as he heated wood until it decomposed, but in the absence of air so that it didn't ignite. From the time of Boyle's discovery until about 1930 his *destructive distillation* of wood was the major source of methanol and is still reflected in one of its more commonly used names, *wood alcohol*. Methyl alcohol is now made commercially from natural gas and coal.

Early in the 19th century the word *methylene*, or one of its derivatives, was applied to compounds related to wood alcohol. *Methylene* itself was coined from the Greek words *methe* ("wine") and *hylē* ("wood") with the intention of showing the connection between a host of chemical compounds and methyl alcohol, considered to be the "wine of wood." Thus methane, the one-carbon alkane, is related chemically to methyl alcohol, the one-carbon wine of wood.

Wood alcohol is the wine of wood only in the most poetic sense: methyl alcohol is highly toxic. (Since it attacks and destroys the optic nerve rapidly, blindness is one of the first symptoms of methanol poisoning.) Nonetheless this alcohol is a valuable industrial solvent and raw material. It's used in the manufacture of such diverse goods as plastics, jet fuels, and embalming fluid. It also shows promise as a replacement for gasoline as a fuel for the internal combustion engine. Mile for mile, methyl alcohol costs about as much as gasoline, but it has the advantage of producing fewer pollutants when it burns in a car's engine. On the other hand, methanol corrodes ordinary steel and delivers fewer miles per gallon than gasoline. Cars using methanol would have to be equipped with much larger fuel tanks and their entire fuel system, including the fuel tank, would have to be made corrosion resistant.

The etymology of the two-carbon alkane, *ethane*, is equally intricate. The *eth-* of ethane comes from the chemical name *ether* (more correctly, *diethyl ether*) given to the very volatile and very flammable compound $CH_3—CH_2—O—CH_2—CH_3$ to represent the ease with which it ignites and burns. *Ether* is taken from the Greek *aither*, meaning "to kindle," "to burn," or "to shine." The chemical ether itself gave its name to the two-carbon alcohol from which it was first prepared, *ethyl alcohol* (or *ethanol*), $CH_3—CH_2—OH$. The name *ethane* connects the two-carbon alkane to this two-carbon source of ether.

While ethyl alcohol is the intoxicating ingredient of beer, wine, whiskey, and other alcoholic beverages, it's also a useful industrial and commercial solvent and an intermediate in the manufacture of diverse consumer goods. The grain alcohol distilled from fermented grain, potatoes, and similar plant products (Section 7.1) isn't pure ethyl alcohol, but contains 5% water. Removing this last trace of water requires additional processing beyond simple distillation. The resulting pure, absolutely dry ethyl alcohol is sometimes called *absolute alcohol*. Another common form of ethyl alcohol is *denatured alcohol*, which is alcohol rendered unfit to drink through the addition of one or more adulterants, usually foul-smelling, bad-tasting, poisonous substances not readily separated from the ethyl alcohol. Denatured alcohol is often used in commercial processes since ethyl alcohol pure enough for human consumption is heavily taxed at federal level and local levels. The tax on denatured alcohol is far lower, making it an inexpensive commercial and industrial solvent.

The root *prop-* of propane, the third member of the alkane family, comes from *propionic acid*, a three-carbon acid that is the first in a series of organic acids that can be obtained from fats and oils. The word *propionic* was coined from the Greek words *protos* ("first") and *pion* ("fat"). Propane, the three-carbon alkane, takes its name from the three-carbon acid.

The next in the series of alkanes is the four-carbon hydrocarbon *butane* with its molecular formula of C_4H_{10}. The root *but-* connects butane with the four-carbon acid *butyric acid*, an acid that comes from butterfat and that gives rancid butter its peculiar taste and odor. *Butyrum* is the Latin word for butter.

As colorful as these roots are, with derivations that reflect the origins of the compounds they name, the rapid development of chemistry as a rigorous science demanded a more orderly approach to the naming of organic compounds. The system of nomenclature chosen as the 1800s progressed, and that is still with us, uses Greek or Latin roots to designate the number of carbons in the alkane molecules rather than to reflect their sources or chemical genealogies. Thus the alkane C_5H_{12} is *pentane* from the Greek *pente*, "five." Table 7.2 presents the names and molecular formulas of the first 10 alkanes and their derivations. Even though the names methane, ethane, propane, and butane do not reflect the number of carbons in molecules of these compounds, and are thus at odds with the system used for the higher alkanes, they are fully accepted as the only correct names of the first four alkanes.

TABLE 7.2 Origins of the Names of the First 10 Alkanes

Number of Carbons	Molecular Formula	Name of Alkane	Root	Meaning	Derivation
1	CH_4	Methane	meth-	wine wood	Greek *methe* Greek *hylē*
2	C_2H_6	Ethane	eth-	to burn	Greek *aither*
3	C_3H_8	Propane	pro- pion	first fat	Greek *protos* Greek *pion*
4	C_4H_{10}	Butane	but-	butter	Latin *butyrum*
5	C_5H_{12}	Pentane	pent-	five	Greek *pente*
6	C_6H_{14}	Hexane	hex-	six	Greek *hex*
7	C_7H_{16}	Heptane	hept-	seven	Green *hepta*
8	C_8H_{18}	Octane	oct-	eight	Greek *oktō*; Latin *octo*
9	C_9H_{20}	Nonane	non-	nine	Latin *novem*
10	$C_{10}H_{22}$	Decane	dec-	ten	Greek *deka*; Latin *decem*

QUESTION

Undecane, dodecane, tridecane, and tetradecane are the names of alkanes whose molecules contain 11, 12, 13, and 14 carbons, respectively. Write the molecular formula of pentadecane. ____________________

7.5 The Classes of Carbons and Hydrogens

Since there's only one way to put together a covalent molecule containing four hydrogens and one tetravalent carbon, there is, necessarily, only one possible three-dimensional molecular structure for methane, the one we saw in Figure 7.3. Furthermore, since each one of the four hydrogens of methane is entirely equivalent in every way to each of the other three, removing any one of the four hydrogens and replacing it with a methyl group gives one and only one ethane (Fig. 7.9). We can make a similar statement about ethane. Since each one of the six hydrogens of ethane is entirely equivalent to each of the other five, removing any one of the six and replacing it with a methyl group gives one and only one propane (Fig. 7.10).

With propane, though, we come to something new in alkane structures. We come to a molecule with more than one kind of hydrogen. Each of the two terminal, methyl carbons of propane bears three hydrogens, and all six of these terminal hydrogens are mutually equivalent methyl hydrogens (Sec-

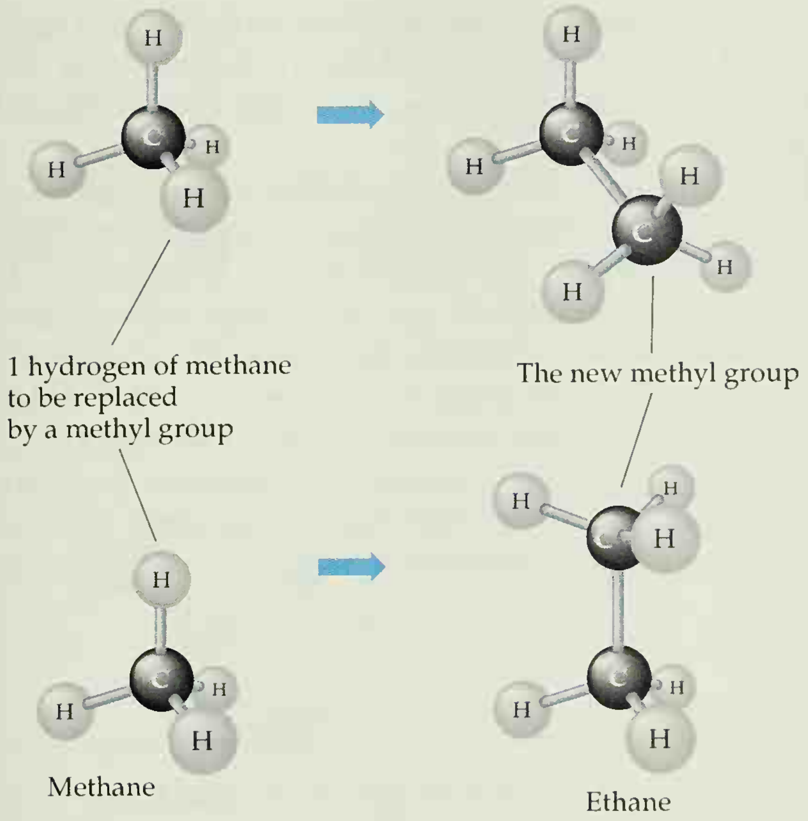


Figure 7.9
Forming one and only one ethane by replacing any one of the four equivalent hydrogens of methane with a methyl group.

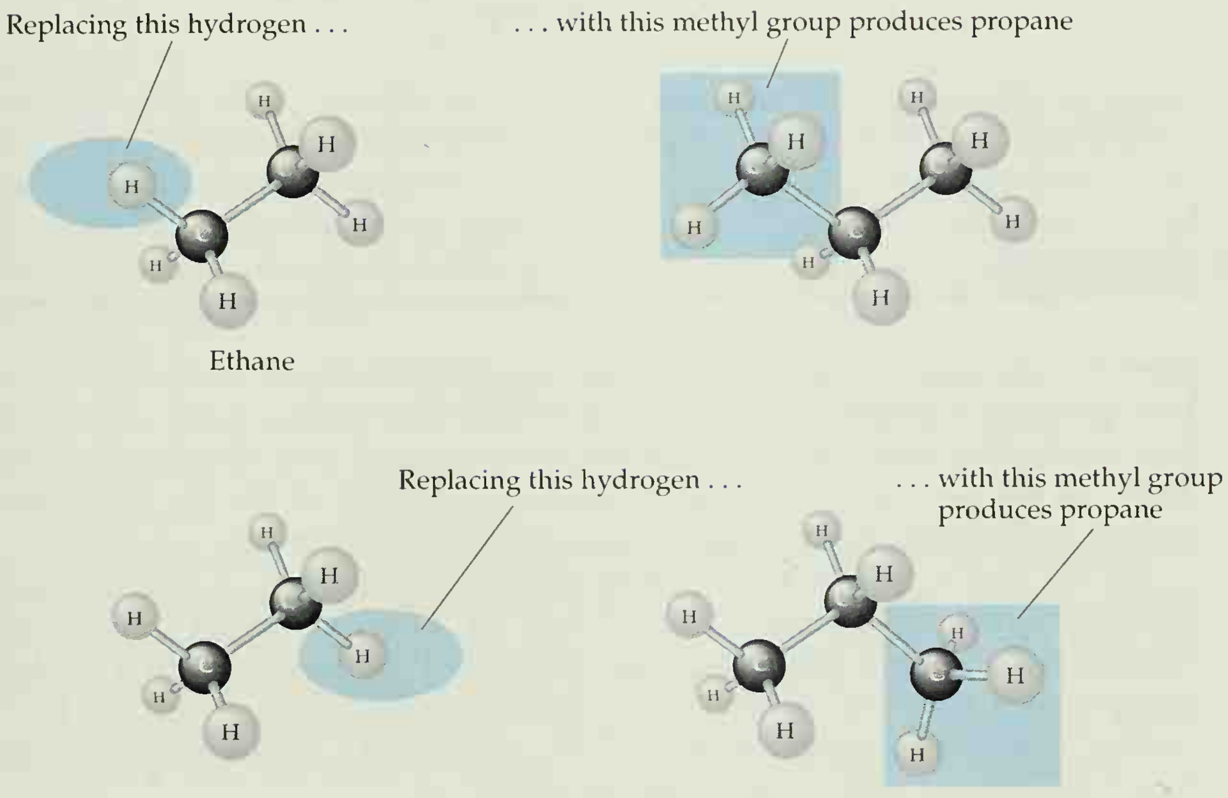


Figure 7.10
Forming one and only one propane by replacing any one of the six equivalent hydrogens of ethane with a methyl group.

tion 7.3). But they are all different from the two hydrogens bonded to propane's central carbon. That is, the six methyl hydrogens of the two methyl groups at the ends of the chain behave differently—have different chemical properties—from the two hydrogens of the central carbon, the —CH_2— group. A —CH_2—group is known as a *methylene group*, its carbon is a *methylene carbon*, and the hydrogens bonded to it are *methylene hydrogens*. Although these two terms, methyl hydrogens and methylene hydrogens, are widely accepted by chemists and useful for discussing the different kinds of hydro-

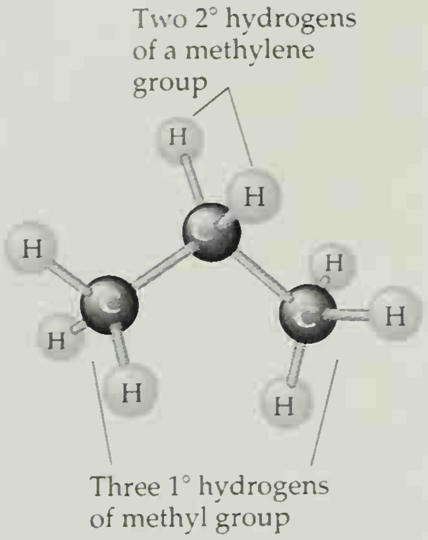


Figure 7.11
The 1° (methyl) and 2° (methylene) hydrogens of propane.

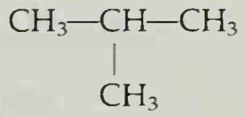
gens in a molecule, there's another, more precise way to describe them. That's by defining three different classes of carbons and the hydrogens that are bonded to them: primary carbons and hydrogens, indicated by the symbol 1°; secondary, with the symbol 2°; and tertiary, 3°.

Any carbon bonded to one and only one other carbon is called a **primary carbon,** and each of the hydrogens bonded to it is a *primary hydrogen.* Thus in propane we have the two 1° carbons of the methyl groups and their six 1° hydrogens (Fig. 7.11). Any carbon bonded to just two other carbons is a **secondary carbon,** and its hydrogens are *secondary hydrogens.* The single carbon of the central methylene group in propane is a 2° carbon and it holds two 2° hydrogens. Finally, a carbon bonded to exactly three other carbons is a **tertiary carbon** and its hydrogen is a *tertiary hydrogen.* In propane there are no 3° carbons and no 3° hydrogens. [Carbons bonded to four other carbons are *quaternary* (4°), but these are rare in hydrocarbon molecules and the term is seldom used.]

A **primary** (1°) **carbon** is bonded to exactly one other carbon; a **secondary** (2°) **carbon** is bonded to exactly two other carbons; a **tertiary** (3°) **carbon** is bonded to exactly three other carbons.

QUESTION

How many carbons and how many hydrogens of each class (1°, 2°, and 3°) are there in $CH_3—CH_2—CH_2—CH_3$? How many of each class are there in the structure below?

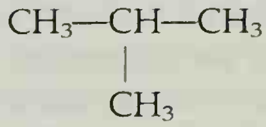


$$\begin{array}{ccc} CH_3— & CH & —CH_3 \\ & | & \\ & CH_3 & \end{array}$$

7.6 Butane and Its Isomers

Now we can return to methane, ethane, and propane to see more clearly just how propane is different. In Figure 7.9 we saw that replacing any one of the four equivalent hydrogens of methane gives one and only one ethane. Similarly, in Figure 7.10, we saw that replacing any one of the six equivalent methyl hydrogens of ethane gives one and only one propane.

But we don't get the same sort of result with propane. It contains two different kinds of hydrogens, two 2° and six 1°, so it matters now which hydrogen we replace. Replacing one of the six 1° hydrogens with a methyl group gives $CH_3—CH_2—CH_2—CH_3$, which is clearly *butane* since it is a four-carbon alkane of molecular formula C_4H_{10} (Table 7.1). Replacing one of the two 2° hydrogens with a methyl group gives



$$\begin{array}{ccc} CH_3— & CH & —CH_3 \\ & | & \\ & CH_3 & \end{array}$$

which is also *butane* since it's a four-carbon alkane of the same molecular formula as the other butane, C_4H_{10}. But it's different from the first butane (Figure 7.12). The first butane, for example, has six 1° and four 2° secondary hydrogens, while this second butane has nine 1° hydrogens and one 3°. Moreover they have different physical and chemical properties. These two butanes

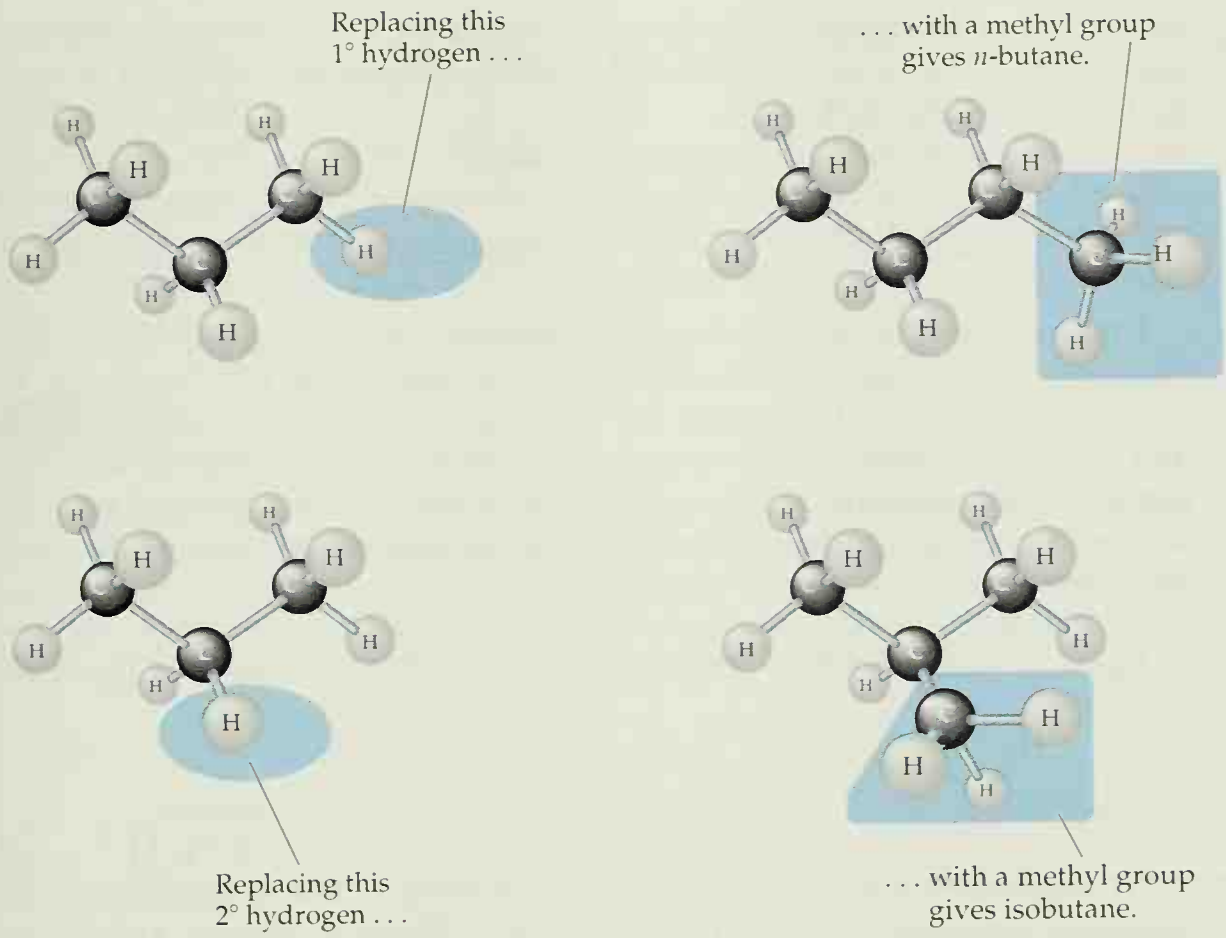
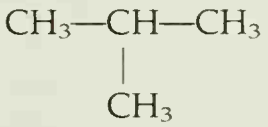


Figure 7.12
From propane to two different butanes.

are **isomers,** which are different compounds that have the same molecular formula. To differentiate the two isomeric butanes, the one that can be written as a straight chain of carbons ($CH_3—CH_2—CH_2—CH_3$) is sometimes called *normal-butane*, although there is nothing "normal" about it, and is often written "*n*-butane"; the one in which a methyl group hangs on the middle carbon of a three-carbon chain,

Isomers are different compounds that have the same molecular formula.

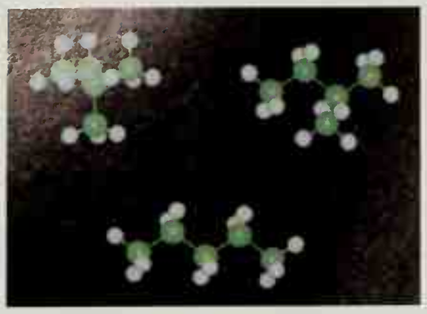


$$\begin{array}{c} CH_3—CH—CH_3 \\ | \\ CH_3 \end{array}$$

is called *isobutane*. As one illustration of the differences in the properties of the two compounds, *n*-butane boils at −0.5°C at atmospheric pressure, while isobutane boils at −11.6°C. As consumers, our principal contact with the butanes is through their use as the fuel of disposable lighters.

The multitude and structural variety of organic compounds result partly from the possibilities of isomerism. The greater the number of carbons and hydrogens there are in an alkane, the greater the variety of covalent structures they can form and the greater the number of isomers that are possible. Isomerism usually isn't possible in small molecules made up of relatively few atoms. As we've seen, only one structure is possible for methane (one carbon and four hydrogens), one for ethane (two carbons, six hydrogens), and one for propane (three carbons, eight hydrogens).

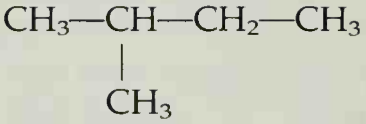
Butane, though, is different. We've just seen that its 4 carbons and 10 hydrogens can be arranged into two different molecules, *n*-butane and isobutane. With pentane, the 5 carbons and 12 hydrogens can form three different compounds: *n*-pentane, isopentane, and neopentane.



Molecular structures of *n*-pentane, isopentane, and neopentane.

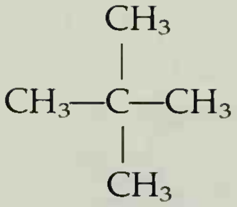
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

n-pentane



$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH_3$

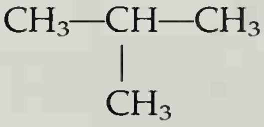
isopentane



$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_3$

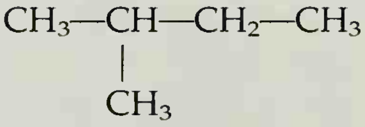
neopentane

The prefix *iso-* of isobutane and isopentane comes from the Greek *isos*, meaning "equal," and the *neo-* of neopentane comes from the Greek *neos*, or "new." Isobutane and *n*-butane are equivalent in their molecular formulas (but *only* in their molecular formulas), as are isopentane, *n*-pentane, and neopentane. Like isobutane and isopentane, all organic compounds that bear the *iso-* prefix consist of a chain of carbons with a single methyl group branching off at one end:



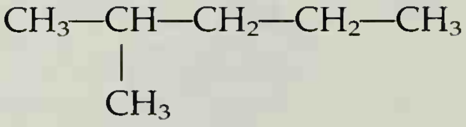
$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3$

isobutane



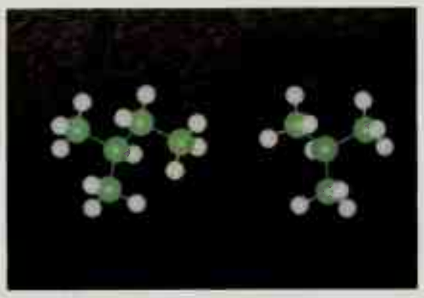
$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH_3$

isopentane



$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH_2{-}CH_3$

isohexane



A comparison of the molecular structures of isobutane and isopentane.

With 6 carbons and 14 hydrogens, hexane exists in five different, isomeric molecular structures. Decane, $C_{10}H_{22}$, forms 75 different isomers, and $C_{20}H_{42}$ is capable of 366,319 (Table 7.3). Certainly, even if we wished to, we couldn't

TABLE 7.3 Numbers of Possible Isomers of the Alkanes

Carbon Content	Molecular Formula	Possible Isomers
1	CH_4	1
2	C_2H_6	1
3	C_3H_8	1
4	C_4H_{10}	2
5	C_5H_{12}	3
6	C_6H_{14}	5
7	C_7H_{16}	9
8	C_8H_{18}	18
9	C_9H_{20}	35
10	$C_{10}H_{22}$	75
15	$C_{15}H_{32}$	4347
20	$C_{20}H_{42}$	366,319

find enough prefixes in Greek, Latin, and all other languages combined to name all possible isomers of even the first 20 alkanes. Nor could we remember them all.

It became clear as organic chemistry developed that the application of the classic languages to the naming of organic compounds has its limits. A simple, yet rigorous, systematic and unambiguous approach to devising names for organic molecular structures was needed. In the next section we will see how it came about.

QUESTION

Isopropyl alcohol, C_3H_8O, is the major ingredient of household rubbing alcohol. Using what you already know about the naming of organic compounds, and the information that in an alcohol a hydrogen of an alkane is replaced by an —OH group, write the molecular structure of isopropyl alcohol. Does any isomer of isopropyl alcohol exist? If your answer is yes, write the isomer's name and molecular structure. ________

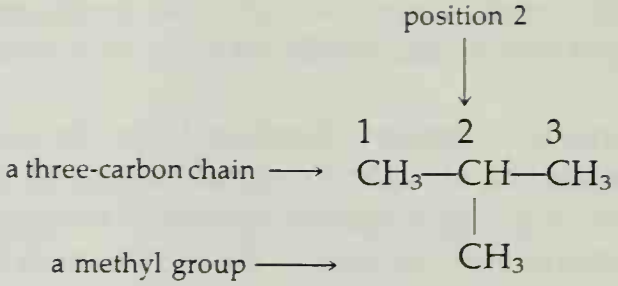
7.7 IUPAC

Using classic roots to establish the number of carbons in an alkane and a prefix to define the specific isomer becomes hopeless in face of the sheer number of possible isomers of any given carbon content. In 1892 a convention of chemists met in Geneva, Switzerland, under the auspices of the International Union of Pure and Applied Chemistry to simplify and systematize the naming of organic compounds. The set of rules they adopted and that is still in general use is known today as the IUPAC system, for the acronym of the host organization.

In essence, the IUPAC system operates through a series of simple rules:

1. As the parent name of the compound, use the name of the alkane corresponding to the longest continuous chain of carbon atoms within the molecule.
2. Locate the position of each group located on the chain—a methyl group, for example—by numbering the chain from whichever end will give the position a lower number.
3. Indicate the total number of each set of mutually identical groups with a prefix. For example, use dimethyl for two methyl groups, triethyl for three ethyl groups.
4. If more than one group is present on the chain, give each group its individual location number.

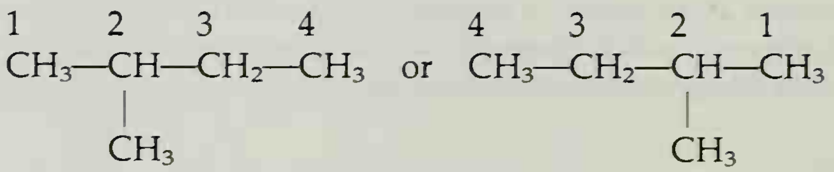
Some examples will surely help. Although isobutane has a total of four carbons, its longest continuous carbon chain contains only three. So isobutane becomes *2-methylpropane* under the IUPAC system. The number 2 places the single *methyl* group at the No. 2 carbon of a three-carbon (*propane*) chain.



$$\overset{1}{CH_3}{-}\overset{2}{\underset{\substack{|\\ CH_3}}{CH}}{-}\overset{3}{CH_3}$$

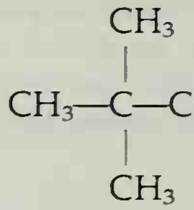
2-methylpropane (also known as isobutane)

The IUPAC names of some of the other alkanes we have discussed appear below.



$$\overset{1}{CH_3}{-}\overset{2}{\underset{\substack{|\\ CH_3}}{CH}}{-}\overset{3}{CH_2}{-}\overset{4}{CH_3} \quad \text{or} \quad \overset{4}{CH_3}{-}\overset{3}{CH_2}{-}\overset{2}{\underset{\substack{|\\ CH_3}}{CH}}{-}\overset{1}{CH_3}$$

2-methylbutane (isopentane)



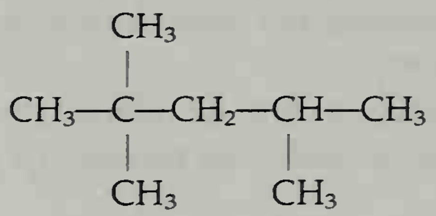
$$CH_3{-}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}{-}CH_3$$

2,2-dimethylpropane (neopentane)

A few very simple examples and one that's much more complex sum up these rules. In the simple cases, the IUPAC system recognizes the unbranched, straight-chain alkanes by their common names, with no prefix whatever. The unbranched $CH_3{-}CH_2{-}CH_2{-}CH_3$ is simply butane; unbranched $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ is pentane; and unbranched $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ is hexane. The more complex case, which follows in the example, provides us with a compound we'll return to in Chapter 8 when we examine the use of hydrocarbons in gasoline.

EXAMPLE WHAT'S IN A NAME?

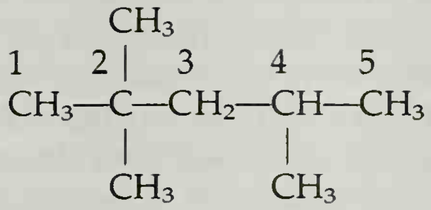
The isomer of octane that establishes a gasoline's octane number has the following condensed molecular structure. What is its IUPAC name?



$$CH_3{-}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}{-}CH_2{-}\underset{\substack{|\\ CH_3}}{CH}{-}CH_3$$

Following rule 1, we find that the longest continuous chain of carbon atoms within the molecule consists of a string of five carbons. Since the five-carbon alkane is pentane, we name this as a *pentane*.

Under rule 2 we find that there are three methyl groups on the chain, so we number the chain so that the methyl groups appear on the chain carbons bearing the lowest possible numbers. Here we start at the left end of the chain so that two CH_3's are on carbon 2 and one CH_3 is on carbon 4.



$$\begin{array}{ccccccccc} & & CH_3 & & & & & & \\ 1 & & 2\,| & & 3 & & 4 & & 5 \\ CH_3 & - & C & - & CH_2 & - & CH & - & CH_3 \\ & & | & & & & | & & \\ & & CH_3 & & & & CH_3 & & \end{array}$$

(If we had started at the right end as the structure is written above, reversing the sequence of the numbers we've just written, then there would have been only one CH_3 on carbon 2 and two CH_3's on carbon 4. The procedure we use above gives us a set of lower numbers.)

With rule 3 we see that the five-carbon chain bears three methyl groups, so it is a *trimethylpentane*.

Rule 4 gives each of the methyl groups its own position number. Three groups require three numbers, which we separate from each other by commas. We now have the full name, *2,2,4-trimethylpentane*.

Notice that we have not only separated the numbers by commas, we've also separated the set of numbers from the first letter of the name with a hyphen. That's all part of the IUPAC system. Also, the system provides a bit of useful redundancy, which minimizes mistakes: The set of numbers to the left of the hyphen and the prefix to the right (*2,2,4* and *tri* in this case) must agree; that is, each indicates the presence of three groups on the chain.

One brief return to etymology tells us something about the chemistry of the alkanes. Originally this family of hydrocarbons was called the *paraffin* family, a name that is still with us in the paraffin wax of candles, wax paper, and the sealing material of home canning and preserving. *Paraffin* comes from two Latin words: *parum*, meaning "barely" or "too little," and *affinis*, for "having affinity" or, in the chemical sense, "having reactivity." The word was coined in 1830 in recognition of the very low chemical reactivity of these hydrocarbons. Indeed, their only reaction of real significance to us as consumers is the one that provides us with most of our energy: hydrocarbons burn. The energy they release on combustion heats us, cools us (through air conditioning), moves our cars, airplanes, and ships, and allows us to cook.

QUESTION

What is the IUPAC name of isohexane? ______________________________

7.8 Balanced Chemical Equations

When a hydrocarbon burns it consumes oxygen, produces carbon dioxide and water, and liberates energy. You carry out this combustion reaction whenever you light a candle, turn on a gas stove, flick a disposable butane lighter, or start up an outdoor gas barbecue grill. You saw this chemistry in action back at the beginning of this chapter when you lit a candle and inserted it into the inverted beaker.

Here's what happened when you lit the candle. The wick started burning and melted a bit of the paraffin wax, which rose up, into the wick. The heat of the burning wick vaporized the hydrocarbons, and the hydrocarbon vapor mixed with the surrounding air and ignited. The carbon and hydrogen atoms of the hydrocarbon molecules combined with the oxygen of the air to form carbon dioxide, CO_2 (a combination of one carbon atom and two oxygen atoms), and water, H_2O (a combination of two hydrogen atoms and one oxygen atom), and released energy in the process.

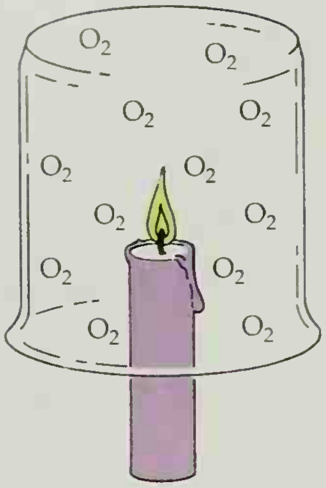
The flame's image blurred because the water produced by the combustion condensed in the form of microscopic droplets on the inside of the glass. With the candle well inside the beaker, the flame grew smaller and died because the oxygen inside the glass was consumed in the chemical reaction and was replaced by carbon dioxide, which doesn't support combustion. And you probably noticed that the beaker grew warm as it absorbed the energy given off by the burning hydrocarbons. Figure 7.13 combines the observations of Figure 7.1 with a description of some of the chemistry taking place.

The hydrocarbons of candle wax are large molecules of complex structure. So that we can examine the chemistry of hydrocarbon combustion more easily, we'll turn from candles to gas stoves, which burn either natural gas, supplied in many areas through underground pipes, or the so-called LP gas provided through refillable tanks. LP gas is the liquefied propane gas contained in the high-pressure tanks we use with outdoor gas grills, home-repair torches, and kitchen gas stoves in areas not served by piped natural gas. We'll examine the chemistry of natural gas first and then turn to propane.

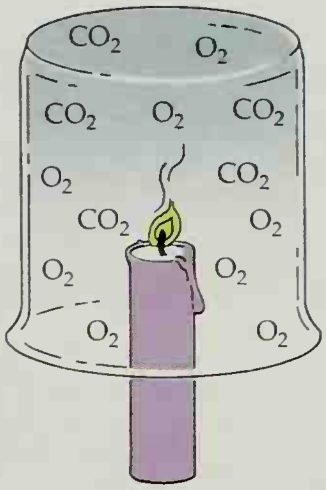
The major hydrocarbon of natural gas is methane, which makes up 80 to 95% of the fuel. When methane burns it consumes oxygen and produces carbon dioxide and water according to the following equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

It's important to recognize that this equation is **balanced.** In a balanced equation *each atom of each element of the products, to the right of the arrow, exactly balances an equivalent atom among the reactants, to the left of the arrow* (Fig. 7.14). Equations must be balanced because of the *Law of Conservation of Mass,* which, as we saw in Section 4.12, states that *matter can neither be created nor destroyed in a chemical reaction.* In a balanced equation each atom that takes part in the reaction appears among both the reactants and the products. No atoms are created and no atoms are destroyed and so the Law of Conservation of Mass holds firm.



Water droplets coat the sides of the beaker as the burning candle converts oxygen and alkanes to water and carbon dioxide.



The candle flame dies as the oxygen in the beaker is replaced by carbon dioxide.

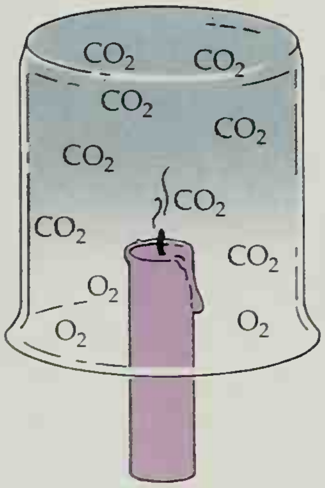
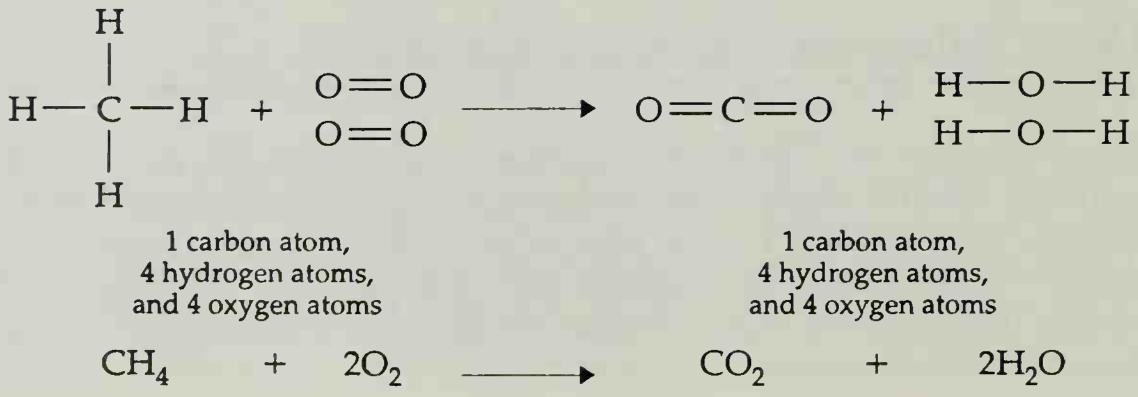


Figure 7.13
A burning candle.



$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Figure 7.14
The reaction of one molecule of methane with two molecules of oxygen to form one molecule of carbon dioxide and two molecules of water.

With the operation of this law, each atom of the products must also be found among the reactants, and no atom may occur among the products that was not present in the reactants. In the balanced equation above, the 2 before the oxygen of the reactants shows us that two diatomic oxygen molecules of the reactants provide the four oxygen atoms of the products: two in the single molecule of CO_2 and one in each of the two molecules of H_2O. Similarly, the 2 before the water of the products represents the two H_2O molecules needed to account for the four hydrogens of CH_4, a reactant. (The absence of a written number before any formula or structure in an equation implies a *1*.)

A **balanced equation** contains the same number of atoms of each of the elements among both the reactants and the products.

Another hydrocarbon oxidation, the combustion of the propane that we consume as LP gas, provides us with a more complex example of a balanced reaction. Like methane and ethane, propane is a gas at ordinary temperatures and pressures. Unlike these other two hydrocarbons, propane can be stored and handled conveniently under high pressure as a liquid, the LP gas of commercial, refillable tanks we described earlier in this section.

EXAMPLE BALANCING ACT

Balance the chemical equation for the combustion of propane.

To balance a reaction we must first know what happens chemically. As with methane, the combustion of propane consumes oxygen and produces carbon dioxide and water:

$$CH_3{-}CH_2{-}CH_3 + O_2 \rightarrow CO_2 + H_2O \qquad \text{(an unbalanced equation)}$$

Clearly, with three carbons in the propane molecule to the left of the arrow and only one in the carbon dioxide to the right, as well as eight hydrogens in the propane molecule and only two in the water molecule, this reaction isn't balanced. To remedy this we'll first place a 3 in front of the CO_2 and a 4 in front of the H_2O so that the carbons and hydrogens are balanced.

$$CH_3{-}CH_2{-}CH_3 + O_2 \rightarrow 3CO_2 + 4H_2O \qquad \text{(better, but still an unbalanced equation)}$$

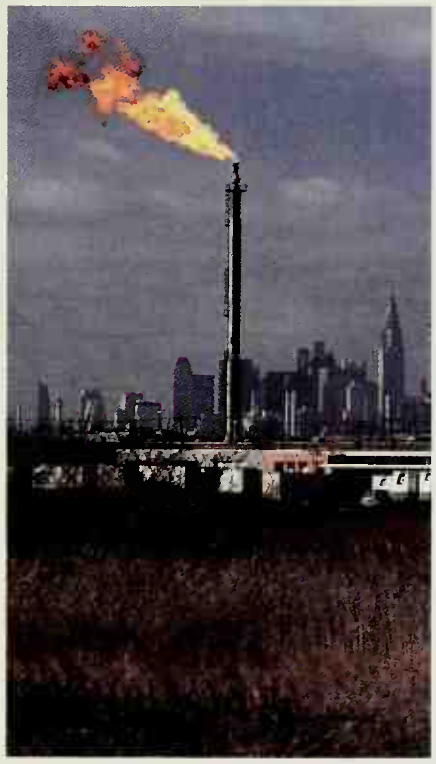
We now have three carbon atoms in the carbon dioxide of the products to balance the three of the propane molecule, and two hydrogens in each of four water molecules to balance the eight hydrogens of propane.

But the reaction still isn't balanced. Notice that there are 10 oxygens among the products, 6 from the three CO_2's and 4 from the four H_2O's, but only 2 oxygen atoms to the left of the arrow. To correct this, and thereby produce our balanced equation for the combustion of propane, we write a 5 in front of the O_2:

$$CH_3{-}CH_2{-}CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad \text{(a balanced equation)}$$

The chemical equation for the oxidation of propane to carbon dioxide and water is now balanced.

The hydrocarbons of natural gas burning at the Brooklyn Union Gas Company, Brooklyn, New York.



EXAMPLE DOUBLE BALANCE

Balance the chemical equation for the combustion of butane.

We don't have to be concerned whether we're dealing with *n*-butane or isobutane here. Since isomers have the same molecular formula, their molecules all have the same numbers of atoms of each of the elements they contain. We can use the molecular formula common to both isomers, C_4H_{10}.

$$C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$$

The combustion of butane presents us with a problem more complex than the combustion of propane. After we have balanced the carbons and hydrogens of the equation by placing a 4 before the CO_2 and a 5 before the H_2O of the products, we are left with an *odd number* of oxygen atoms, 13, among the products:

$$CH_3—CH_2—CH_2—CH_3 + O_2 \rightarrow 4CO_2 + 5H_2O \quad \text{(an unbalanced equation)}$$

Since each oxygen molecule contains 2 oxygen atoms, we can't get the 13 oxygen atoms we need by placing any whole number in front of the oxygen of the reactants. We could solve this problem by placing a $6\frac{1}{2}$ in front of the oxygen, but although this would give us a correct arithmetic solution it doesn't make much sense chemically to consider using half a molecule. A better solution is to use *two* propane molecules and multiply everything else by two. This gives us our balanced equation that includes a whole number of oxygen molecules:

$$2CH_3—CH_2—CH_2—CH_3 + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

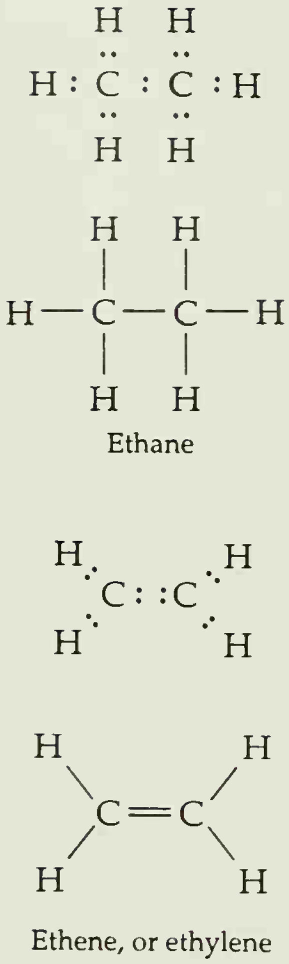
QUESTION

We have seen balanced equations for the oxidation of methane, propane, and butane. Write a balanced equation for the oxidation of ethane. ____________________

7.9 Alkenes and Alkynes

Later in this chapter we'll examine the societal consequences of using hydrocarbon combustion as a source of energy, and in Chapter 8 we'll see how the internal combustion engine converts that energy into the force of motion. Before we explore these topics, though, we'll first examine some families of hydrocarbons other than the alkanes.

As we've seen, compounds that fit the general formula C_nH_{2n+2} are alkanes. Ethane, C_2H_6, is an alkane; for ethane n is 2 and $2n + 2$ is 6. But


Ethane

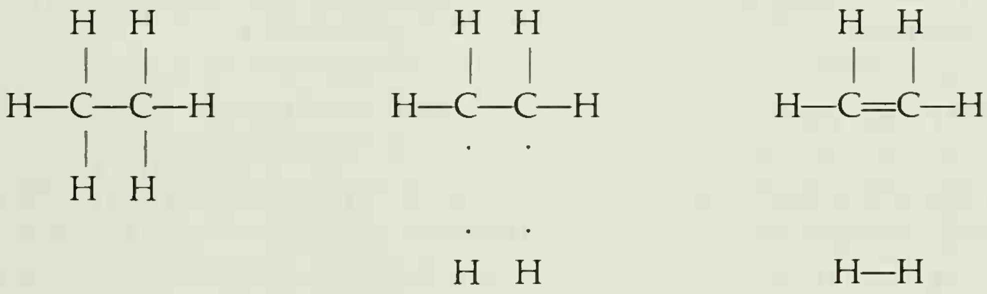
Ethene, or ethylene

Figure 7.15
The carbon–carbon single bond of ethane and the carbon–carbone double bond of ethylene.

carbon and hydrogen atoms can combine in other proportions as well. To understand how, we can start by removing two hydrogens from ethane, one from each of its methyl groups. In removing these two hydrogen atoms we remove not only the proton that makes up the nucleus of each, but its electron as well. These two hydrogen atoms could now unite to form a diatomic hydrogen molecule, held together by the covalent bond formed by the sharing of their electrons (Section 7.3):

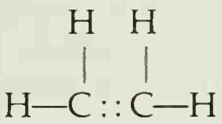
$$H^{\cdot} + {}^{\cdot}H \rightarrow H{:}H \qquad \text{(also written as H—H or } H_2\text{)}$$

This hydrogen molecule doesn't interest us further here. What does interest us is the fate of the two unpaired electrons that remain on the carbons that held the hydrogens. Those two electrons could come together, pair up, and form a new, second covalent carbon–carbon bond.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H} \qquad \mathrm{H-\overset{H}{\underset{\cdot}{C}}-\overset{H}{\underset{\cdot}{C}}-H} \quad \underset{\mathrm{H}\ \ \mathrm{H}}{\cdot\ \ \cdot} \qquad \mathrm{H-\overset{H}{C}{=}\overset{H}{C}-H} \quad \mathrm{H-H}$$

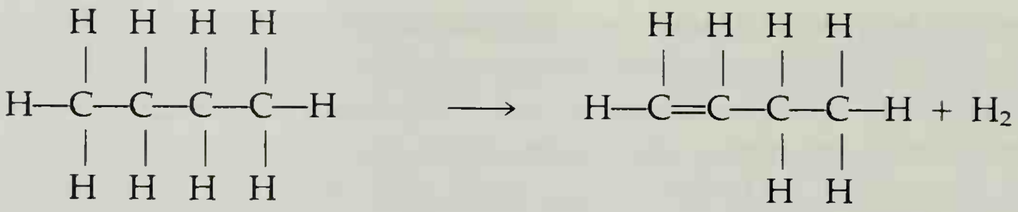
The result is the appearance of a carbon–carbon *double bond,* two covalent bonds formed through the sharing of a total of *two* pairs of electrons by the neighboring carbons (Fig. 7.15).



$$\mathrm{H-\overset{H}{C}{::}\overset{H}{C}-H}$$

The hydrocarbon that results from this procedure is known as *ethylene* or, in the IUPAC system, *ethene*. Ethylene is the first compound in a family of hydrocarbons called the *alkenes,* all of which share the general formula C_nH_{2n} and each of which contains a carbon–carbon double bond. The hydrocarbons of this family are named much like those of the alkane family, but the *-ane* ending of the alkane names is replaced by *-ene*. While the alkane C_3H_8 is propane, the alkene of the same carbon content, C_3H_6, is *propene,* $CH_2{=}CH{-}CH_3$. The alkene family is also known by an older name as the *olefin* family.

Carrying out an operation of this sort on any two adjacent C—H bonds of any alkane produces an alkene. Notice that if we were to start with butane, we'd have a choice of removing hydrogens from carbons 1 and 2, or 2 and 3. Introducing a double bond between carbons 1 and 2 gives us *1-butene,* with the *1* of 1-butene indicating that the double bond connects carbon atoms 1 and 2 of the chain. Since the double bond connects two consecutive atoms of the chain, using the lower of their two numbers defines the position of the double bond without any ambiguity.



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array} \longrightarrow \begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & = & C & - & C & - & C & - & H \\ & & & & & & | & & | & & \\ & & & & & & H & & H & & \end{array} + H_2$$

carbon number: 1 2 3 4

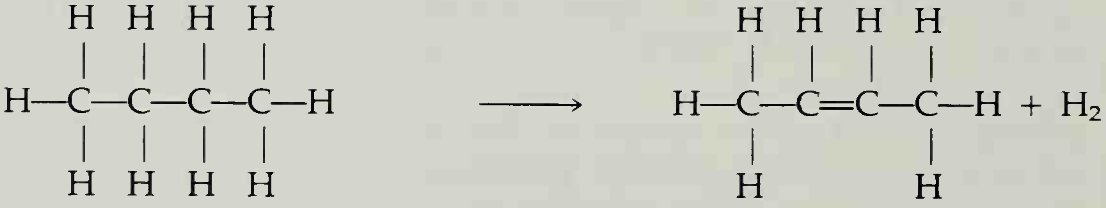
1-butene

$$CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_2=CH-CH_2-CH_3 + H_2$$

carbon number: 1 2 3 4

1-butene

With the double bond located between carbons 2 and 3, the compound is 2-butene. Here, 2 represents the lower-numbered of the two carbons joined by the double bond.



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array} \longrightarrow \begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & = & C & - & C & - & H \\ & & | & & & & & & | & & \\ & & H & & & & & & H & & \end{array} + H_2$$

carbon number: 1 2 3 4

2-butene

or

$$CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH=CH-CH_3 + H_2$$

carbon number: 1 2 3 4

2-butene

$$H\!:\!C\,\vdots\vdots\,C\!:\!H$$

$$H-C\equiv C-H$$

Ethyne, or acetylene

Figure 7.16
The triple bond of acetylene.

We can carry this a step further. Applying this same procedure to ethylene removes two hydrogens from $CH_2=CH_2$ and produces the *triple bond* of *acetylene*, $HC\equiv CH$, which is named *ethyne* in the IUPAC system (Fig. 7.16). Acetylene, with its general formula C_nH_{2n-2}, is the first of the *alkynes* (pronounced al-KĪNZ), sometimes referred to as the *acetylene* family. Like acetylene, all members of this family contain carbon–carbon triple bonds. In naming the members of the alkyne family by the IUPAC system, we replace the *-ane* of the corresponding alkane with *-yne*. The three-carbon member of this family, C_3H_4, is *propyne*.

Unlike alkanes, the first few members of the alkene and alkyne families have characteristic odors, ranging from slightly sweet to sharp and pungent, depending on their concentrations in the atmosphere. Most of these hydrocarbons are of little direct use to consumers. Many ripening fruits and vegetables, especially citrus fruit and tomatoes, release ethylene, which itself speeds further ripening. Commercial growers sometimes use this same phenomenon to hurry the maturation of fruit and vegetables by bathing their unripened produce in ethylene gas. Industrially, more ethylene is manufac-

TABLE 7.4 Alkanes, Alkenes, and Alkynes

Family	General Formula	First Member	Structure
Alkane (also known as *paraffin*)	C_nH_{2n+2}	Methane, CH_4	H HCH H
Alkene (also known as *olefin*)	C_nH_{2n}	IUPAC name: ethene Common name: ethylene	$CH_2{=}CH_2$
Alkyne (also known as *acetylene*)	C_nH_{2n-2}	IUPAC name: ethyne Common name: acetylene	$HC{\equiv}CH$

tured each year in the United States and worldwide than any other organic chemical. In 1990, U.S. firms manufactured about 18 million tons of the alkene, with most of it going into the production of plastics, synthetic fibers, and the kinds of film we find in freezer wrappings and trash bags. (We'll have more to say about these and other plastics in Chapter 20.) Ethylene ranks fourth in total industrial chemical tonnage produced each year, behind the inorganic chemicals sulfuric acid, nitrogen, and oxygen. Propylene ranks second only to ethylene in the industrial production of organic chemicals, with much of that alkene also going into plastics.

Among the alkynes, only acetylene, the first member of the family, has extensive commercial use. Because it burns with a very hot flame, acetylene is commercially important as the fuel of the oxyacetylene torch, widely used in welding. Table 7.4 sums up the names and structures of the simplest alkanes, alkenes, and alkynes.

Alkanes are said to be **saturated,** while alkenes, alkynes, and all other organic compounds containing double or triple bonds are **unsaturated.** A compound containing a double or triple bond is unsaturated since it's possible to add molecular hydrogen to it until it will take up no more—to saturate it with hydrogen. A molecule to which we cannot add any hydrogen is considered to be saturated. Alkane molecules, then, are already saturated with as much hydrogen as they can hold (Fig. 7.17). Chemicals other than hydrogen can also add to unsaturated hydrocarbons, converting them to saturated

A **saturated** hydrocarbon is one that contains the maximum number of hydrogen atoms possible and that contains only single covalent bonds. An **unsaturated** molecule is one to which hydrogen can be added.

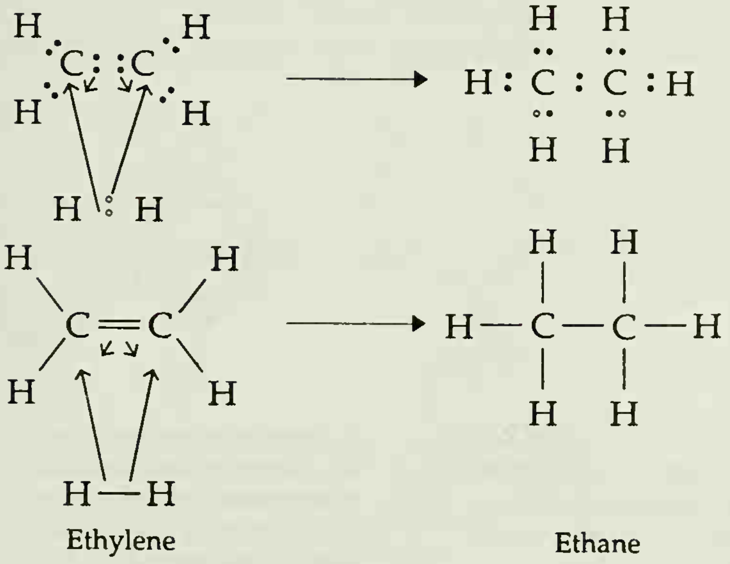


Figure 7.17

The conversion of unsaturated ethylene to saturated ethane.

compounds. These, of course, would no longer be classified as hydrocarbons since they would then contain elements other than hydrogen and carbon. Water can add to alkenes, for example, to form alcohols.

QUESTION

Draw the condensed molecular structures of propene and propyne. ____________

7.10 Cycloalkanes and Aromatic Hydrocarbons

While all compounds fitting the general formula C_nH_{2n+2} must be alkanes since they are all fully saturated, not all compounds of the formula C_nH_{2n} are alkenes. Some are *cycloalkanes*. Each cycloalkane molecule contains a ring or cycle of carbons. Cyclopropane, the first member of the cycloalkane family, consists of a ring of three methylene groups (Section 7.5), each located at an apex of an equilateral triangle. In *cyclobutane* the methylene groups are in a ring nicely represented by a square, in *cyclopentane* a pentagon, in *cyclohexane* a hexagon, and so on (Fig. 7.18).

Still another family of compounds, the *aromatic hydrocarbons*, is important to the chemistry of gasoline. All aromatic compounds contain at least one highly unsaturated ring of six carbons. The hydrocarbon *benzene* is the simplest of all of these (Fig. 7.19). The circle within the hexagonal ring of one of

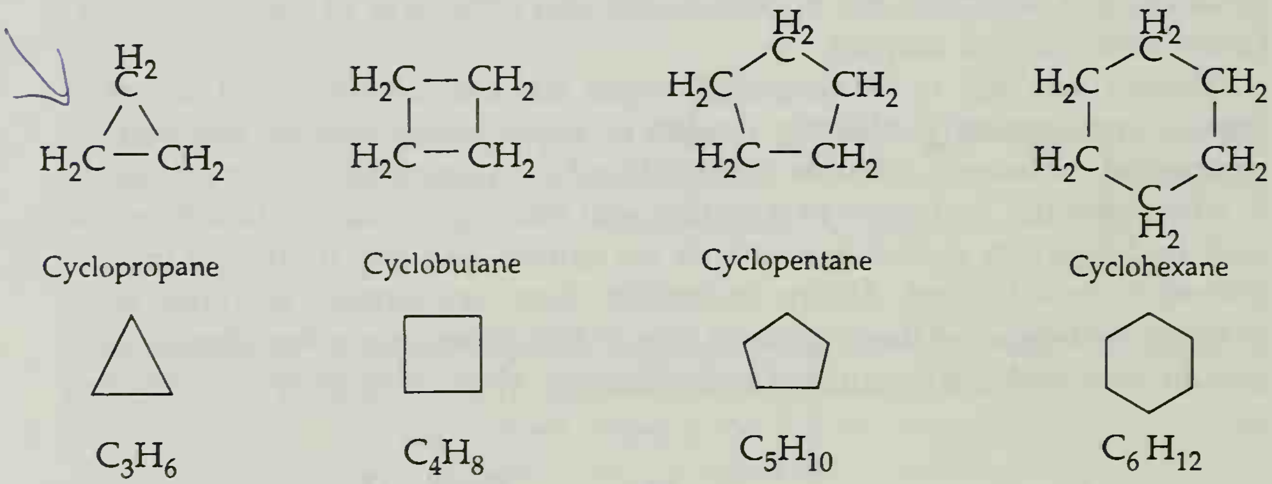
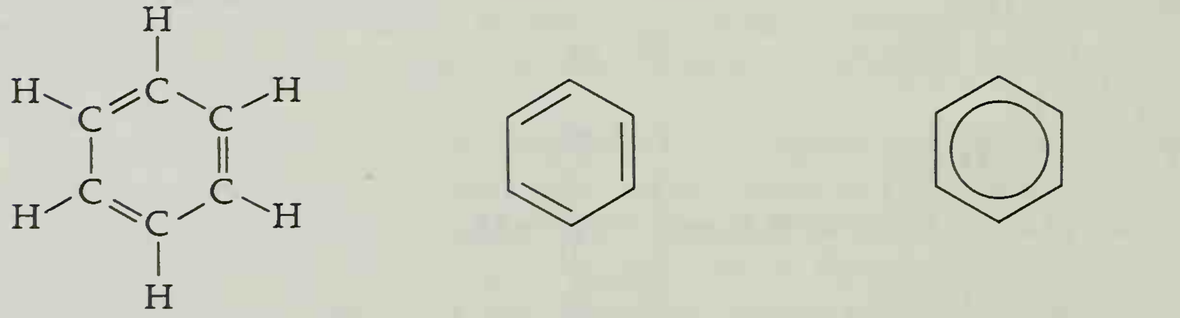


Figure 7.18
Cycloalkanes. (In the lower set of figures, only the carbon–carbon bonds are shown; the carbon atoms, hydrogen atoms, and carbon–hydrogen bonds are implied.)



All atoms and bonds are shown.

Only carbon–carbon bonds are shown. Carbon atoms, hydrogen atoms, and carbon–hydrogen bonds are implied.

A representation showing six electrons (two from each of the three carbon–carbon double bonds) distributed evenly over the entire ring.

Figure 7.19
Three representations of benzene.

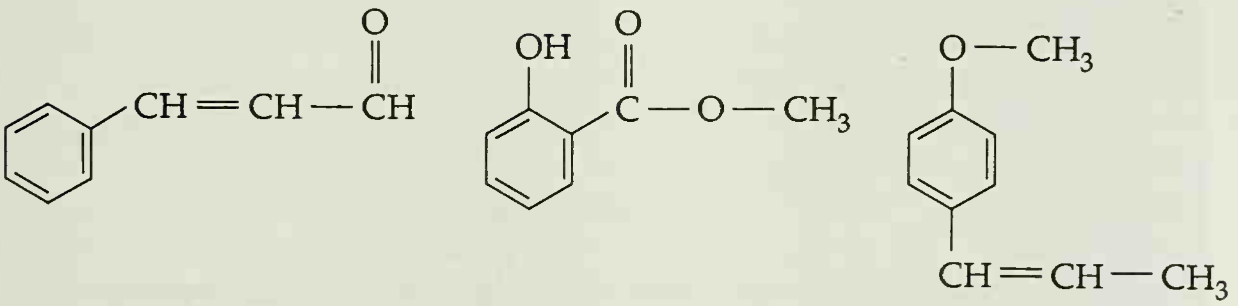
the structures shown in Figure 7.19 represents a peculiar facet of benzene's molecular structure and chemical reactivity. We'll see why.

By drawing benzene's molecular structure with alternating double bonds (four shared electrons) and single bonds (two shared electrons) around the ring, we suggest that two different kinds of covalent bond alternate among the carbons of the ring. In fact, though, plenty of experimental evidence shows very clearly that all the carbon–carbon bonds of the ring are mutually equivalent in every way. Every bond is just like every other bond. This runs counter to the representation that shows three single bonds and three double bonds in the ring.

Moreover, it would seem from the structure containing three double bonds that benzene must be highly unsaturated, that it should add hydrogen molecules or water molecules as readily as the alkenes do, for example. But benzene adds hydrogen only under extreme conditions that are far more rigorous than those needed with alkenes and alkynes. And benzene doesn't add water molecules at all. Benzene is far less reactive than this structure would suggest. So representing benzene as a six-membered ring with three double bonds nicely positioned between adjacent pairs of carbons doesn't quite do justice to the compound's actual properties.

The sets of two shared electrons and four shared electrons simply aren't located as neatly between the carbons as the structure with alternating single and double bonds would suggest. Instead, the 18 electrons of all those covalent bonds are more accurately represented as being smeared around the entire ring, distributed in equal portions among all six carbons. The circle is intended to represent this smearing, this equal distribution, and to remind us that aromatic rings react in ways different from the alkenes and alkynes.

The term *aromatic* also needs some qualification. Although benzene itself is the first member of the aromatic family of hydrocarbons, the compound has a somewhat disagreeable odor. "Aromatic" reflects structural similarities between molecules of benzene and molecules of many other compounds, occurring mostly in plants, that have distinctly pleasant odors and that also contain one or more benzene rings in their structures. These are, therefore, aromatic in the chemical sense and in sensory perceptions as well. Among these pleasant-smelling compounds are the organic compounds that give their fragrances to cinnamon (cinnamaldehyde), oil of wintergreen (methyl salicylate), and oil of anise (anethole), an oil used in the blending of perfumes and as a flavoring in foods and candies (Fig. 7.20). While not hydrocarbons (since they contain elements in addition to hydrogen and carbon), such compounds are nonetheless considered to be aromatic chemically because of the



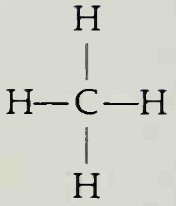
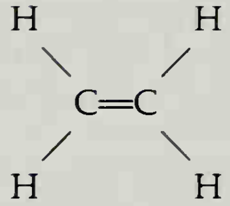
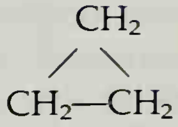
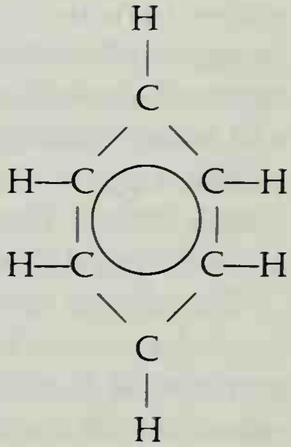
Cinnamaldehyde
(occurs in cinnamon)
C_9H_8O

Methyl salicylate
(in oil of wintergreen)
$C_8H_8O_3$

Anethole
(in oil of anise)
$C_{10}H_{12}O$

Figure 7.20
Aromatic compounds.

TABLE 7.5 Families Within the Hydrocarbon Family

	Alkane	Alkene	Alkyne	Cycloalkane	Aromatic
Alternative family name	Paraffin	Olefin	Acetylene	—	—
General formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	C_nH_{2n}	—
First member	Methane	Ethene Ethylene	Ethyne Acetylene	Cyclopropane	Benzene
Molecular formula of first member	CH_4	C_2H_4	C_2H_2	C_3H_6	C_6H_6
Molecular structure of first member	 $\begin{array}{c} H \\ \vert \\ H-C-H \\ \vert \\ H \end{array}$		$H\text{-}C{\equiv}C{-}H$		

major role the benzene ring plays in their chemical behavior. Thus the family of **aromatic compounds** includes both hydrocarbons and compounds that are not hydrocarbons.

Table 7.5 sums up the kinds of compounds—alkanes, alkenes, alkynes, cycloalkanes, and aromatic compounds—that make up the hydrocarbon family.

An **aromatic** compound is one that contains at least one benzene ring as part of its molecular structure.

QUESTION

How many molecules of hydrogen would have to be added to a molecule of benzene to produce cyclohexane? ______________________________

7.11 The Greenhouse Effect

In Chapter 5 we examined the use of nuclear reactions as a source of energy. Fission, as we saw, is expensive because of the costs of building and maintaining safe reactors, and hazardous as well because of the possibility of accidents and because of the radioactive wastes that are generated. Fusion, although environmentally clean, requires materials and technologies still to be developed. Then, in Chapter 6, we saw how electrochemical reactions can provide us with energy. Here in this chapter we have examined still another source of energy, the combustion of hydrocarbons.

As we noted at the beginning of this chapter, most of the world's energy comes from the burning of organic compounds, whether they constitute the complex organic matter of wood or are the hydrocarbons of natural gas, coal, petroleum, and other *fossil fuels*, so-called because these fuels are believed to have been formed from the partially decayed animal and vegetable matter of living things that inhabited the Earth in eras long past. In 1990 the combustion of fossil fuels accounted for about 90% of all the energy consumed in the United States.

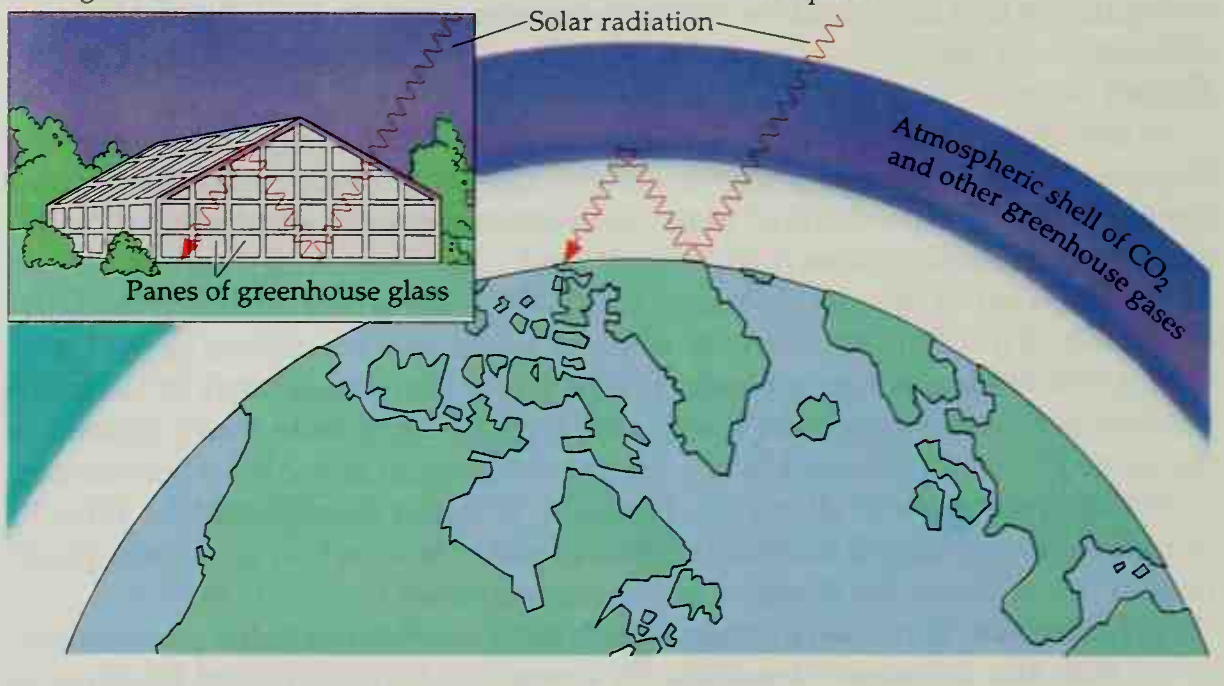
In any case, wood and fossil fuels are abundant and cheap and the devices we use to burn them and to capture their energy are easily built, sturdy, and simple to use. The products of their combustion are water and carbon dioxide, as we've seen, and various pollutants. It might seem that with rigorous control of the emission of the more noxious pollutants—we'll find an example of just such control in Chapter 8—the burning of wood and fossil fuels should provide a nearly ideal source of energy. The water that's generated in the combustion is a necessity for life itself, and the carbon dioxide that's formed is the same gas that's released by the life processes of all animals and consumed in the life processes of all plants. Nothing, it might seem, could be safer to our global environment than the release of water and carbon dioxide as products of the efficient combustion of organic materials.

Yet emissions of carbon dioxide, which have accelerated in the past century or so with the increased demands for energy and the increased burning of fossil fuels to produce it, threaten to change the world's climate radically, perhaps within another century, through the **greenhouse effect.** This is the same effect that allows us to grow temperature-sensitive plants in a cold climate. The glass walls and roof of a greenhouse allow the sun's warming radiation to penetrate into the space enclosed by the greenhouse. There, inside the greenhouse, the radiation is absorbed and its energy is converted into heat, which doesn't leave the glass enclosure nearly as easily as the solar radiation enters it. The trapped heat keeps the temperature within the greenhouse high enough for the plants to grow and thrive.

The **greenhouse effect** is the warming of the earth by solar heat trapped through the insulating effect of atmospheric gases.

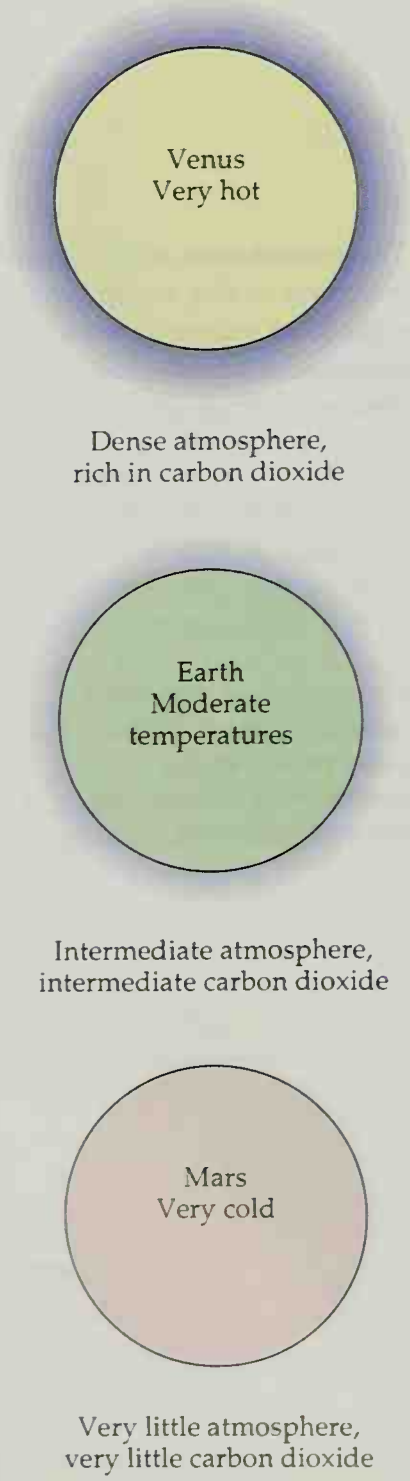
A greenhouse. The sun's radiation passes through the glass panels and is transformed to heat, which is trapped inside the building.

Figure 7.21
The greenhouse effect.


Solar radiation passes through the greenhouse glass and is converted to heat, which is trapped within the greenhouse.

Solar radiation passes through the atmosphere and is converted to heat, which is trapped within the planetary atmosphere.

Figure 7.22
Planetary greenhouse effects.



Dense atmosphere, rich in carbon dioxide

Intermediate atmosphere, intermediate carbon dioxide

Very little atmosphere, very little carbon dioxide

The earth's atmosphere behaves in a similar way. Solar radiation penetrates through it easily and is converted to heat in the lower atmosphere and at the surface of the earth. The carbon dioxide and other gases of the atmosphere trap the generated heat at and near the earth's surface in much the same way as the glass traps the heat within the greenhouse (Fig. 7.21). And it's a good thing they do. Life as we know it couldn't be sustained on Earth if it weren't for the presence of just the right amount of carbon dioxide and other greenhouse gases in our atmosphere. To see why, we'll compare Earth with its two nearest planetary neighbors, Venus and Mars.

Venus is surrounded by an atmosphere that's about 95% carbon dioxide and is compressed to about 95 times the density of Earth's atmosphere. The surface of Venus roasts at close to 450°C, well above the melting point of lead. The surface of Mars, on the other hand, is covered by an atmosphere that's also about 95% carbon dioxide but is less than 1% as dense as ours. Temperatures on the Martian surface range from a high of a bit below 40°C at noon on a summer day down to a nighttime low near −80°C. Neither one of those two planets provides a surface temperature that's hospitable to the kinds of life we find on Earth. Venus is too hot and Mars is too cold.

While Venus, Earth, and Mars receive progressively smaller amounts of solar radiation because of their progressively greater distances from the sun, the dramatic differences in their surface temperatures almost certainly result from differences in the atmospheric greenhouse effect on the three planets (Fig. 7.22). The dense, insulating layer of carbon dioxide around Venus traps whatever solar warmth penetrates through to the planet's surface. Like a greenhouse, Venus holds the heat that reaches it from the sun and keeps it from radiating back into space. As a result, it gets very warm on Venus. Mars, with its thin, almost nonexistent atmosphere, returns its heat to space easily. Mars is cold.

Venus, Earth, and Mars. The greenhouse effects of the atmospheres of these three planets produce striking differences in their surface temperatures.

Earth's atmosphere, which contains only 0.03% carbon dioxide and has a density between the two extremes of Venus and Mars, maintains just the right temperature ranges for the forms of life we know so well.

(Carbon dioxide isn't alone in its action as a greenhouse gas. Other greenhouse gases include methane, oxides of nitrogen, and both ozone and chlorofluorocarbons. We'll have more to say about still other effects of the last two in Chapter 19. For the moment we'll focus on the effect of atmospheric carbon dioxide.)

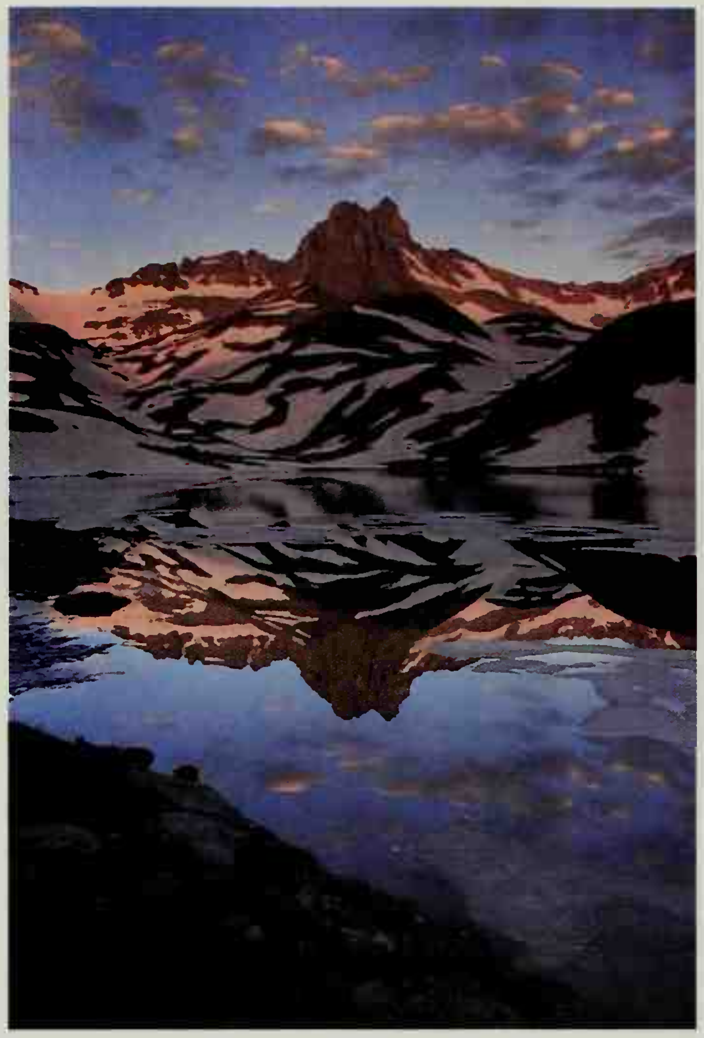
QUESTION

Planting 100 million trees has been suggested as a means for decreasing the greenhouse effect of our atmosphere. Describe the reasoning behind this proposal. (Refer to Section 5.14 in your description.) ____________________

PERSPECTIVE: Will Palm Trees Soon Grow in Alaska?

Given the reality of the greenhouse effect, we can ask whether there are changes now occurring in the chemical composition of the earth's atmosphere that are likely to produce a dramatic effect on our climate in the near future. To answer the question, even hesitantly, we must combine a number of scientific observations, scientific speculations, and possible courses of action that could be taken by society.

First, the amount of carbon dioxide in the earth's atmosphere appears to be increasing, and it appears to be increasing more rapidly now than it did in the distant past. It's estimated that in the early part of the 19th century the amount of atmospheric carbon dioxide had increased by about a third since the worst of the last Ice Age, some 18,000 years ago, and that during the last 150 years or so, since the beginning of the Industrial Revolution, the level has risen by about another 25%. What's more, the earth does seem to



A glacier melting as the sun rises on the San Juan Mountains of San Juan National Forest, Colorado.

be getting warmer. Accurate temperature records go back a century or so. During that period the average temperature at the surface of the earth has risen by 0.5°C and the decade of the 1980s was, on average, the warmest recorded.

While an increase of half a degree in the earth's average temperature every hundred years might not seem like much, if the rate keeps up a summer in New York early in the next century will be much like Miami's today. Moreover, by the middle of the next century the melting of the polar ice caps is likely to cause the seas to rise some 1.5 meters, with serious results for beaches, seaside settlements, and water supplies.

Is all this inevitable? Maybe; maybe not. The heat of the 1980s may have been no more than part of a natural fluctuation rather than a segment of a relentless increase in world temperatures. We'll probably know with considerably more certainty by the beginning of the new century. By relying less on wood and fossil fuels for energy and more on other sources, such as nuclear energy, solar energy, wind energy, and the like, as well as by decreasing our overall demand for energy by employing energy conservation, we may be able to decrease the rate of accumulation of carbon dioxide in our atmosphere. By slowing the removal of trees from the earth's surface and by planting enormous numbers of new trees to replace those already lost we may be able to remove some of the carbon dioxide already present in the atmosphere (see Section 5.14). In any case, whatever wisdom we may use either in counteracting the greenhouse effect or in adapting our society to it, our actions will have as their foundation an understanding of the chemistry of the combustion of organic compounds.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

Any compound containing the element carbon is an ______ compound. Those compounds containing both carbon and hydrogen, but with no other element present, are ______. Those containing carbon and hydrogen in a ratio that fits the general formula C_nH_{2n+2}, are known as ______ or, by an older system of nomenclature, ______. The modern system of naming organic compounds, the ______ system, came about as a result of an international gathering of chemists at Geneva, Switzerland, in 1892.

Because the component atoms of all but the smallest molecules can be joined to each other in a variety of ways, most molecular formulas can represent a variety of molecules. Different compounds that share the same molecular formula are known as ______. The molecular formula C_4H_{10}, for example, applies to two different compounds, known commonly as ______ and ______ or, by the IUPAC system, as ______ and ______.

Through the ______ we recognize that matter can neither be created nor destroyed in a chemical reaction and that all of the atoms among the reactants in the combustion of an organic compound (or in any other chemical reaction) must be present among the products. We accommodate this principle by writing a ______ for the combustion of an organic compound and for any other chemical reaction as well.

alkanes
balanced equation
butane
n-butane
hydrocarbons
isobutane
isomers
IUPAC
Law of Conservation of Mass
2-methylpropane
organic
paraffins

2. Define, describe, or give an example of each of the following:

a. 1° carbon
b. alkene
c. aromatic compound
d. cycloalkane
e. double bond
f. greenhouse effect
g. heptane
h. LP gas
i. methyl group
j. saturated hydrocarbon
k. stereochemistry
l. unsaturated hydrocarbon

3. Name a fossil fuel that is (a) a liquid, (b) a gas, (c) a solid.

4. Name a commercial source of energy that does *not* depend on burning a fossil fuel.

5. Name five organic compounds that are isolated from plants or specific parts of plants. Name one organic compound that is isolated from animals or animal products. Name one organic compound that isn't contained within plants but is produced from plant material.

6. What are three properties of carbon that result in the large number and great variety and complexity of organic compounds?

7. In what way do free radicals react when two of them encounter each other?

8. Match each of the following organic compounds with the property or source that is the origin of its common name:

Compound	Property or source
____ a. methane	1. Related to the first in a series of acids found in fats
____ b. ethane	2. Related to an acid found in rancid butter
____ c. propane	3. Related to prepare a very highly flammable compound
____ d. butane	4. Related to an alcohol obtained from wood

9. How can you determine whether any particular organic compound is a member of the alkane family?

10. What are the IUPAC names of isohexane, *n*-decane, and neopentane?

11. What does it mean when we say that a chemical reaction is "balanced"?

12. What scientific principle or law requires that a reaction be balanced? Explain.

13. Write a balanced equation for the combustion of methane.

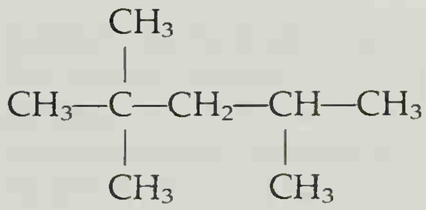
14. Name each of the following:

a.
$CH_3{-}CH_2{-}CH_3$

b.
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

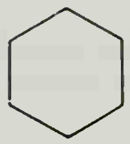
c.
$H_2C{=}CH_2$

d.

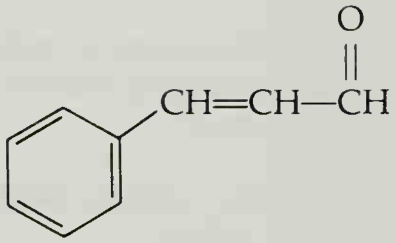


$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{CH}{-}CH_3$

e.



f.



15. Classify each of the following as to whether it is (1) a hydrocarbon or *not* a hydrocarbon, (2) an alkane or *not* an alkane, and (3) an aromatic compound or *not* an aromatic compound.

a. isobutane
b. acetylene
c. hexane
d. cyclohexane
e. carbon dioxide
f. benzene
g. $C_{17}H_{36}$
h. cinnamaldehyde

16. Arrange the three planets Earth, Mars, and Venus in order of increasing surface temperature. Suggest a reason for the order you have shown.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

17. Write balanced equations for each of the following reactions. Show all valence electrons:

a. two hydrogen atoms combining to form a hydrogen molecule
b. two chlorine atoms combining to form a chlorine molecule
c. one hydrogen atom combining with one chlorine atom to form a molecule of HCl

18. Write a balanced equation for the combustion of *ethylene*, $H_2C{=}CH_2$.

19. How many isomers of heptane, C_7H_{16}, are capable of existence? (*Note*: You do *not* have to draw molecular structures of all of them to answer this question.)

20. Draw *all* the condensed molecular structures of heptane, C_7H_{16}, that have exactly six 1° hydrogens.

21. The number of 1° hydrogens in a molecule must be a multiple of 3, and the number of 2° hydrogens in a molecule must be a multiple of 2. Why is this so?

22. Hydrocarbon molecules that contain *two* carbon–carbon double bonds are called *dienes*. What is the general molecular formula for the family of dienes? What other family of hydrocarbons has this same general molecular formula?

23. To what class or classes of compounds might each of the following hydrocarbons belong: (a) C_5H_{10}, (b) C_8H_{18}, (c) C_6H_{10}, (d) $C_{10}H_{20}$, (e) C_9H_{20}?

24. Why can't a compound with a molecular formula of C_3H_{10} exist?

THINK, SPECULATE, REFLECT, AND PONDER

25. How would using a warm beaker rather than a cool one in the demonstration that opened this chapter have affected our observations? (Recall that in the demonstration, a burning candle was inserted into an inverted beaker.)

26. How would you distinguish between food that is "organic" and food that is not "organic"? Apply the chemist's definition of "organic" to food and describe how this affects your interpretation of the term *organic food*.

27. Can any *inorganic* substance be isolated from living or once-living material? Explain.

28. Give the molecular structures and the IUPAC names of all five isomeric hexanes.

29. Draw molecular structures for all the isomers of (a) C_2H_6 (one isomer), (b) C_2H_5Cl (one isomer), (c) C_3H_7Cl (two isomers), (d) C_4H_{10} (two isomers), and (e) C_5H_{12} (three isomers).

30. Dietary fats are often described as "saturated" or as "unsaturated" or "polyunsaturated." The term *saturated* of "saturated fats" is used in the same sense as in hydrocarbon chemistry. What does the term *saturated* suggest about the molecular structure of a saturated fat? (We'll discuss dietary fats in Chaper 11.)

31. Should we classify benzene as a saturated hydrocarbon or as an unsaturated hydrocarbon? Explain.

32. Suppose a sealed vial of a liquid is recovered from an ancient tomb in Egypt, and writing on a clay tablet accompanying the vial is translated to indicate that the liquid was made from the juice of berries, but there is no indication of the age of the liquid. How might you go about determining how long ago the liquid was prepared from the berries? What technique might you use?

33. What would happen to the temperature of the earth's surface if the planet's atmosphere were to vanish? Describe your reasoning.

34. A global average daily increase in temperature of, say, 1° does not mean that every daily temperature, everywhere throughout the earth, would rise by just 1°. Some regions would feel the effects more than others. How would your own activities change if the daily temperatures where you live were to increase by perhaps 5°C (9°F) for a significant number of days, scattered uniformly throughout the year?

35. Describe how the use of energy-efficient cars and appliances can help alleviate the greenhouse effect.

36. If, to combat the greenhouse effect, the nations of the world found it necessary to ask their citizens to use less energy voluntarily, both directly through lower consumption of fossil fuels such as gasoline and indirectly through lower consumption of electricity, much of which is produced by burning fossil fuels, how would you respond? What would be the easiest way for you to conserve energy? What would be the most difficult?

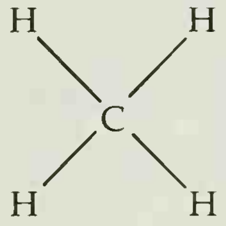
37. Compare and contrast the hazards of the commercial generation of electricity from nuclear fuels with the hazards of the commercial generation of electricity from fossil fuels.

38. Suppose an electric utility wanted to build a new power plant in your area and the residents could vote on whether it should be a nuclear plant or a plant that relies on a fossil fuel such as petroleum or natural gas, but that in any event a plant of one type or the other would be built. Knowing no more about the merits and dangers of each than you do now, and recognizing that much speculation is involved in your decision, would you vote for a plant that produces electricity from nuclear power or from a fossil fuel? Describe the reasoning that you would use in your decision.

39. We can speculate that life exists in some other part of the universe, perhaps in a form far different from what we find here on earth. On earth, life is based on compounds of the element carbon. If life were to occur in another part of the universe, and if that life were based on an element other than carbon, suggest what element that might be. Justify your answer with reference to the periodic table and the relationships among elements within it.

40. Suppose that the carbon atoms of alkanes weren't tetrahedral, but were *square-planar* instead. That is, suppose the carbon atom were at the center of a simple square and the hydrogens or other carbons bonded to it were at the corners of the square and that they all lay in the same plane, as they do on this sheet of paper:

Knowing that atoms and groups bonded to each other by covalent bonds can rotate freely around those bonds, predict how many isomeric methanes could exist if all carbons of alkanes were square-planar? How many ethanes? Propanes? Butanes?



38. Suppose an electric utility wanted to build a new power plant in your area and the residents could vote on whether it should be a nuclear plant or a plant that burns a fossil fuel such as coal, oil or natural gas. Suppose further that a plant of one type or the other would be built. Knowing as much about the benefits and dangers of each as you do now, and recognizing that much uncertainty is involved in your decision, would you vote for a plant that produces electricity from nuclear power or from a fossil fuel? Describe the reasoning that you would use in your decision.

39. We can speculate that life exists in some other part of the universe, perhaps with forms very different from what we find here on earth. On earth, life is based on compounds of the element carbon. If life were to exist in another part of the universe, and if that life were based on an element other than carbon, suggest what element that might be. Justify your answer with reference to the periodic table and the relationships among elements within it.

40. Suppose that the carbon atom were not tetrahedral, but were planar. [illegible] suppose the carbon atom were [illegible] simple square and that hydrogens or other atoms were bonded to it at the corners of the square and that they all lay in the same plane, as they do on this sheet of paper. Knowing that atoms and groups bonded to each other by covalent bonds can rotate freely around those bonds, predict how many isomers [illegible] could exist if all carbons were planar? How many [illegible]

31. Should we classify methane as a saturated hydrocarbon or as an unsaturated hydrocarbon? Explain.

32. Suppose [illegible] of a liquid is discovered in an ancient tomb and writing on a clay tablet accompanying the vial is available to indicate that the liquid was made from the juice of berries, but there is no indication of the age of the liquid. How might you go about determining how long ago the liquid was prepared from the berries? What technique might you use?

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37. Compare and contrast the hazards of the commercial generation of electricity from nuclear fuels with the hazards of the commercial generation of electricity from fossil fuels.

8

Petroleum

THE DRIVING FORCE

A refinery converts crude petroleum into commercial products.

Petroleum and Strong Tea

Our society runs on petroleum. The word itself comes from a combination of two Latin words, *petra*, meaning "rock," and *oleum*, "oil." Petroleum is an oil that comes from rocks just under the surface of the earth. It's our only source of gasoline and our leading source of commercial energy. In 1990 about 40% of all the commercial energy consumed in the United States came from the hydrocarbons of petroleum, and of all this petroleum consumed in the United States, roughly 60% went to moving us around in cars, trucks, buses, airplanes, and other forms of transportation. In appearance and composition, petroleum varies about as widely as the forms of transportation that run on its hydrocarbons. Depending on the region from which it comes, petroleum ranges from an almost colorless fluid, through shades of red and brown, to black and tarry.

We'll start our discussion of petroleum by looking at some of the science behind a common kitchen phenomenon that will help us understand just how we obtain our gasoline, kerosene, heating oil, jet fuel, and other valuable products from this liquid fossil fuel. If you've ever cooked anything by boiling it in a covered pot of water, you've probably already seen something like this happen.

Make a glass of strong, deeply colored tea. Put it into a small pot that comes with a lid, making sure you don't fill the pot more than about a quarter full. Put the pot's lid into the freezer. Heat the tea to boiling in the open pot and, as the tea is heating, wrap several ice cubes in a towel. When the tea comes to a boil, cover the pot with the cold lid, allow the tea to continue to boil for a few seconds, then remove it from the heat. Now cool the top of the lid by rubbing it with the wrapped ice cubes, being careful to keep the towel far from the heating element so as not to ignite it. Rub the top of the lid with the wrapped ice cubes for about 45 seconds, or until it's cool, then quickly wipe the top of the cool lid clean of any water from melted ice cubes. Now remove the cover and tilt the cover over a clean, clear glass so that the water condensed on the inside, bottom of the lid drains out into the glass. The few

Distilling pure water from strong tea. Boil the tea, cool the lid and the vapors that come in contact with it, and collect the condensed water.

drops of water that run into the glass from the bottom of the cover are clear and clean.

Put the lid back on the pot and repeat the procedure several times. (You don't need to chill the lid in the freezer again.) You'll find that you are collecting water that's about as pure as you can make it there in your own kitchen. If the tea is boiling briskly, there might be a little color because of tea splattering up from the pot onto the bottom of the cover. Otherwise, the water you collect is quite pure, containing perhaps only a little of the more fragrant, low-boiling organic compounds of the tea leaves.

With this demonstration you have separated water from the mixture we call "tea" by the process of **distillation.** The water you collected is *distilled water*. To summarize what happened, you boiled the water, converting it from liquid water into steam, or water vapor. The hot water vapor condensed to liquid water when it came into contact with the cold lid. You collected this condensed and purified water by removing the lid from the pot and allowing the water to drain into another container, the clean glass. The importance of this entire process of distillation is that it allows us to separate liquids of different boiling points and it allows us to separate liquids from solids dissolved in them. By carrying out a distillation carefully, with sophisticated equipment, we can separate a liquid substance completely from any other liquids it may be mixed with, and from any solids. We can thus purify a liquid to a very high degree. The principles are the same as those you used in distilling the water from the tea.

Distillation is the process of purifying a liquid by boiling it in one container, condensing its vapors again to a liquid, and collecting the separated, condensed liquid in another container.

This same process of distillation provides a fine method for separating petroleum into mixtures of hydrocarbons that have similar boiling points, known as **petroleum fractions.** Hydrocarbons can make up as much as 98% of petroleum, as they do the highest grade of crude oil from Pennsylvania, or as little as 50% of the oil from some regions of California. These hydrocarbons vary over a wide range of **volatility,** or ease and speed of evaporation from a liquid to a vapor. The most volatile is methane, a low-boiling, gaseous

Petroleum fractions are mixtures of components of petroleum with similar boiling points that are obtained through the distillation of petroleum.

The **volatility** of a substance is a measure of the ease and speed of its transformation from a liquid to a vapor.

hydrocarbon that is a component of the natural gas often associated with crude oil (Section 7.2). At the other extreme are the very-high-boiling, waxy, solid alkanes, such as *n*-hexacontane, $C_{60}H_{122}$. In addition to hydrocarbons, petroleum can also contain organic compounds of nitrogen, oxygen, and sulfur, as well as traces of metals that are incorporated into the organic molecules.

QUESTION

The distillation of water from the tea in the pot allows you to collect water that is quite pure, except for possible contamination by the more volatile components of the tea. What is left behind in the pot as you distill the water from the pot and collect it in the glass? ______________________________

8.1 Our Thirst for Oil

Our interest in petroleum extends beyond the chemistry of its hydrocarbons, reaching to the societal, economic, political, and strategic consequences of our thirst for oil. On August 2, 1990, military forces of Iraq invaded the neighboring country of Kuwait. This oil-producing and -exporting country lies on the eastern shore of the Arabian peninsula, on the Persian Gulf. Kuwait is a member of OPEC, an acronym for an organization of Oil Producing and Exporting Countries throughout the world. OPEC itself exists to regulate the international production and pricing of oil. The invasion of Kuwait represented, among other things, a threat to a large portion of the world's petroleum supplies.

The significance of such a threat and its implications for our society were summarized by an editorial that appeared in *The New York Times* on the day of the invasion. The editorial began:

> Even before Iraq's invasion of Kuwait, America's energy situation was looking increasingly ominous. Fact one: Imports accounted for a record 50 percent of the oil consumed by the U.S. during the first half of 1990. Fact two: The oil cartel, the Organization of Petroleum Exporting Countries, this week raised its target price for oil by 17 percent.
>
> This combination of increasing dependence and price was cause for concern by itself. Now add the possibility of military upheaval, and there are all the ingredients of a new energy noose, like the one that caused Americans to choke in the 1970's.

The events since August 2 are history; their causes have been many and complex. Yet as the comments in the *Times* reveal, our dependence on petroleum for energy is one of the central issues of our society, affecting (in part) our response to the upheaval in the Middle East and extending beyond it, influencing other spheres of activity as well.

Although the political and economic issues generated by our dependence on oil are well beyond the scope of our discussions here, the chemistry that

The structure of our society rests on the mobility provided by automobiles.

underlies them is not. In this chapter we'll focus on our use of petroleum for the manufacture of gasoline. We'll examine the operation of the internal combustion engine of our automobiles and learn how it converts the chemical energy stored in gasoline's hydrocarbons into the mechanical energy that moves our cars and other vehicles. We'll also see how gasoline is modified to make our cars run more efficiently, what its environmental effects are, and how we modify our cars to minimize atmospheric pollution.

As we proceed, we can keep in mind the societal impact of the chemistry we examine. In 1989 the United States consumed over 6.3 billion barrels of oil, which amounts to more than the total used by Japan, Germany, Italy, France, Canada, and Great Britain, *combined*. In the United States alone, over 140 million cars burned more than 70 billion gallons of gasoline as they traveled a total of over 1,400,000,000,000 (1.40×10^{12}) miles. With figures like these it's clear that each day enormous numbers of people in the United States and throughout the rest of the world are initiating countless chemical reactions as they slide into the driver's seat and turn the ignition key.

QUESTION

(a) Using the figures in Section 8.1 for the approximate number of cars in the United States and the number of gallons they used, calculate the average number of gallons of gasoline consumed by each car. (b) Now, using the total number of cars and the total number of miles traveled, calculate the approximate number of miles the average car traveled. (c) Finally, calculate the number of miles per gallon the average car delivered in the United States in 1989. ____________

8.2 The Four-Stroke Cycle

When you do turn the ignition key, you begin a sequence of chemical reactions. First you send a stream of electrons from the battery (Chapter 6) through a starting motor, which is connected to the engine itself. The electric current

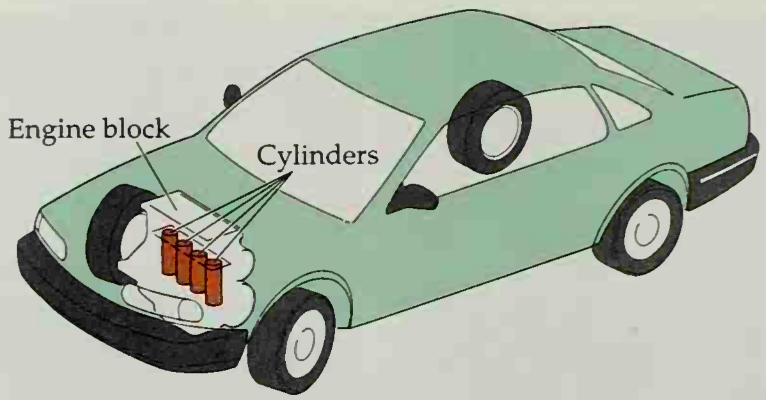


Figure 8.1
Schematic of four-cylinder engine in a car with front-wheel drive.

from the battery turns the starting motor and the starting motor turns the engine. As the engine comes to life, it draws a mixture of gasoline and air into it. As soon as the spark plugs begin firing, the chemical energy of the gasoline hydrocarbons takes over and keeps the engine running. We'll now see how it all happens.

Almost all cars that run on gasoline have engines with four, six, or eight cylinders (Fig. 8.1). Each cylinder is a hollow tube, only a few inches in diameter, bored into the engine block. Each holds a close-fitting piston that rides smoothly up, nearly to the top of the cylinder, and down to the bottom. Each full passage of the piston from one end of its travel to the other, upward or downward, is a *stroke*.

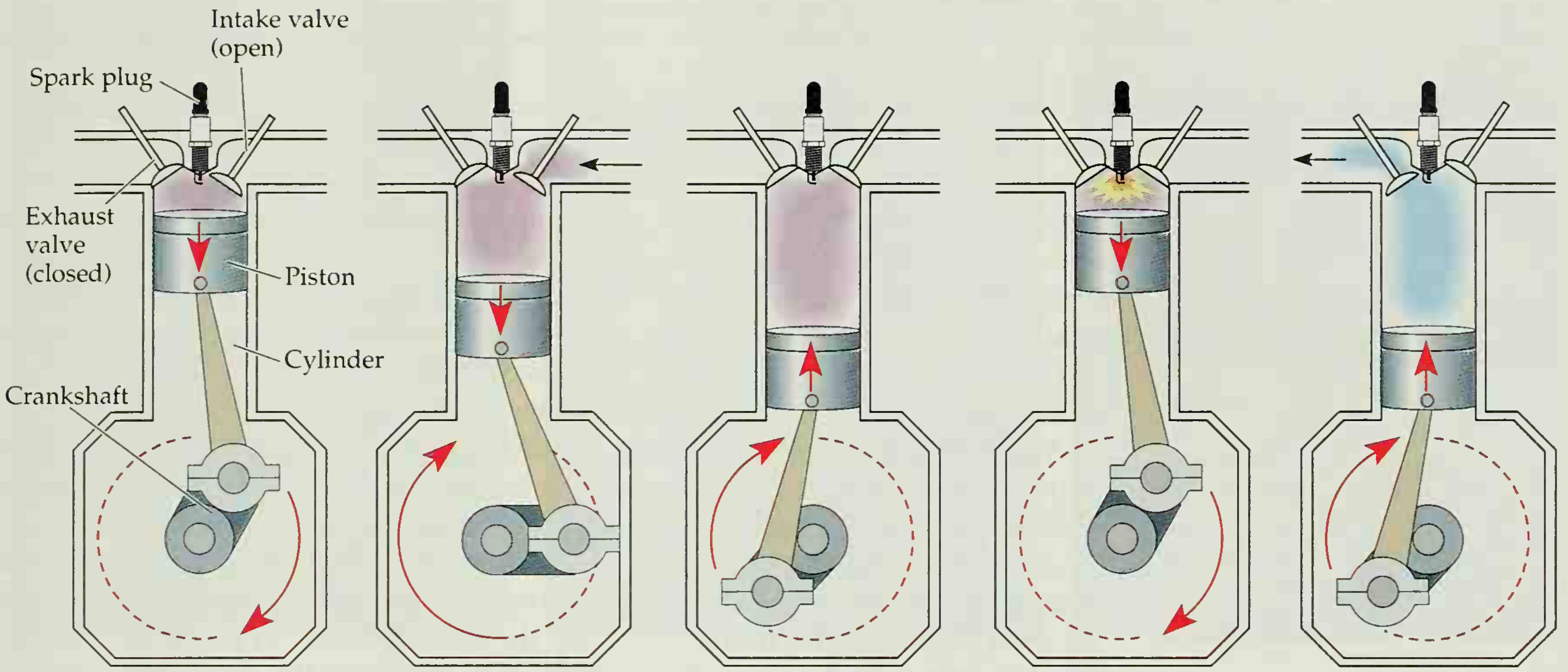
A piston rod connects the piston to the engine's crankshaft, which is in effect a sturdy rod extending through the length of the engine. A series of gears and various linkages connect the crankshaft to the car's wheels. As the piston moves up and down in the cylinder, the rod transmits the energy of its reciprocating motion to the crankshaft. The crankshaft converts the piston's reciprocating motion into a rotary motion that turns the car's wheels.

At the top of the cylinder in the simplest engines are two valves that open and close in rhythm with the movements of the piston, and a spark plug that sets off an electrical spark to ignite the gasoline at precisely the right moment. When all this operates just as it should, the engine converts the energy of the gasoline into the energy of motion and the car runs smoothly and well. (Some engines are more complex, with more than two valves in the cylinder and with other refinements of the basic design. But since the process of converting the chemical energy of gasoline into the energy of motion is fundamentally the same in all gasoline engines, we'll stick to the simplest case.)

The entire process takes four strokes of the piston to accomplish, hence the name "four-stroke internal combustion engine." ("Internal combustion" refers to engines designed to burn their fuel inside the engine. Engines that run from fuel burned outside the engine—steam engines, for example—could be called "external combustion" engines.)

In the first stroke of the cycle, the *intake stroke* (Fig. 8.2a), the piston moves down from the top of the cylinder, drawing a mixture of air and gasoline past the open *intake valve* and into the cylinder. The intake valve and the exhaust valve cover their respective ports. Gases move freely through these ports, into and out of the cylinder, only when the valves are open.

As the piston moves down from the top of the cylinder to the bottom, it fills the empty cylinder with a combustible gasoline–air mixture (Fig. 8.2b). At the conclusion of the intake stroke, with the piston now at the end of its downward travel, the cylinder is filled to capacity with the mixture of gasoline



Gasoline–air mixture enters cylinder through open intake port

Cylinder sealed as both intake valve and exhaust valve are closed

Spark plug fires, igniting the compressed mixture of gasoline and air and begins the power stroke

Combustion products are swept out of the cylinder through the open exhaust port

(a) (b) (c) (d) (e)

Figure 8.2

(a) The beginning of the intake stroke.
(b) The middle of the intake stroke.
(c) The beginning of the compression stroke.
(d) The beginning of the power stroke.
(e) The beginning of the exhaust stroke.

and air. At this point the intake valve closes and the piston starts upward in the *compression stroke* (Fig. 8.2c). Now both valves at the top of the cylinder remain closed as the piston moves up, squeezing the combustible mixture into a small volume.

Just as the piston is about to reach the end of its upward movement the spark plug fires, igniting the mixture. The burning gasoline releases its chemical energy and the vapors in the cylinder expand vigorously, sending the piston down in the *power stroke* (Fig. 8.2d). This released energy pushes the piston down and turns the crankshaft and, through it, the wheels. The energy of the burning gasoline makes the car move.

Finally, the cylinder must be emptied of the spent gases and prepared to take another charge of gasoline and air. After having reached the bottom of its motion in the power stroke, the piston starts upward again. With the *exhaust valve* now open and the intake valve closed, the piston pushes the combustion products out of the cylinder (Fig. 8.2e). At the top of the stroke the exhaust valve closes, the intake valve opens, and the four-stroke cycle begins again. In summary, the combination of these four strokes allows the engine to draw in a mixture of gasoline and air, ignite it, convert the energy of the burning hydrocarbons into energy of motion, and expel the burned gases as engine exhaust, which leaves the car through the tailpipe.

QUESTION

Are *both* valves ever *closed* simultaneously throughout any of the four strokes? Are *both* valves ever *open* simultaneously throughout any of the four strokes? Explain your answers. ______________________________

8.3 A Problem of Design and Its Solution

A one-cylinder engine on a lawnmower.

In theory an automobile engine could be designed to run on a single cylinder, even though the engine would supply power only a quarter of the time it is running, during the single power stroke in its cycle of four. Some consumer products, power lawnmowers and model airplane engines for example, do run very nicely on one-cylinder engines. The answer to the question, "What keeps them running during the intake, compression, and exhaust strokes?" is simple: inertia. Enough momentum is built into these small engines to keep them moving through the three strokes of each cycle that don't produce any power, and to return them to the power stroke.

While that's a fine solution for small engines that don't have to produce much power, one of the solutions for an automobile engine is to design it with at least four cylinders, each of which is in a different phase of the four-cycle pattern at any given moment. In that way one of the four cylinders is always in its power stroke. All other things being equal (including the volume of the cylinders), the more cylinders, the more power. In an eight-cylinder engine, two cylinders are always delivering power to the crankshaft.

QUESTION

On average, how many cylinders are in the power stroke at any given moment in a six-cylinder engine? ______________________________

8.4 Gasoline

Potential energy is energy stored in an object or a substance, often as a consequence of its location or composition. **Kinetic energy** is the energy of motion.

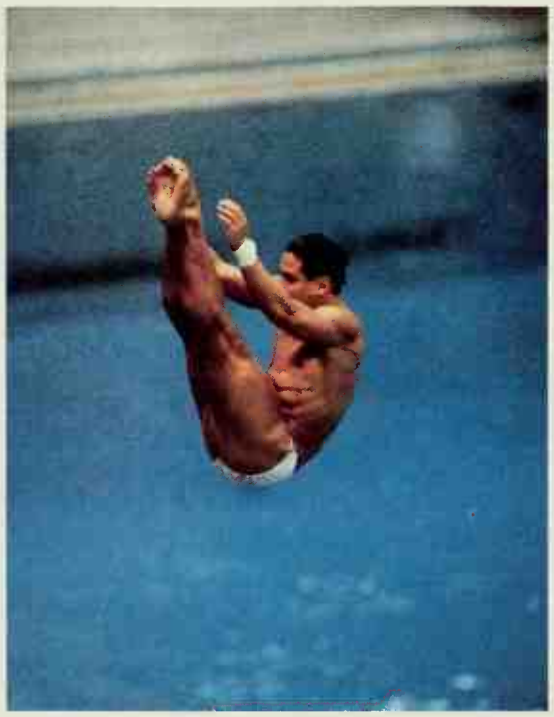
The energy transmitted to the crankshaft and passed along to the wheels during the power stroke comes from the chemical potential energy that lies latent in the hydrocarbons of gasoline. This chemical potential energy is one of two general kinds of energy that science recognizes in the world about us, **potential energy** and **kinetic energy.**

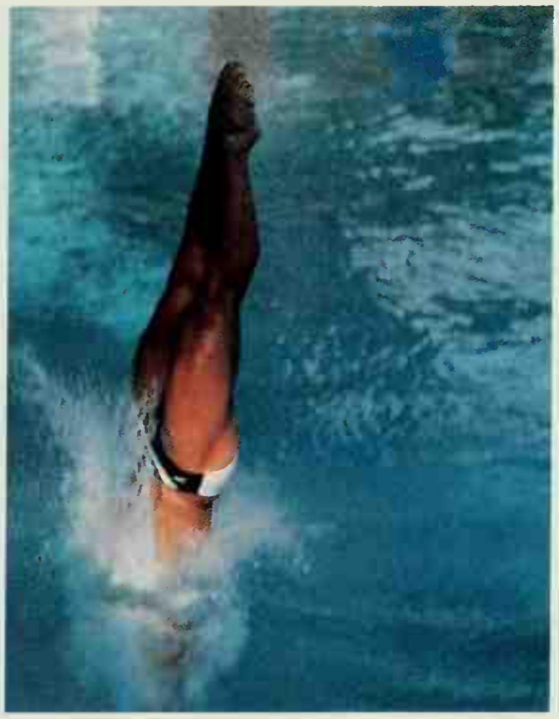
You can experience the difference between the two by placing an egg (preferably hard-boiled) on the floor next to a chair and then climbing up on the chair. As you stand on the chair above the egg, your body contains a certain amount of potential energy. While you stand there the energy is *potential* since nothing is happening. But jump off the chair and you convert that potential energy into *kinetic* energy, the energy of motion. As you land on the egg the kinetic energy that your body acquires as you fall smashes it (Fig. 8.3). You do work on the egg as you land on it, and as we saw in Section 1.1, energy is simply the capacity to do work.

Similarly, the hydrocarbons of gasoline contain great amounts of chemical potential energy. When a mixture of these hydrocarbons and oxygen is ignited by the spark plug, the hydrocarbons burn releasing their chemical potential energy. This energy is converted into kinetic energy as the hot, expanding gases produced by the combustion force the piston downward, turning the crankshaft and the wheels. The following general equation describes the chemical reaction:

$$\text{hydrocarbons} + O_2 \rightarrow CO_2 + H_2O + \text{energy}$$


Potential energy.


Kinetic energy.


Work.

With its intricate design and construction, the internal combustion engine requires a carefully regulated blend of hydrocarbons as its fuel. Gasoline is a mixture of over a hundred different alkanes, alkenes, and aromatic hydrocarbons ranging from low-boiling isobutane to relatively high-boiling aromatic compounds of complex molecular structures. A blend of these hydrocarbons makes an effective fuel for the internal combustion engine because they

- Deliver large amounts of chemical energy for each gallon of fuel used,
- are reasonably inexpensive, and
- have volatilities (ease of vaporization) in the range required by the engine.


Potential energy Kinetic energy

Figure 8.3
Potential energy and kinetic energy.

These qualities make the automobile a practical means of transportation. We wouldn't find cars very useful if the fuel delivered so little energy and carried us such a short distance that we had to fill the tank twice a day, or if gasoline cost, say, $50 or $100 a gallon. Nor would we be happy with a gasoline that doesn't vaporize and ignite in the engine, or one that's so volatile that it simply doesn't burn efficiently when the spark fires. We'll examine this third factor, the importance of a gasoline's volatility, more closely in the next section.

QUESTION

Isopentane (2-methylbutane) is a major component of gasoline. Give its molecular structure and write a balanced equation for its combustion. (See Section 7.8.)

8.5 The Volatility of Hydrocarbons

As we've just seen, a gasoline must be blended from hydrocarbons of the right volatility. Generally, the lower the boiling point of a liquid, the more volatile it is at any particular temperature, which is another way of saying that the lower the liquid's boiling point, the more readily it evaporates. In any given family of compounds, such as the hydrocarbons, boiling points *increase* (and volatilities decrease) with *increasing* molecular weight as long as we're dealing with molecules of the same general shape, such as straight-chain alkanes. Boiling points *decrease* with *increasing* branching of the carbon chain among isomeric hydrocarbons (those of the same molecular formula and therefore the same molecular weight; Section 7.6). We can see these effects in Tables 8.1 and 8.2.

Table 8.1 lists the boiling points of some of the unbranched alkane hydrocarbons. For hydrocarbons of the same molecular shape—straight chains of carbons, for example—the boiling point increases along with molecular weight. For isomeric hydrocarbons Table 8.2 shows that the greater the degree of branching, the lower the boiling point. Isobutane and neopentane (2-methylpropane and 2,2-dimethylpropane), with their combination of relatively low molecular weights and relatively high degrees of branching, have much lower boiling points and are much more volatile than *n*-heptane, for example, which is a higher-molecular-weight, unbranched alkane. They also boil at lower temperatures than their straight-chain isomers, *n*-butane and *n*-pentane.

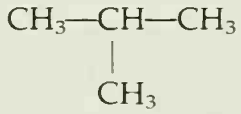
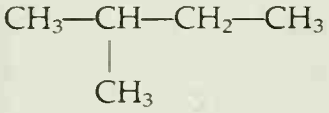
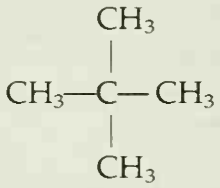
On the one hand, gasoline must be rich in volatile hydrocarbons to ensure that enough hydrocarbon vapors mix with the air in the cylinders to start a cold engine on a cold morning. If the gasoline–air mixture contains too little of the organic compounds, nothing burns when the spark plug fires.

On the other hand, gasoline must not be too rich in volatile hydrocarbons. If it were, there wouldn't be enough oxygen in the cylinder to burn the vaporized gasoline efficiently. The results would be poor ignition, roughness, poor fuel economy, and even vapor lock, a condition in which a bubble of gasoline vapor blocks the flow of fuel to the engine. With vapor lock a hot engine dies and won't start again until it cools off. Since gasoline must be

TABLE 8-1 The Effect of Chain Length on Boiling Point

Straight-Chain Alkane	Structure	Molecular Weight	Boiling Point (°C)
Methane	CH_4	16	−164
Ethane	CH_3-CH_3	30	−89
Propane	$CH_3-CH_2-CH_3$	44	−42
Butane	$CH_3-CH_2-CH_2-CH_3$	58	−0.5
Pentane	$CH_3-CH_2-CH_2-CH_2-CH_3$	72	36
Hexane	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	86	69
Heptane	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	100	98
Octane	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	114	126
Nonane	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	128	151
Decane	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	142	174

TABLE 8-2 The Effect of Chain Branching on Boiling Point

Name	Structure	Branching	Boiling Point (C°)
Isomeric C_4H_{10} Alkanes			
Butane (*n*-butane)	$CH_3-CH_2-CH_2-CH_3$	Four-carbon chain, no branching	−0.5
Isobutane (2-methylpropane)	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_3$	Three-carbon chain, one methyl branch	−11.6
Isomeric C_5H_{12} Alkanes			
Pentane (*n*-pentane)	$CH_3-CH_2-CH_2-CH_2-CH_3$	Five-carbon chain, no branching	36
Isopentane (2-methylbutane)	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_2-CH_3$	Four-carbon chain, one methyl branch	28
Neopentane (2,2-dimethylpropane)	 $CH_3-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}-CH_3$	Three-carbon chain, two methyl branches	9.5

equally efficient in Miami in July and in Chicago in January, manufacturers blend their gasolines to match the season and the locale of use.

QUESTION

Which one of the following alkanes has the highest boiling point? Which one has the lowest? (a) 2,3-dimethylbutane, (b) *n*-octane, (c) 3-methylpentane, (d) 3-methylheptane, (e) isohexane. Describe the reasons for your answer.

8.6 Knocking

An engine's **compression ratio** is the ratio of the maximum volume of the gasoline–air mixture, at the beginning of the compression stroke, to the volume of the compressed mixture, as the spark plug fires.

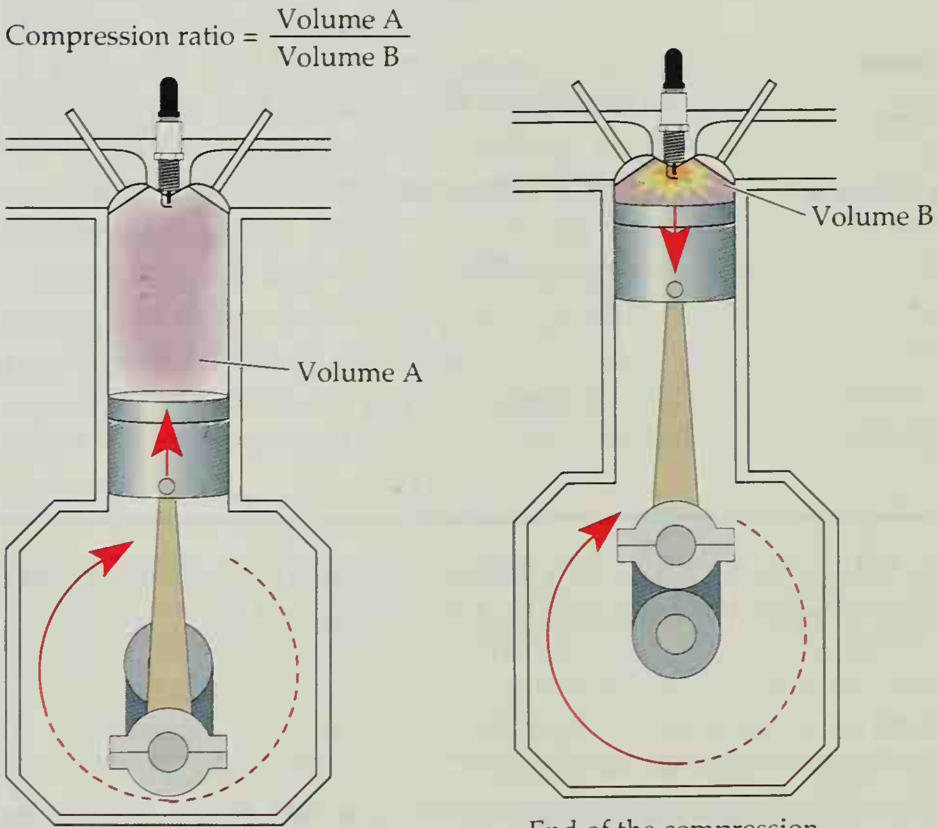
To squeeze as much energy out of the burning gasoline as possible, an engine must be designed with a high **compression ratio.** The compression ratio is simply the maximum volume of the gasoline–air mixture, at the beginning of the compression stroke, divided by the volume of the fully compressed mixture at the end of the compression stroke, as the spark plug fires (Fig. 8.4). The higher the compression ratio, the greater the compression of the gasoline–air mixture before it is ignited, and the more powerful the thrust it delivers to the piston on its way down in the power stroke. In effect, the higher the compression ratio, the more energy we can squeeze out of the hydrocarbons, up to the limit of the chemical energy they contain. Imagine, for example, a wet sponge. The more you squeeze it, the more water you get out of it, up to the limit of the water that it holds. The more energy we can squeeze out of the hydrocarbons of gasoline, the more power the engine can provide.

The average automobile engine of 1925 had a compression ratio of 4.4. That's low by today's standards. In modern engines compression ratios run as high as 10. In 1925 the gasoline–air mixture was compressed to between one-fourth and one-fifth of its original volume before it was ignited; today the mixture can be compressed to as little as one-tenth of its original volume. Today's engines can get more energy out of hydrocarbon combustion than the engines of 1925.

Knocking is a rapid pinging or knocking sound produced by preignition or irregular combustion of the gasoline–air mixture in the cylinders of an internal combustion engine.

But there's a limit to all this compression: **knocking.** "Knocking" is a rapid pinging or knocking sound that comes from an engine when it is pushed to produce a lot of power quickly. It usually occurs when a car is accelerating,

A piston head damaged by severe knocking.



$$\text{Compression ratio} = \frac{\text{Volume A}}{\text{Volume B}}$$

Beginning of the compression stroke

End of the compression stroke and beginning of the power stroke

Figure 8.4

The compression ratio is volume A divided by volume B.

especially while going uphill or when pulling a trailer. In severe cases an engine can knock while the car is simply cruising along a level highway.

Knocking is the sound of actual explosions in the cylinders. Normally the gasoline–air mixture burns smoothly when the spark plug fires. The combustion of the compressed hydrocarbons begins at the spark plug and proceeds outward smoothly and evenly, like ripples in a pond. Sometimes knocking results from *preignition*, an ignition of the mixture before the piston has risen to the point where the spark plug normally fires. Knocking can also result from a combustion that begins spontaneously at one or more spots in the cylinder either before or just as the plug fires, as though several stones had dropped into a pond, producing a set of irregular, overlapping ripples (Fig. 8.5). Or it can be a combination of the two. In any case, the resulting irregular, uncontrolled combustion produces a series of small explosions that we hear as knocking. It causes loss of power, inefficient and uneconomical use of fuel, and, in severe cases, damage to the engine. In extreme cases, for example, knocking can produce pits in the top surface of the piston or even fracture it. With any particular grade of gasoline, the higher the compression ratio, the greater the likelihood of knocking.

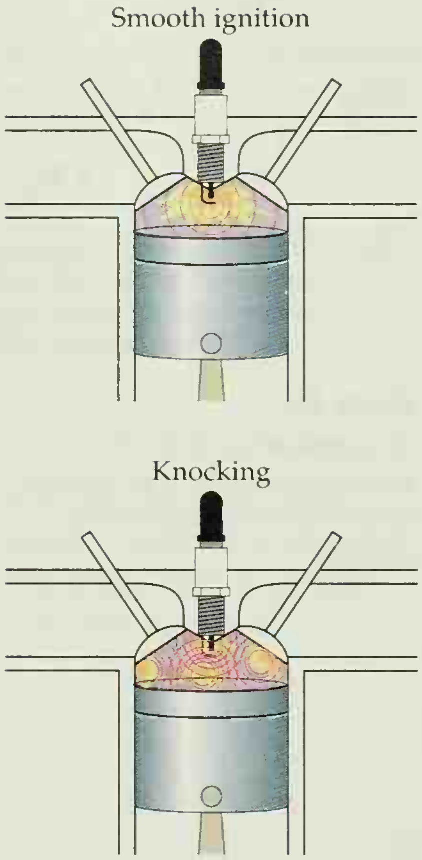


Figure 8.5
Smooth ignition and knocking.

QUESTION

Describe one advantage and one disadvantage of a high compression ratio in an engine. ____

8.7 Octane Rating

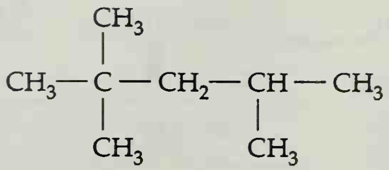
The **octane rating** or **octane number** of a gasoline is a measure of the gasoline's resistance to knocking.

The elimination of knocking through the production of high-quality blends of gasoline requires, first, some measure of a gasoline's ability to burn smoothly even under the rigorous conditions of the modern high-compression engine. To look at the problem from another angle, we need a means for describing a gasoline's *resistance* to knocking. Studies of the tendencies of various hydrocarbons to knock in test engines reveal one consistent trend: the more highly branched an alkane, the greater its tendency to burn smoothly and evenly and to resist knocking. 2,2,4-Trimethylpentane, also called (mistakenly) "isooctane" and even simply "octane" because it's one of the isomers of C_8H_{18}, consists of a chain of five carbons that bears three methyl branches and shows very little tendency to knock. *n*-Heptane, on the other hand, is completely unbranched and knocks readily, even under mild conditions (Fig. 8.6).

Three grades of gasoline and their octane ratings.

Mixtures of these two alkanes are used in assigning **octane ratings** or **octane numbers** to commercial gasolines. Because of its considerable ability to burn smoothly and to resist knocking, 2,2,4-trimethylpentane is assigned an octane rating of 100; *n*-heptane, with its great tendency to knock, receives an octane rating of 0. Mixtures of the two are given octane ratings equal to the percentage of the octane they contain.

To determine the octane rating of any blend of gasoline we simply compare the knocking tendencies of the particular blend itself with those of mixtures of "octane" and *n*-heptane. If, for example, a particular blend of gasoline has knocking tendencies identical to those of a mixture of 85% "octane" and 15% *n*-heptane, under standard test conditions, we assign the blend an octane



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

2,2,4- Trimethylpentane, known as "octane" or "isooctane", a highly branched alkane, shows little tendency to knock.
Octane rating = 100.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

n-Heptane,
a straight-chain, unbranched alkane, knocks readily, even under moderate conditions.
Octane rating = 0.

Figure 8.6

A combination of 2,2,4-trimethylpentane and heptane is used to evaluate octane ratings.

TABLE 8.3 Octane Ratings

	Approximate Octane Rating
n-Octane	−20
n-Heptane	0
n-Pentane	60
Regular gasoline	87
Premium gasoline	93
2,2,4-Trimethylpentane	100
Ethanol	105
Methanol	105
Benzene	105
Methyl *tert*-butyl ether	115

rating of 85. In summary straight-chain, unbranched alkanes have a great tendency to knock and are assigned low octane numbers, while both highly branched alkanes and aromatic hydrocarbons such as benzene have little tendency to knock and receive high octane numbers. Octane numbers of representative hydrocarbons and other compounds appear in Table 8.3.

It's worth noting that there are several slightly different ways to measure the antiknock quality of a gasoline. Two stand out. One provides a "research" octane rating, with the symbol R, that emphasizes the ability of a gasoline to burn smoothly when you're just starting out with the gas pedal to the floor. The other yields a "motor" octane rating, M, more appropriate to cruising along an expressway. Since neither one is useful under all driving conditions, the number actually posted at the pump is an average of these two, R and M. For a gasoline with an average rating of 87, for example, you might see the following on the pump:

$$\frac{R + M}{2} = 87$$

QUESTION

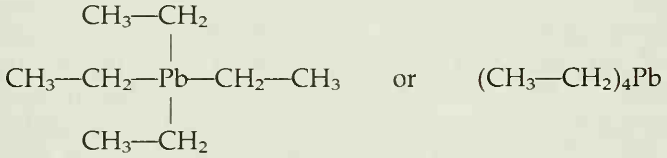
Which of the compounds in the question at the end of Section 8.5 would you expect to have the highest octane number? The lowest? Describe your reasoning.

8.8 A Problem of the 1920s and Its Solution

The problem back in the 1920s was finding an economical way of increasing octane ratings to match the increased compression ratios of the powerful engines that the public wanted. One way was to modify the molecular structure of hydrocarbons obtained from petroleum. Increasing their branching, for example, would raise the octane ratings of the gasoline. But this is an expensive process, one we'll examine later when we discuss the chemistry of petroleum refining (Section 8.13).

In 1922 Thomas Midgley, working at General Motors, discovered another way to raise octane ratings that's both simple and inexpensive. He found that adding less than 0.1% **tetraethyllead** to a gallon of gasoline, roughly one teaspoon per gallon, increases the octane number of the gasoline by 10 to 15 points. Note in the following structure that *Pb* is the chemical symbol for lead, and $CH_3—CH_2—$ is the *ethyl* group. The molecule is made up of four ethyl groups covalently bonded to one lead atom.

Tetraethyllead, or more simply "**lead,**" is a chemical that was added to gasoline to inhibit knocking.



$$\begin{array}{c} CH_3—CH_2 \\ | \\ CH_3—CH_2—Pb—CH_2—CH_3 \\ | \\ CH_3—CH_2 \end{array} \quad \text{or} \quad (CH_3—CH_2)_4Pb$$

tetraethyllead
(also known as *lead tetraethyl,* or simply "lead")

The high octane ratings achieved with inexpensive leaded gasoline allowed the production of more powerful engines that would be free of knocking.

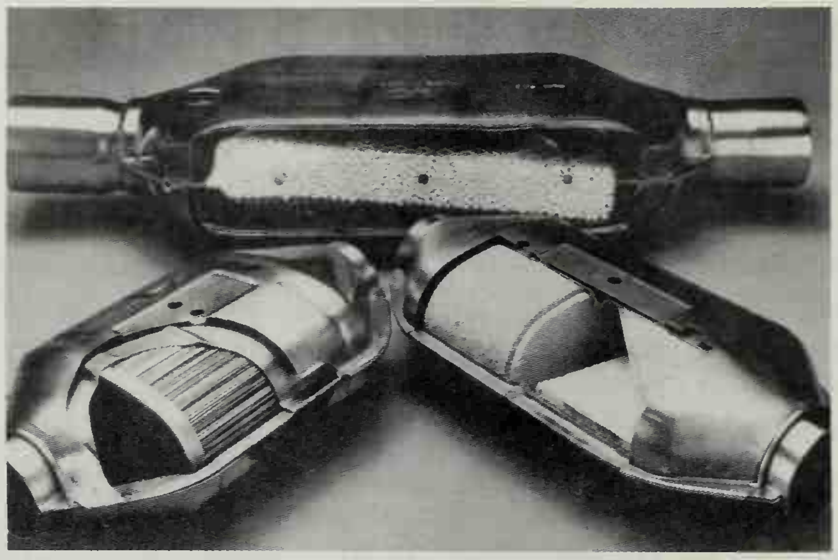
QUESTION

What is the molecular formula of tetraethyllead? ______________________

8.9 A Problem of the 1970s: The Case of the Poisoned Catalyst

Ideally, the hydrocarbons of gasoline burn completely to yield only carbon dioxide, water, and energy (Section 8.4). Unfortunately, an internal combustion engine is not the ideal device for the combustion of hydrocarbons. Under the operating conditions of a real engine some of the hydrocarbons remain unoxidized and pass out of the tailpipe, into the atmosphere, as part of the exhaust gases. Others oxidize only partly, yielding toxic carbon monoxide, CO.

What's more, gasoline isn't a pure mixture of hydrocarbons, but often contains traces of elements other than carbon and hydrogen. Sulfur, a contaminant that comes to gasoline from poorer grades of petroleum, burns to form sulfur dioxide, SO_2; nitrogen, another contaminant, undergoes oxidation to form various nitrogen oxides. Both sulfur dioxide and the oxides of



The interior construction of three different kinds of catalytic converters.

nitrogen are major atmospheric pollutants, each contributing to urban smog and to the worldwide problem of acid rain (Chapter 10). Neither one can be oxidized to a chemical that doesn't pollute.

By the middle of the 20th century increasing numbers of automobiles were spewing these gases—unburned hydrocarbons, carbon monoxide, sulfur dioxide, and various oxides of nitrogen—out of their tailpipes and into the air we breathe. In 1970, spurred by the threat of steadily increasing atmospheric pollution from industrial and commercial sources as well as from automobiles, the U.S. Congress acted. In the Clean Air Act of 1970 Congress specifically required that 1975 model cars emit no more than 10% of the carbon monoxide and hydrocarbons that came from their 1970 counterparts, and that emissions of other pollutants be reduced as well.

For a chemical solution to a chemical problem, auto manufacturers turned to the *catalytic converter*. Since 1975, virtually all automobiles built or imported into the United States have been equipped with this device. A **catalyst** is any substance that speeds up a reaction but is not itself a reactant. The catalyst simply allows the reactants to come together to produce the very same products they would have generated in its absence, but much faster or under much milder conditions. In another context, our bodily enzymes are also catalysts. They allow us to digest and metabolize food under the mild conditions of temperature, acidity, and alkalinity that our bodies tolerate easily. In the absence of enzyme catalysts, digestion and metabolism would take place far too slowly to maintain life.

A **catalyst** is a substance that speeds up a reaction but is not itself a reactant.

The automobile's catalytic converter consists of a large canister mounted between the engine's exhaust system and the tailpipe, containing finely divided platinum, palladium, and sometimes other substances as well (Fig. 8.7). As the exhaust gases from the engine pass through the converter, the finely divided particles of platinum and palladium catalyze the complete oxidation of unburned hydrocarbons and carbon monoxide into water and carbon dioxide, and thereby decrease the amounts of these atmospheric pollutants leaving the exhaust pipe.

The catalysts themselves are sensitive to a form of deterioration called *catalytic poisoning*, in which another chemical coats their surfaces and renders them ineffective. Lead, in particular, can poison a platinum or a palladium catalyst. It's been estimated that using as little as two tanks of leaded gasoline can completely destroy the activity of a catalytic converter. For this reason

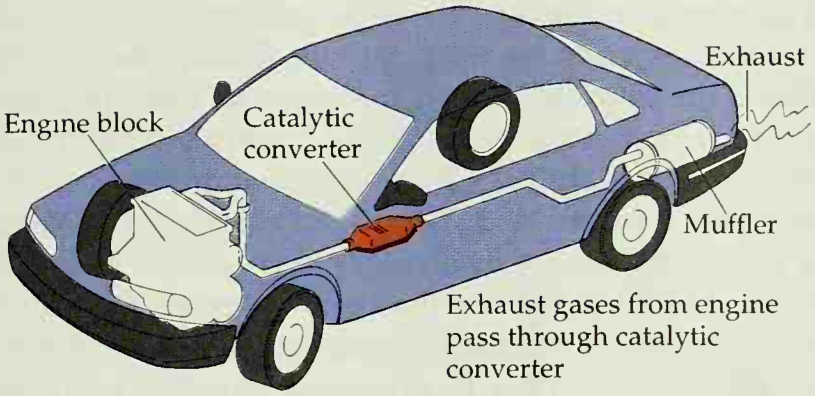


Figure 8.7
Catalytic converter.

Congress made it illegal to use leaded gasoline in cars equipped with catalytic converters (unless, in an emergency, no unleaded gasoline is available).

(Initially, unleaded gas cost substantially more than the leaded variety. To discourage illegal use of leaded gasoline in cars equipped with catalytic converters, hoses on pumps that dispense unleaded gas have smaller nozzles than those on the few remaining pumps that deliver leaded gas. Cars equipped with catalytic converters also come with smaller filler openings into their gas tanks, which can accept the unleaded nozzle but not the one on a pump that dispenses leaded gas. The leaded nozzles are too large to fit into the tank of a car with a converter. A motorist using unleaded gas legally, in an emergency, would have to use a funnel.)

As older cars not equipped with the converters leave active use, and as the demand for leaded gasoline decreases, high-octane unleaded gasoline is steadily replacing leaded gasoline as the fuel of choice in autos. Today leaded gasoline is no longer available in many areas. Nationally, sales of leaded gasoline have dropped from about 45% of all gasoline sold in 1983 to about 5% in 1990.

QUESTION

Catalytic converters decrease the amounts of carbon monoxide and unburned hydrocarbons that enter the atmosphere from unburned exhaust gases. The converters perform this function by catalyzing the combustion of unburned components of gasoline. Describe how an effective catalytic converter may also act to *increase* atmospheric pollution, even as it lowers the amounts of carbon monoxide and unburned hydrocarbons in exhaust gases. Base your answer on the contents of this section. ______

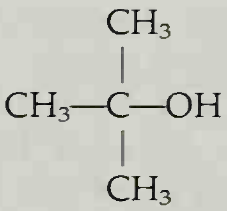
8.10 Beyond Lead

Lead and its compounds are poisonous not only to catalysts, but to humans as well. Lead poisoning, which affects the nervous system, the organs, the reproductive system, and fetuses, was once so common an occupational hazard that it's known by the medical term *plumbism*, from the Latin word for the metal, *plumbum*. Years ago colorful lead compounds were used widely in consumer products, as pigments in household paint and in ceramic glazes. Poisoning of infants and young children occurred as paint on baseboards and indoor walls flaked off and children picked at the flakes, eating them as attractive candies. Lead pigments in glazes can leach into acidic food and drink that are stored in ceramic utensils for long periods. Today the federal government rigorously limits the amount of lead that may be used in commercial paints or that may leach from a glaze. Yet, paint in very old buildings and glazes on ceramic souvenirs brought back from vacations in other countries may still contain hazardous levels of lead. Because of this threat, several commercial home-testing kits have become available to consumers. Many of those familiar with lead and its effects believe that lead entering the atmosphere from cars using leaded gasoline is equally hazardous to living things. Lead is leaving consumer products not only to protect automobile catalysts and the environment, but to protect consumers as well. We'll have more to say about lead and lead poisoning in Chapters 9 and 18.

With the market for inexpensive tetraethyllead (and other lead products) vanishing rapidly, other approaches must be used for producing high-octane gasoline. Among these are (1) the use of octane-boosting additives other than tetraethyllead and (2) the more extensive and more intricate processing of petroleum as it is converted to gasoline. Lead-free additives include *tert*-butyl alcohol, methyl *tert*-butyl ether (also known as MTBE), and a 50:50 mixture of *tert*-butyl alcohol and methyl alcohol (Section 7.4).

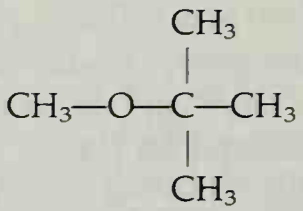
$CH_3{-}OH$

methyl alcohol



$$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}OH$$

tert-butyl alcohol



$$CH_3{-}O{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_3$$

methyl *tert*-butyl ether

(The *tert*-butyl group forms when the 3°—tertiary—hydrogen of isobutane is removed.)

In the next few sections we'll examine the second of these approaches to higher-quality gasoline, *petroleum refining*.

QUESTION

Even if the internal combustion engine were so efficient in burning gasoline that no catalytic converters were needed to protect the environment, it's likely that "leaded" gasoline would become unavailable. Why? ______________________________

8.11 Petroleum Refining: Distillation

The conversion of raw petroleum into useful consumer products, such as gasoline and other fuels, is known as *petroleum refining* and includes distillation among its principal processes. We saw an illustration of distillation in this chapter's opening demonstration as we distilled water from tea. Distillation, as we noted then, allows us to separate liquids of different boiling points and to separate liquids from dissolved solids. For their simplest distillations, chemists use an apparatus only a little more intricate than the pot of boiling water of our demonstration (Fig. 8.8). Liquid contained in a flask

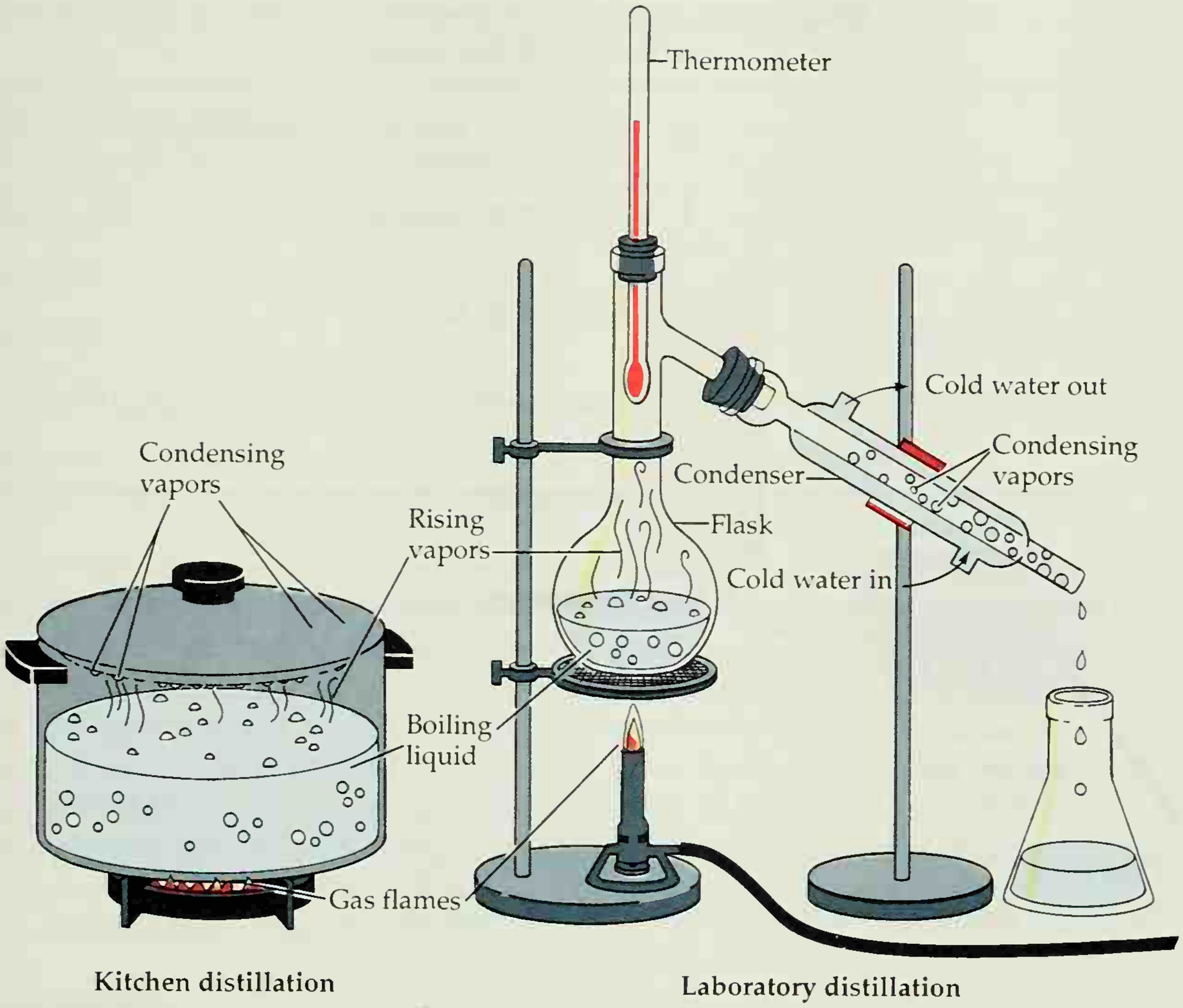


Figure 8.8
Distillations.

A pump bringing crude oil out of the ground.

is boiled and its vapors rise above the bulb of a thermometer, passing into a condenser (usually cooled by a stream of running water). There they condense back to a liquid, which is collected in another flask. The thermometer registers the boiling point of the condensed liquid. Distillations are ideal procedures for separating the various fractions of hydrocarbons that make up crude oil.

A fractionating tower. Distillation of crude oil in towers like this separates the hydrocarbons of the petroleum into fractions useful as gasoline, kerosine, heating oil, jet fuel, and so on.

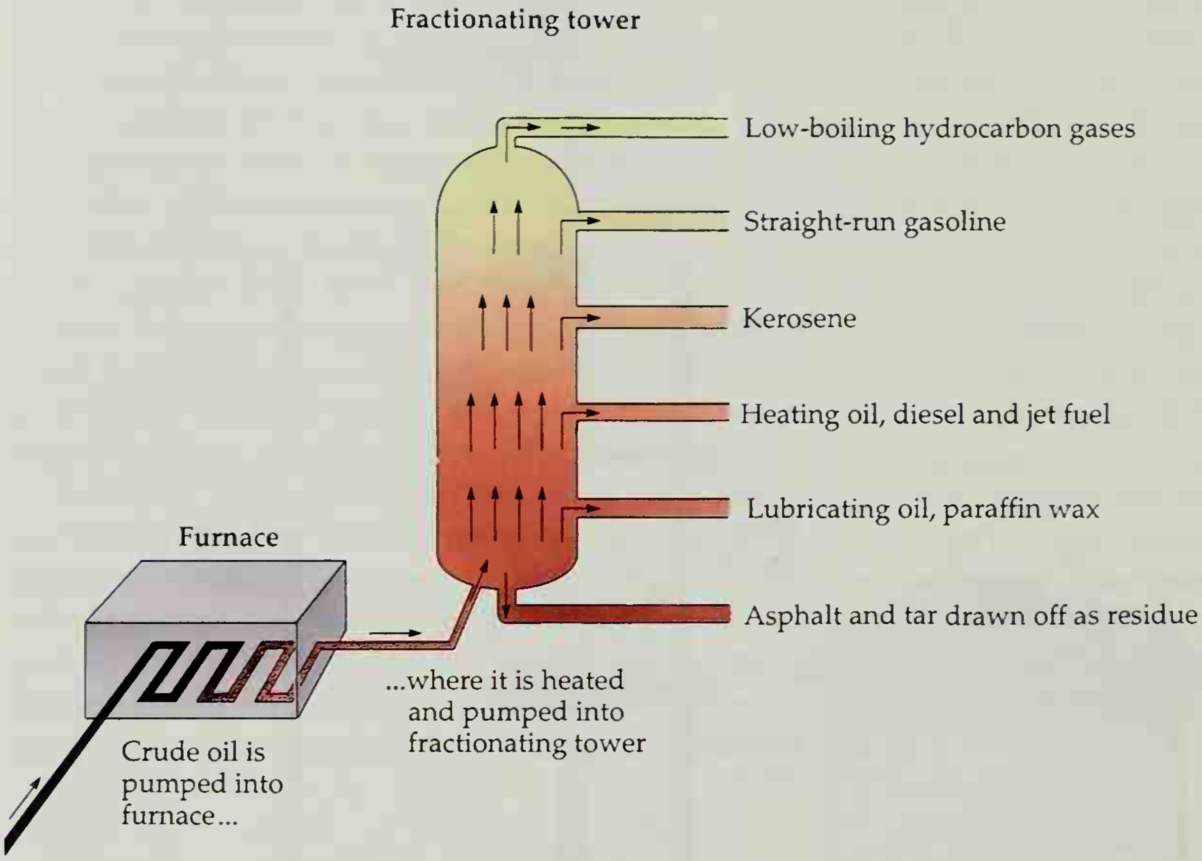


Figure 8.9
Schematic diagram of the fractional distillation of crude oil.

At a typical petroleum refinery the crude oil is heated in a vessel connected to the base of a tall *fractionating tower* (Fig. 8.9). The hydrocarbon vapors pass into the fractionating tower and separate into groups of compounds according to their boiling points. The vapors of the most volatile hydrocarbons—those with the lowest boiling points—rise to the top of the tower where they are condensed to liquids and are drawn off. Hydrocarbon mixtures with higher boiling points, the less volatile fractions, condense and are drawn off from the lower regions of the tower.

Filling wing-tanks with jet fuel, a product of petroleum refining.

Paving a road with asphalt, a residue obtained from petroleum distillation.

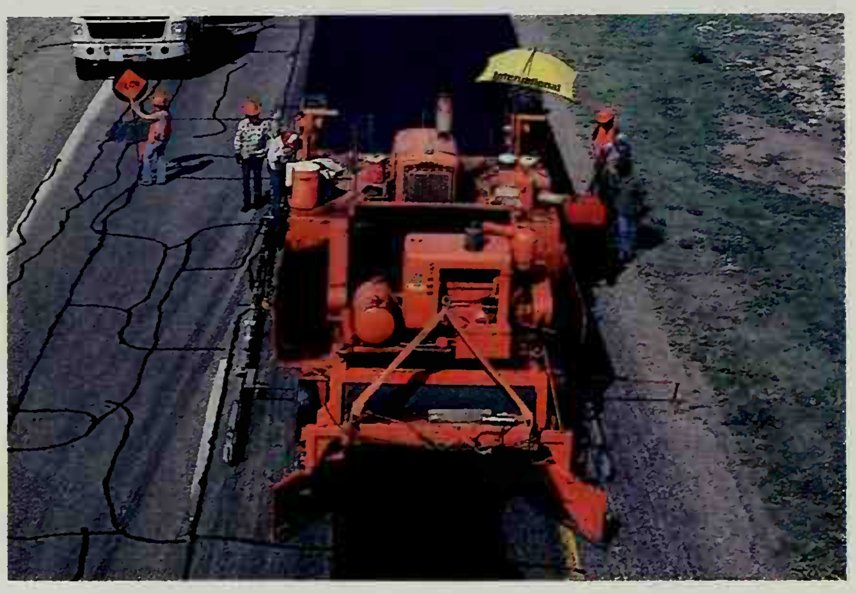


TABLE 8.4 Hydrocarbon Fractions Obtained on the Distillation of Petroleum

Approximate Boiling Range (°C)	Carbon Content	Fraction
Below 200	4–12	Straight-run gasoline
150–275	10–14	Kerosene
175–350	12–20	Heating oil, diesel, and jet fuel
350–550	20–36	Lubricating oil, paraffin wax
Residue	Over 36	Asphalt, tar

In this way the crude petroleum is separated by *fractional distillation* into mixtures of hydrocarbons represented in Table 8.4. Since the boiling point of a hydrocarbon is related to its molecular weight and, therefore, to the number of carbon atoms in its molecules, fractional distillation produces a separation of the hydrocarbon constituents of petroleum according to their carbon content. Gasoline that is produced directly from the hydrocarbons of crude oil, separated from other fractions by distillation, is known as *natural gasoline* or *straight-run* gasoline. Distilling at higher temperatures than straight-run gasoline are the hydrocarbons that make up such products as kerosene, heating oil, and jet fuel (Table 8.4).

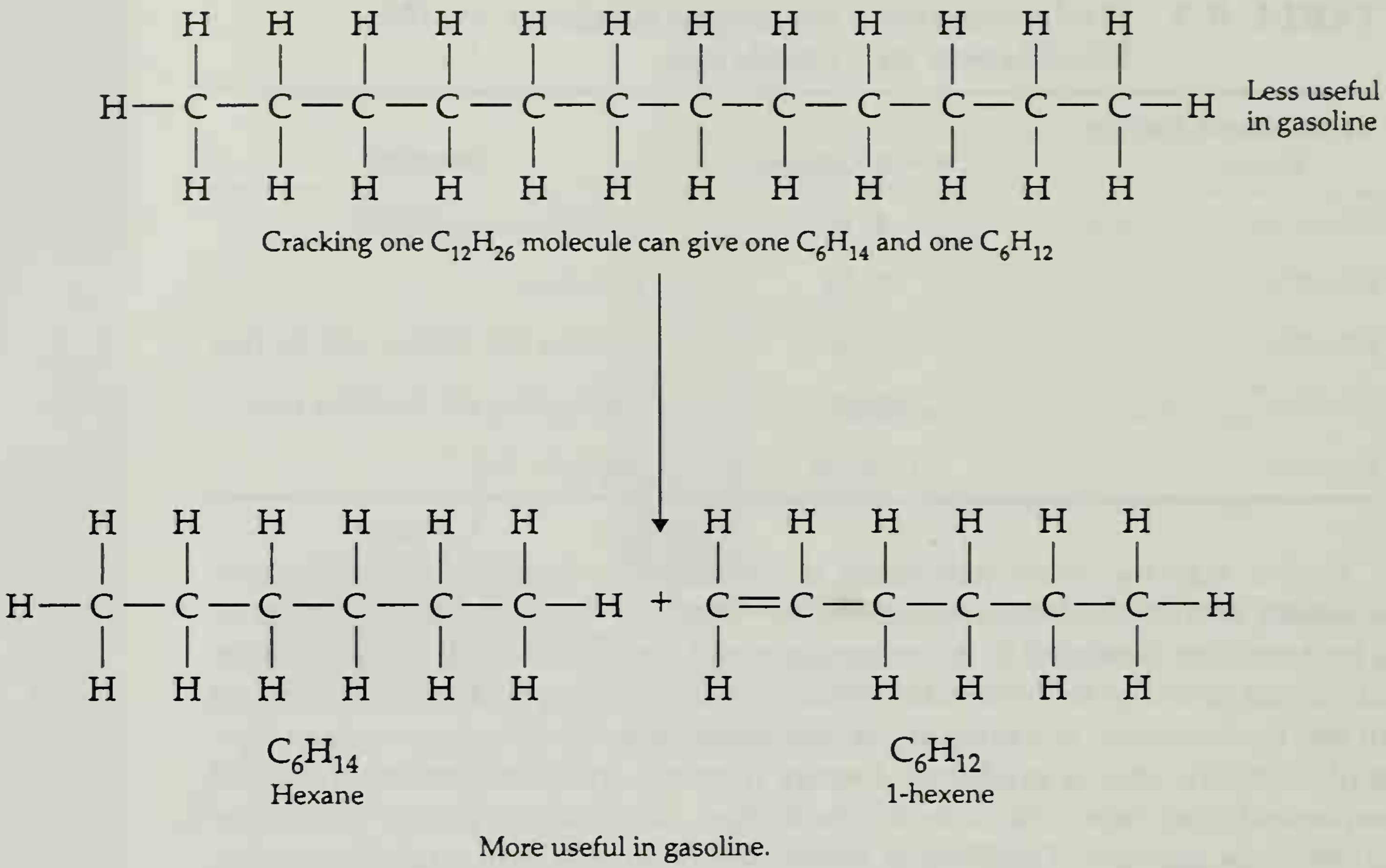
QUESTION

What facet of molecular structure other than the molecular weight or carbon content of its molecules affects the boiling point of an alkane? ____________

8.12 Petroleum Refining: Catalytic Cracking

In the introduction to this chapter we saw that the composition of petroleum varies considerably, depending primarily on the region of the world from which it comes. Generally, though, not much more than about 20% of any barrel of crude oil consists of hydrocarbons that can be blended into a gasoline mixture as they come from the fractionating tower. In the early part of this century, with relatively few cars on the road, kerosene, which was used for heating, was the most valuable product of petroleum refining. The 20% or so of straight-run gasoline obtained from the distillation easily satisfied the relatively small demand for gasoline. As the automobile swept away the horse and buggy, the demand for gasoline grew until natural limitations in the supply of straight-run gasoline threatened to strangle the relatively young automobile industry. Just before the outbreak of World War I a solution to the problem appeared in the form of a chemical process known as *cracking*. As the name implies, large covalent molecules are cracked, or broken apart into smaller ones. The process yields several smaller molecules from one larger parent.

Figure 8.10
Catalytic cracking.



Cracking a C_{12} hydrocarbon molecule of the kerosene fraction, for example, could yield two C_6 hydrocarbon molecules (Fig. 8.10). A C_6 hydrocarbon is more useful than a C_{12} hydrocarbon in blending a gasoline mixture because of its greater volatility. Cracking a C_{30} hydrocarbon could increase the amount of heating oil, or kerosene, or gasoline from a barrel of petroleum. In any case, cracking can increase the amount of low-molecular-weight hydrocarbons obtained through petroleum refining, but only at the expense of the higher-molecular-weight hydrocarbons. By using a **catalytic cracking** process, the yield of gasoline from a barrel of petroleum can be increased from 20% to about 50%, *but at the expense of the higher-boiling hydrocarbons, including kerosene and home heating oil.*

Catalytic cracking is a process by which large hydrocarbon molecules are converted into two or more smaller hydrocarbon molecules.

With warm winters and ample supplies of crude oil, there's plenty of kerosene, heating oil, and gasoline to satisfy everyone. But cold winters and short supplies of petroleum can drain our commercial reserves of heating oil, forcing petroleum refiners to perform a careful balancing act to maintain ample supplies of both gasoline and heating oil through catalytic cracking as well as other processes. Coupled with severe restrictions in our imports of petroleum, as a result of political actions, wars, or economic conditions, cold winters can force on our society the uneasy choice between enough gasoline to satisfy everyone, at the expense of cold homes, and warmth for all, at the expense of gasoline shortages. The technology we need in making these choices requires only a knowledge of the chemistry of petroleum refining and the existence of the refineries, catalysts, and equipment to do the job. But the choice itself, deciding how we use this technology in a moment of crisis, for mobility or for warmth, is societal and political in character. It requires wisdom in addition to knowledge.

QUESTION

Suppose that one product of cracking a C_9 alkane is

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2.$$

What is the other hydrocarbon product? ______________________

8.13 Petroleum Refining: Reforming

The use of the catalytic converter to alleviate air pollution means the disappearance of leaded gasoline. Although other gasoline additives have been used to increase octane ratings, none is as successful as tetraethyllead. The blending of lead-free gasoline from hydrocarbons of inherently high octane ratings seems now to offer the best approach to a combination of low hydrocarbon emissions (through the catalytic converter) and high compression ratios. Producing the high-octane hydrocarbons now necessary for lead-free gasoline requires an additional step in the process of petroleum refining: **catalytic reforming**.

In catalytic reforming, the carbon skeletons of unbranched or only slightly branched hydrocarbons are reorganized into much more highly branched molecules and into cyclic hydrocarbons (Section 7.10). When the carbon skeleton of an alkane is rearranged with formation of a more highly branched isomer, the reforming process is **isomerization** (Fig. 8.11). In another reforming step, **cyclization,** chains of five or six carbons are converted to cycloalkanes with an accompanying loss of hydrogen (Fig. 8.12). Loss of several hydrogens from a cyclohexane ring can produce an aromatic hydrocarbon through **aromatization** (Fig. 8.13). Aromatization of petroleum hydrocarbons through catalytic reforming serves as a major commercial source of aromatic hydrocarbons, which are used as industrial solvents and in the manufacture of pharmaceuticals, plastics, synthetic rubber, and other consumer products.

In **catalytic reforming** hydrocarbon molecules are reorganized into more useful structures of the same carbon content.

In **isomerization** the reforming results in the formation of a more highly branched isomer.

Cyclization converts noncyclic structures into cyclic molecules.

Aromatization converts cyclohexane rings into aromatic rings.

Figure 8.11

Isomerization of *n*-hexane (hexane) to isohexane (2-methylpentane).

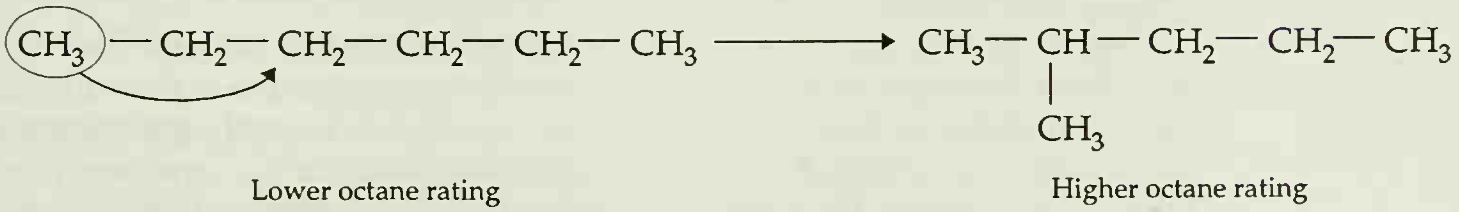
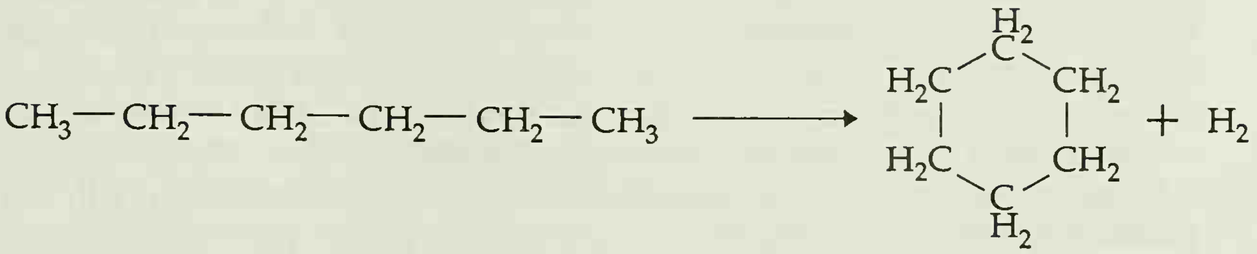


Figure 8.12

Cyclization of hexane to cyclohexane.



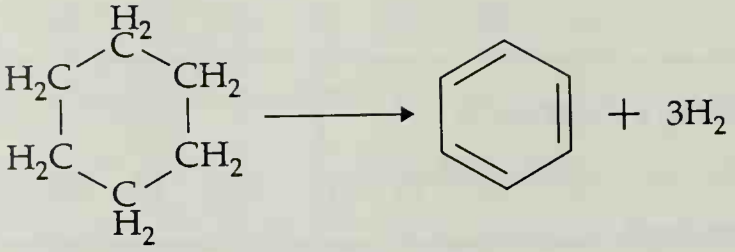


Figure 8.13 Aromatization of cyclohexane to benzene.

Since many of the products of catalytic reforming processes have high octane ratings (including benzene and other aromatic hydrocarbons), they can be used to blend gasolines for high-compression engines without the need for tetraethyllead as an additive. The result is a steady decrease in the pollution of our atmosphere by lead and by the unburned hydrocarbons of automobile exhausts.

QUESTION

(a) Name two products produced by the isomerization of *n*-pentane. (b) What is produced through the aromatization of cyclohexane? ______________________

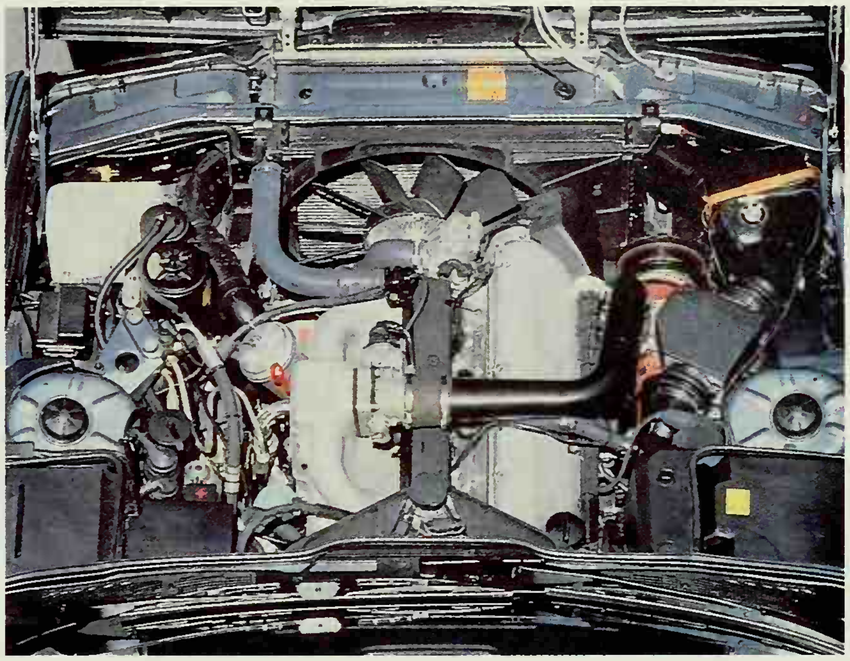
PERSPECTIVE: Fuels for the Cars of Tomorrow

In this chapter we have examined hydrocarbons as a source of energy, with particular emphasis on the hydrocarbons of gasoline and their use in the internal combustion engine. It's been an appropriate emphasis since about 40% of all the petroleum used in the United States now ends up as gasoline for our cars. Add diesel fuel and jet fuel to the list and you increase the amount of petroleum we use to move people and products over our roads and through the air by another 20%. (Somewhere between 10 and 15% of our petroleum consumption goes into the generation of electricity and the heating of homes, offices, and other buildings. Petroleum chemicals are also used in the manufacture of plastics, synthetic rubber, and pharmaceuticals, and are converted into other chemicals useful as raw material in manufacturing a host of consumer items.)

Despite an increase in the gasoline mileage delivered by our cars since the petroleum shortages of the early 1970s (which were alluded to in the editorial quotation earlier in this chapter), our cars, buses, trucks, and other vehicles are actually consuming 20% *more* fuel and other hydrocarbon products than they did back then. The reason is simple: There are more of these vehicles on the road today than there were in the early 1970s.

We're not only using more petroleum now, but we're doing more damage with it. Driving is a dirty business. We add more pollution to our environment by running our internal combustion engines than we do with any other single activity. Auto exhaust, even "clean" exhaust, contributes about a quarter of all the carbon dioxide discharged into the air above the United States, as well as almost all of the carbon monoxide in and above our cities. (Review Section 7.11 for a discussion of the greenhouse effect.) The benzene that's in our gasoline is a known *carcinogen*, a cancer-causing agent. The Environmental

An experimental electric van.



Another possibility: an experimental engine that runs on hydrogen.

Protection Agency, a division of the federal government, estimates that auto exhaust produces about 1800 cancers annually. Next time you fill your tank, look for a note on the gas dispenser telling you that "Long term exposure to vapors has caused cancer in some laboratory animals."

It seems clear that reducing our societal dependence on petroleum and improving or at least maintaining the health of our environment and ourselves require, among other things, lowering tailpipe emissions. This can take several forms. Auto manufacturers can design and produce cars that are more fuel-efficient than those now on the roads, and therefore simply use less gasoline. In addition, gasoline manufacturers can formulate cleaner-burning gasolines. Adding organic compounds containing oxygen within their molecules, like the methyl alcohol, *tert*-butyl alcohol, and methyl *tert*-butyl ether of Section 8.10 could lower carbon monoxide emissions, but it won't decrease carbon dioxide emissions and it might just increase other forms of pollution such as smog. Another route would be to switch from the hydrocarbons of gasoline entirely. We'll look at four of the most promising alternatives, and since none is a sure winner against hydrocarbons, we'll use simple alphabetical order.

ELECTRICITY

We discussed battery-powered cars in Chapter 6's Perspective, with a view of some of the advantages and disadvantage of electric cars. Perhaps their greatest advantage lies in the virtual absence of emissions from the car itself. In 1990 California required that by 1998 at least 2% of the cars sold in the state emit no exhaust pollutants whatever. By 2003 this proportion increases to 10%. With current technologies only electric cars can meet the zero-pollutant standard. The criterion of tailpipe emissions as a test of a car's societal acceptance seems to be gaining strength. In response to federal clean air laws, more than half the states now require inspection of tailpipe exhausts for noxious emissions of one kind or another. As additional states follow the same path the market for electric cars may enlarge and the pattern of the early years of this century could reverse in the next century, with electric cars displacing those running on gasoline. The major disadvantages of electric cars are their short driving ranges, the long times required for home recharging of their batteries, and the uncertainty of where all the electric power needed to recharge large numbers of batteries will come from.

ETHANOL

Unlike fuels obtained from petroleum, ethanol (ethyl alcohol) comes from the fermentation of grain and other crops (Section 7.4) and is thus a "renewable resource." That is, given sunlight, rain, a good climate, and other conditions, we can renew our supplies of ethanol as long as we have abundant annual harvests. Petroleum, on the other hand is a nonrenewable resource. None of this fossil fuel is being formed today to regenerate what we draw from the earth's current reserves. Add to this ethanol's octane rating of 105, its low impact on the greenhouse effect (because plants used in making ethanol absorb atmospheric CO_2 as they grow; see Section 5.14), and its relatively low toxicity, and ethanol becomes an attractive replacement for hydrocarbon fuels. Among its disadvantages are its relatively (compared to gasoline) high cost, low energy content, which would require large fuel tanks, and scarcity. Converting all the grain grown in the United States each year into ethanol would supply only about a quarter of the fuel needed.

METHANOL

Like ethanol, methanol has an octane rating of about 105. As noted in Section 7.4, methanol costs about as much as gasoline, mile for mile, and produces fewer pollutants. Moreover it can be manufactured from a variety of sources, including wood, coal, natural gas, and even garbage. Unfortunately it is corrosive, has a relatively low energy content (which, again, means large fuel tanks), and is toxic. Moreover, one of the few pollutants methanol does produce is especially nasty. Incomplete combustion of methanol generates formaldehyde, which is a carcinogen, an irritant, an air pollutant, and the active ingredient of embalming fluid. Exhaust systems would have to be redesigned to keep it out of the environment.

NATURAL GAS

Compressed gas of the sort used for cooking and heating now runs tens of thousands of "fleet vehicles" in the United States. These are cars, trucks, and buses that operate over short distances and return to a home base each night. The fuel is plentiful, relatively inexpensive, and far cleaner than gasoline. Unlike methanol, it produces no pollutant that is particularly troublesome. Its disadvantages are the short driving range it provides—about 100 miles, the heavy and awkward fuel tanks it requires, and the complexity of refueling. It is more suitable to fleet vehicles than to private automobiles.

Another possibility is a car that runs on more than one source of energy, such as a battery with a small gasoline engine for backup or recharging. Or tomorrow's cars may run on mixtures such as ethanol and gasoline or methanol and gasoline. In the end a balancing of cost, convenience, and cleanliness will very likely determine our choice of fuel for tomorrow's car. "Cost" will include the cost of fuel itself and the engine that burns that fuel, together with the expense of maintaining a clean environment and a safe means of fuel storage and engine operation. "Convenience" will be a matter of the simplicity of charging or exchanging a battery or filling a tank with our chosen chemicals, and the driving range they provide. "Cleanliness" will be a matter of the kind of environment in which we choose to live. In any case, we will have choices before us, as individuals and as a society. Whatever fuel or combination of fuels we do choose, it will be chemistry, in one form or another, that delivers the energy. Making the choices intelligently will require an understanding of the chemistry that lies behind them.

EXERCISES

FOR REVIEW

1. Complete this statement with the words and phrases that follow. Each is used once.

______ is a mixture of ______ whose ______ is converted into ______ within the cylinders of the ______. In a four-stroke engine, the ______ ignites the gasoline–air mixture at the end of the ______, sending the piston downward. The resulting ______ translates the energy of the gasoline into the power that moves the vehicle.

As the ______ (the ratio of the maximum volume of the gasoline–air ratio at the beginning of the compression stroke to that of the fully compressed mixture at the end of the compression stroke) of an engine increases, the tendency of a gasoline to ______ also increases. The ability of a particular gasoline blend to resist this tendency is reflected by its ______, which is measured by comparing the gasoline blend to a mixture of ______ and ______, which is also known as "octane" and "isooctane."

Gasoline itself is derived from a naturally occurring mixture of hydrocarbons known as ______. Although a certain amount of gasoline hydrocarbons (known as natural or straight-run gasoline) can be obtained directly from this mixture by ______, additional gasoline can be produced by ______, a process in which the molecules of higher-boiling fractions, such as ______, are broken down into smaller molecules that have properties more suitable to gasoline.

catalytic cracking
chemical energy
compression ratio
compression stroke
distillation
gasoline
n-heptane
hydrocarbons
internal combustion engine
kerosene
kinetic energy
knock
octane rating
petroleum
power stroke
spark plug
2,2,4-trimethylpentane

2. Define or identify each of the following:

a. catalyst
b. catalytic converter
c. chain branching
d. Clean Air Act of 1970
e. intake stroke
f. isomerization
g. potential energy
h. tetraethyllead

3. Identify the four strokes of the internal combustion engine and describe what happens during each.

4. What is the function of each of the valves located at the top of the cylinder? The spark plug? The piston?

5. What are the *three* products of the *complete* oxidation of a hydrocarbon? What lethal substance is produced on *incomplete* oxidation of a hydrocarbon?

6. What are the three characteristics of hydrocarbons that make them effective fuels for the internal combustion engines of automobiles?

7. What two factors affect the *volatility* of a hydrocarbon?

8. What is a major advantage of increasing the compression ratio of an engine? What characteristic of a gasoline must be changed as the compression ratio increases?

9. What purpose does the catalytic converter of an automobile serve?

10. Into which chemical is the carbon monoxide (CO) of exhaust gases converted as the gases pass through the catalytic converter? What effect does this product have on the environment?

11. What is the significance of the term *unleaded* in unleaded gasoline.

12. (a) Why was tetraethyllead originally introduced into gasoline? (b) What was the immediate reason for removing this chemical additive from gasoline? (c) What additional benefit comes from removing this additive? (d) Name another chemical additive that can serve the same function as tetraethyllead. (e) What refining process produces the same characteristic in gasoline as that obtained by adding tetraethyllead?

13. What is the function of distillation in the refining of petroleum?

14. Petroleum, which does not contain large quantities of aromatic hydrocarbons, is a major source of aromatic hydrocarbons. Explain why and describe the chemistry involved.

15. Does the catalytic cracking of petroleum produce straight-run gasoline? Explain.

16. What *two* refining steps are needed to convert *n*-hexane into benzene?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

17. Arrange the following hydrocarbons in order of increasing boiling point, with the lowest-boiling hydrocarbon first and the highest-boiling last: (a) nonane, (b) ethane, (c) butane, (d) heptane, (e) methane.

18. Arrange the following hydrocarbons in order of increasing boiling point, with the lowest-boiling hydrocarbon first and the highest-boiling last: (a) 2-methylbutane, (b) butane, (c) 2,2-dimethylpropane, (d) 2-methylpropane, (e) pentane.

19. Arrange the following hydrocarbons in order of increasing boiling point, with the lowest-boiling hydrocarbon first and the highest-boiling last: (a) octane, (b) 2-methylbutane, (c) hexane, (d) 2,2-dimethylpropane, (e) heptane.

20. Arrange the following hydrocarbons in order of increasing boiling point, with the lowest-boiling hydrocarbon first and the highest-boiling last: (a) 2,2-dimethylpentane, (b) 2-methylhexane, (c) 2,2,3-trimethylbutane, (d) heptane.

21. Based on what you know of the effect of the molecular structure of alkanes on their boiling points, why is it difficult to predict whether 2,2,3-trimethylheptane or *n*-octane will have the lower boiling point?

22. Aromatization of a cyclic hydrocarbon, A, molecular formula C_7H_{14}, produces *toluene*, C_7H_8. Write the name of hydrocarbon A and give its molecular structure.

23. Draw the condensed structure of the isomer of C_8H_{18} that has the *greatest number* of methyl groups. Write the IUPAC name of this isomer. What prediction can you make about the numerical value of its octane number?

24. Repeat Question 23 for the isomer of C_8C_{18} that has the *smallest number* of methyl groups.

25. What correlation do you think may exist between the number of primary carbons and the number of secondary carbons on a pair of isomeric alkanes, and the relative magnitude of their octane numbers? Explain.

26. What percentage of the time does a one-cylinder, four-stroke engine deliver power to the rotating blade of a gasoline-powered lawnmower? What keeps the blade spinning during the remainder of the time?

27. (**Note:** This question deals with data presented in Section 8.1.) Assuming that the same number of cars are on the road today as in 1989 and that we drive them the same number of miles as we did then, how many gallons of gasoline would we save each year for each one mile/gallon increase in the energy efficiency of our cars?

THINK, SPECULATE, REFLECT, AND PONDER

28. You have a mixture of two different liquid compounds and you attempt to separate them from each other by distillation. You find, however, that no matter how carefully you distill them and no matter how complex and intricate a distillation apparatus you use, you cannot separate the two components. What can you conclude about these two liquids?

29. Which of the following are examples primarily of kinetic energy and which are examples primarily of potential energy:

a. a waterfall
b. a person standing on a diving board, about to jump into a swimming pool

c. a diver who is in the process of entering the water at the end of the dive
d. an electric battery standing alone on the floor of a room
e. a stream of α particles
f. a coiled, compressed spring
g. the earth as it orbits the sun
h. a car traveling at 0.5 mile per hour

30. Which of the following components of auto exhaust emissions would you expect to be *decreased* by the use of a catalytic converter: H_2O, isopentane, CO_2, CO?

31. Which of the components of exhaust emissions described in Question 9 would you expect to be *increased* by the use of catalytic converters?

32. Would you expect the chemical composition—the specific hydrocarbons used to blend the gasoline and their proportions in the mixture—of a specific brand of gasoline to be the same in Miami in July as it is for the same brand sold in Chicago in January? Explain.

33. Suppose you were given samples of two different liquids. Describe how you could determine which one is the more volatile.

34. Engines are more likely to stall as the result of vapor lock after the car has been traveling for a while than when it is just started. Why?

35. How would doubling the electrical power used to fire the spark plug and ignite the gasoline–air mixture in the cylinder affect the power delivered by an internal combustion engine? Explain.

36. Do you think it would be a good idea to use pure, undiluted rocket fuel in the standard internal combustion engine of a commercial automobile? How do you think it would affect the engine's performance? Explain.

37. You are in charge of designing a new form of the internal combustion engine. One of your workers has suggested moving the valves and the spark plug from the top of the cylinder to the side of the cylinder, midway between the top and the bottom of the piston's travel. Are there any advantages to this idea? Are there any disadvantages? Explain.

38. Describe one way our society can produce a significant decrease in our consumption of petroleum. Explain your answer.

39. In the event of a severe and prolonged petroleum shortage, we may have to choose between producing enough heating oil to keep us warm during a particularly cold winter and producing enough gasoline to keep our cars running. Explain why we might have to make this choice and describe the chemistry involved.

40. What would you think is a major advantage of the combustion of hydrogen (H_2) as an automotive fuel? What would you think is a major disadvantage?

41. Can a compound have an octane rating higher than 100? Lower than 0? If your answer to either of these is *no,* explain why not. If your answer to either of these is *yes,* explain their significance.

42. If the combination of a new engine design and the development of the ideal hydrocarbon fuel produced *only* CO_2 and H_2O as combustion products, would you agree to the removal of catalytic converters from automobiles or to the sale of new cars without them? If your answer is *no* describe your reasoning. If your answer is *yes* would you agree to the return of leaded gasoline?

43. Suppose that you now own a car and could replace it with a new one that is equivalent or better in all respects, is far less expensive to own and operate, and doesn't pollute the atmosphere in any way. Suppose, though, that this new car has to be refueled (or recharged if it is an electric car) every 10 miles you drive. Would you replace your current car with this one? Would you replace it if the new car required refueling or recharging every 20 miles? 50 miles? 100 miles? 250 miles? 1000 miles? How does the *range* of a car affect your attitude toward it?

44. Prepare a table listing sources of energy that may replace today's gasoline for our cars of tomorrow. List several of the advantages and disadvantages of each.

c. a diver who is in the process of entering the water at the end of the dive
d. an electric battery standing alone on the floor of a room
e. a stream of α particles
f. a coiled, compressed spring
g. the earth as it orbits the sun
h. a car traveling at 55 miles per hour

30. Which of the following components of auto exhaust emissions would you expect to be decreased by the use of a catalytic converter: NO_x, hydrocarbons, CO, CO_2?

31. Which of the components of exhaust emissions described in Question 9 would you expect to be increased by the use of catalytic converters?

32. Would you expect the chemical composition—the specific hydrocarbons used to blend the gasoline and their proportions in the mixture—of a specific brand of gasoline to be the same in Miami in July as it is for the same brand sold in Chicago in January? Explain.

33. Suppose you were given samples of two different liquids. Describe how you would determine which one is the more volatile.

34. Engines are more likely to stall as the result of vapor lock after the car has been traveling for a while than when it is just started. Why?

35. How would doubling the electrical energy used to fire the spark plug and ignite the gasoline-air mixture in the cylinder affect the power delivered by an internal combustion engine? Explain.

36. Do you think it would be a good idea to use pure, undiluted rocket fuel in the standard internal combustion engine of a commercial automobile? How do you think it would affect the engine's performance? Explain.

37. You are in charge of designing a new form of the internal combustion engine. One of your engineers has suggested moving the valves and the spark plug from the top of the cylinder to the side of the cylinder, midway between the top and the bottom of the piston's travel. Are there any advantages to this idea? Are there any disadvantages? Explain.

38. Describe one way our society can gradually eliminate its dependence on the consumption of petroleum. Explain your answer.

39. In the event of a severe and prolonged petroleum shortage, we might be forced to choose between producing enough heating oil to keep us warm during a particularly cold winter and producing enough gasoline to keep our cars running. Explain why we might have to make this choice and describe the chemistry involved.

40. What would you think is a major advantage of the combustion of hydrogen (H_2) as an automobile fuel? What would you think is a major disadvantage?

41. Can a compound have an octane rating higher than 100? Lower than 0? If your answer to either of these is no, explain why not. If your answer to either of these is yes, explain their existence.

42. If the combination of a new engine design and the development of the ideal hydrocarbon fuel produced only CO_2 and H_2O as combustion products, would you agree to the removal of catalytic converters from automobiles or to the sale of new cars without them? If your answer is no, describe your reasoning. If your answer is yes, would you agree to the return of leaded gasoline?

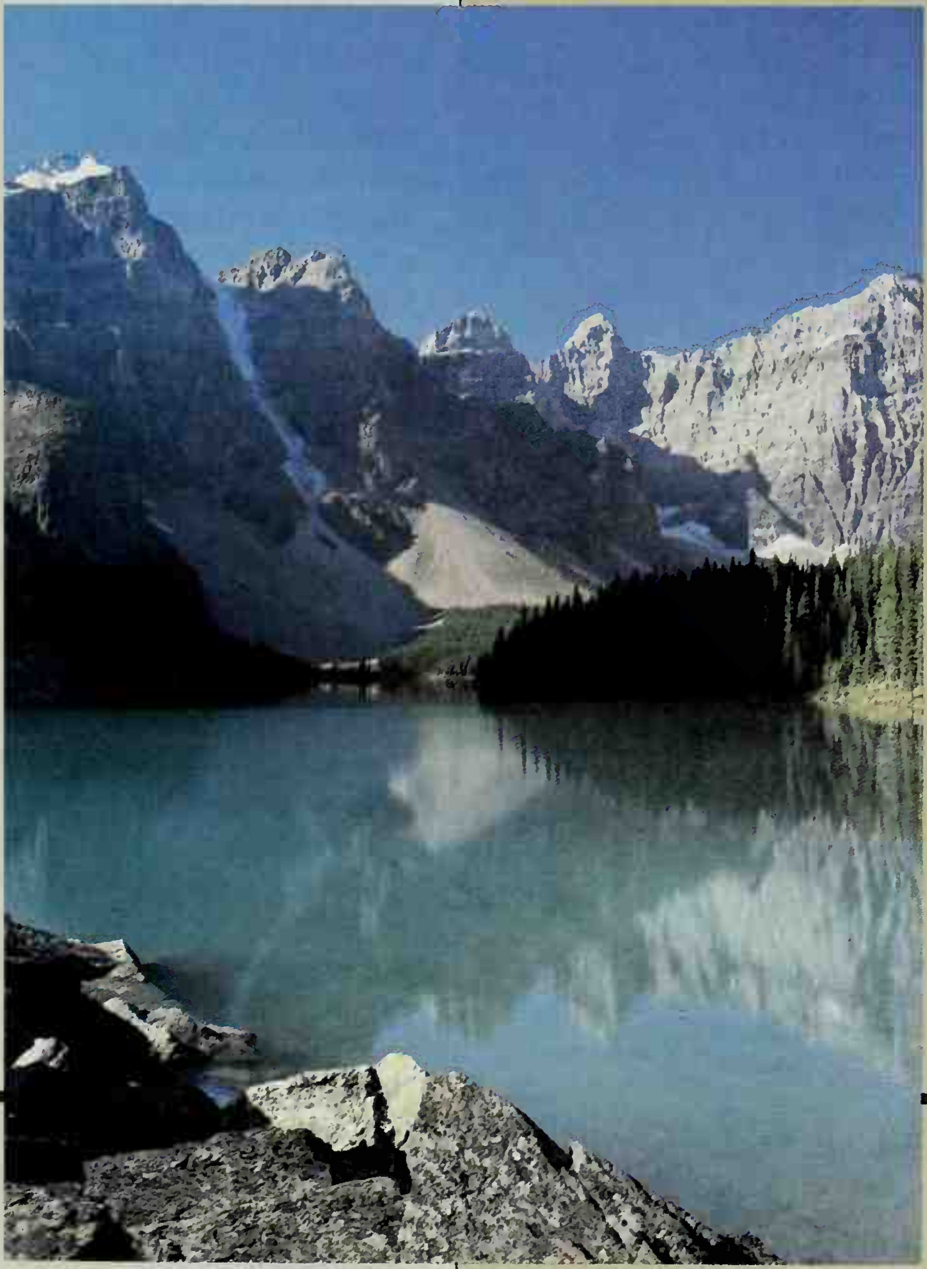
43. Suppose that you own a car and decide to replace it with a new one that is [illegible] in all respects, is far less expensive to own and operate, and doesn't pollute the atmosphere in any way. Suppose, though, that the new car has to be refueled (or recharged, if it is an electric car) every [illegible]. Would you replace your current car with this one? Would you replace it if the new car required refueling or recharging every 20 miles? 50 miles? 100 miles? 250 miles? 1000 miles? How does the [illegible] of a car affect your attitude toward it?

44. Prepare a table listing sources of energy that may replace petroleum for [illegible]. List some of the advantages and disadvantages of [illegible].

Counting Chemical Particles

9

THE ARITHMETIC OF POLLUTION



Would you drink this water?

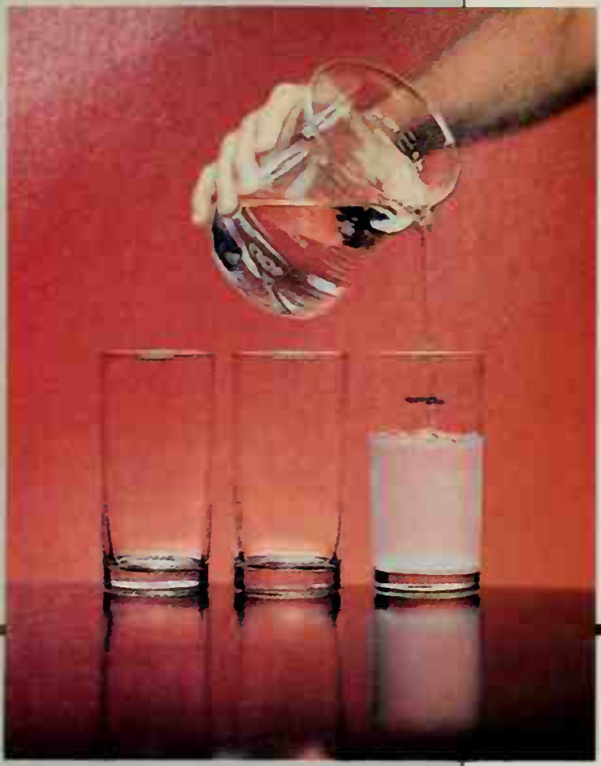


Figure 9.1

1. Put a tablespoon of salt into the standard measuring glass and fill it to the mark with water. Allow the salt to dissolve.

The Glass Where Pollution Begins

According to one of the less formal principles of chemistry, "There's a little bit of everything in anything." This implies that if we could detect and measure the most exceedingly small quantities down to the very molecules and atoms that make up any particular substance, we'd find a bit of whatever we might look for in anything we choose to examine. Read it as saying that nothing is pure and that everything is contaminated with something else, to one degree or another. If we consider pollution to be the contamination of any substance with another, undesirable material, then the question we ought to ask isn't *whether* any particular substance is polluted but, rather, *"What's the extent* of the pollution?" To put it a bit differently, our own concerns in our everyday world of ordinary things aren't so much with the very fact of contamination (the unavoidable presence of undesirable materials in our air, water, food, consumer goods, and other aspects of our environment), but rather with the actual *level* of contamination that exists, the concentrations of these disagreeable materials. Coupled with this, we must ask what levels of contamination we as individuals and as a society are willing to tolerate and what levels we will not accept.

Let's take a concrete example, one we'll return to repeatedly in this discussion. Start with eight drinking glasses, a ruler, a marking pen, and some table salt and table sugar. The glasses need not all be the same size and shape, but it's easier if they are. Put a mark near the top of one of the glasses (the smallest, if they aren't all the same size) so that you can fill it with the same volume of water repeatedly. That's your standard glass; you'll use it to fill the others. Put labels on the remaining seven from No. 1 to No. 7, or line them up in a row so you can always tell which is which.

Put a tablespoon of salt into the standard glass, fill it to the mark with warm tap water, and stir until the salt dissolves. Now pour this salt water into glass 1. Using the ruler and the marking pen, put a mark on the side of glass 1, 1/10th of the way down from the water's surface. This will make it easy to transfer 1/10th of the water in glass 1 (and therefore 1/10th of the salt) back to the standard glass. (The measurement will be most accurate if all the

2. 3. 4.

Figure 9.1 (*continued*)

2. Pour the standard glass of salt water into glass 1 and place a mark one-tenth of the way down from the top of the salt-water solution. 3. Using the mark on glass 1 as a guide, pour one-tenth of the solution from glass 1 back into the empty standard measuring glass. 4. Dilute the salt-water solution in the standard measuring glass by adding enough fresh water to bring the level of the solution up to the mark. Now you can pour this solution from the standard measuring glass into glass 2. Repeat the process so that the concentration of the salt in each glass of the set is one-tenth of the concentration of the salt in the preceding glass.

glasses have straight, vertical sides, but even if they don't, the mark will do nicely for this demonstration.)

Using the mark as a guide, pour 1/10th of the salt water from glass 1 into the standard glass. Now fill the standard glass to its own mark, as you did before, with warm tap water and stir the solution a bit so that the salt is evenly distributed. You have just diluted the salt water from glass 1 by a factor of 10. Empty this new, diluted salt-water mixture into glass 2. Repeat the procedure until each of the seven glasses holds a standard glass of salt water. The first glass contains salt water at a concentration of one tablespoon of salt per glass of water. Each of the remaining six contains 10% of the salt in the one before it. Figure 9.1 shows the preparation of the first two.

Taste the water in each, starting with the most dilute. A good way to do this is to use a fresh set of three glasses. Have a friend pour a little water from glass 7 into one of them and put tap water into the other two so that you don't know which is which. Now taste the water in the three glasses. Can you tell which has the salt in it? Repeat this procedure, going successively to the lower numbered glasses (with higher concentrations of salt) until you're sure you can taste the salt. At what dilution can you first taste the salt: 1/1000th tablespoon per glass? 1/100th tablespoon? 1/10th tablespoon? 1 tablespoon? You probably find that the water in glass 1 is too salty to drink. Would you call the water in glass 1 polluted with salt? Do you think you can drink the water in glass 7? Would you call the water in that glass polluted? What fraction of a tablespoon of salt is there in glass 7?

Try this again with solutions of sugar instead of salt. As we proceed through this chapter this demonstration will help us understand how we count chemical particles, what concentrations are and how we describe them, and the importance of measuring levels of pollution and dealing with pollution in a quantitative fashion.

9.1 A Pair, a Six-Pack, a Dozen, and More Than All the Stars in the Sky

We buy, sell, and count out things in units. They can be units of weight, as in a pound of hamburger; or units of volume, as in five gallons of gas; units of length, as in two yards of fabric; or units of area, as in three acres of timberland. Sometimes the units that we use reflect a natural or a common way of using things. We buy socks, for example, in pairs. Since we have two feet, the pair is a good unit for socks. Lose one sock and you'll have to buy two of them to replace it. You don't find socks being sold one at a time.

We usually buy soft drinks in six-packs and eggs in dozens. Sometimes we buy and sell very small, inexpensive things in packages of 50 or 100 or 250 simply for convenience. We're not likely to find run-of-the-mill paper clips or rubber bands for sale in ones and twos. More likely we'd buy a box of 50 or 100 or so (Fig. 9.2).

Atoms, molecules, and ions give us the problem of units on a scale unlike any other. In even the smallest quantity of material we might handle, the enormous numbers of chemical particles present simply overwhelm our ability to count. Terms like pair and dozen are meaningless; counting into the thousands or millions or billions is hopeless. There are more atoms of carbon in a single lump of charcoal than there are stars in the sky. Our common language fails us. We have to use new ideas and new words to count out the particles of chemistry.

We also have to use arithmetic. Like all sciences, chemistry functions through experimental observations of the world about us and through mathematical manipulations of the results we get. Whether we're counting socks, cans of soda, sheets of paper, or atoms and molecules, we have to use arithmetic to manipulate the numbers. Understanding the extraordinary chemistry of even the simplest things often requires familiarity with exponential or scientific notation, facility in the use of the metric system, and the ability to

A pair of socks, a 6-pack of soda, a dozen eggs, and a box of 100 paper clips.

perform simple calculations involving values and measurements that carry a variety of units.

Appendixes A, B, C, and D, at the back of this book, provide a brief introduction to the mathematical tools of the chemist. A review of them may be helpful before continuing with this chapter. Appendix E contains a detailed solution to Exercise 34, at the end of this chapter.

QUESTION

What number of individual items or smaller units make up (a) an ordinary deck of cards, without the jokers b) a football team (on the playing field); (c) a string quartet d) a kilogram; (e) a millennium?

9.2 The Chemistry of a Backyard Grill

Our examination of how we count molecules begins with a very pleasant chemical reaction that takes place on many a summer evening in a backyard grill. Steak is sizzling over hot charcoal. The glowing charcoal that cooks the steak consists almost entirely of the element carbon. It burns slowly in the oxygen of the evening air. In the overall reaction one atom of carbon combines with a diatomic molecule of oxygen to produce one molecule of carbon dioxide. When plenty of oxygen is available, the following reaction occurs in the grill:

$$C + O_2 \rightarrow CO_2$$

It's about as simple a reaction as you can find. Carbon combines with the oxygen, in the ratio of one atom of carbon to one molecule of diatomic oxygen, or 1:1, and the heat given off cooks the steak. That's all there is to it.

Grilling burgers over charcoal.

Simple as it is, though, it's real chemistry and it raises some good questions. For example, how much oxygen does the carbon in the sack of charcoal consume as it burns? It's an important question, even a matter of life or death. When charcoal burns in an enclosed space, a closed room for example, where there isn't enough oxygen to convert all the carbon to carbon dioxide, lethal carbon monoxide, CO, forms. Whenever there's insufficient oxygen, the reaction becomes

$$2C + O_2 \rightarrow 2CO$$

With a deficiency of oxygen, *two* carbon atoms combine with *one* diatomic oxygen molecule to form *two* molecules of CO.

Occasionally, on very cold nights, people living in houses with poor heating light up a charcoal grill in a closed bedroom to keep warm. That can be deadly. Not only does the glowing charcoal use up the life-sustaining oxygen, but as the burning carbon consumes the oxygen in the enclosed room, the chemical reaction changes from one yielding CO_2 to the one that produces lethal CO. The result is often tragic.

QUESTION

As we saw in Chapter 8, carbon monoxide is also produced by the incomplete combustion of hydrocarbons in automobile engines. Catalytic converters (Section 8.9) can promote the combination of carbon monoxide with oxygen, transforming the CO into CO_2. Balance the following equation for this reaction:

$$CO + O_2 \rightarrow CO_2$$

9.3 Counting Atoms and Molecules: Part I

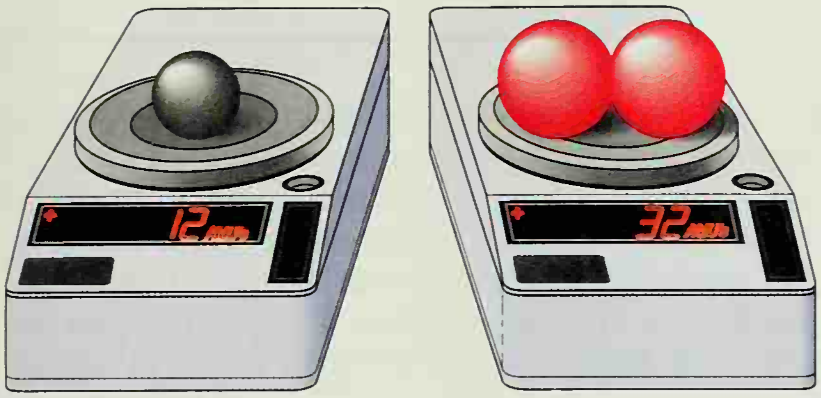
A single lump of commercial charcoal, the kind that's made for use in outdoor grills, weighs about 36 g. If we make the reasonably accurate assumption that the charcoal is pure carbon, it's easy enough to calculate exactly how much oxygen it takes to convert the entire 36 g of charcoal into carbon dioxide.

Here's how. We start by recognizing that exactly one atom of carbon combines with exactly one diatomic molecule of oxygen to form one molecule of CO_2. We saw this earlier in the chemical equation $C + O_2 \rightarrow CO_2$ (Section 9.2).

A charcoal briquette that weighs 36 grams.

We also know, from the periodic table, that the mass of carbon is 12 atomic mass units, or 12 amu (Section 2.4), and that the mass of one atom of oxygen is 16 amu. Naturally, the mass of a diatomic molecule of oxygen is twice this, 32 amu. If we had a scale that could weigh single atoms and molecules, we'd see something like Figure 9.3. One atom of carbon weighs 12 amu; one molecule of oxygen, 32 amu. Now we can answer a question that helps us along: "What weight of oxygen will react completely with 12 amu of carbon to give carbon dioxide as a product?" The answer has to be "32 amu of oxygen." That *must* be the answer since we have to work with whole atoms and entire molecules. One whole carbon atom weighs 12 amu and one entire oxygen molecule (two oxygen atoms) weighs 32 amu.

The scales in Figure 9.3 are completely imaginary. Figure 9.4 shows two

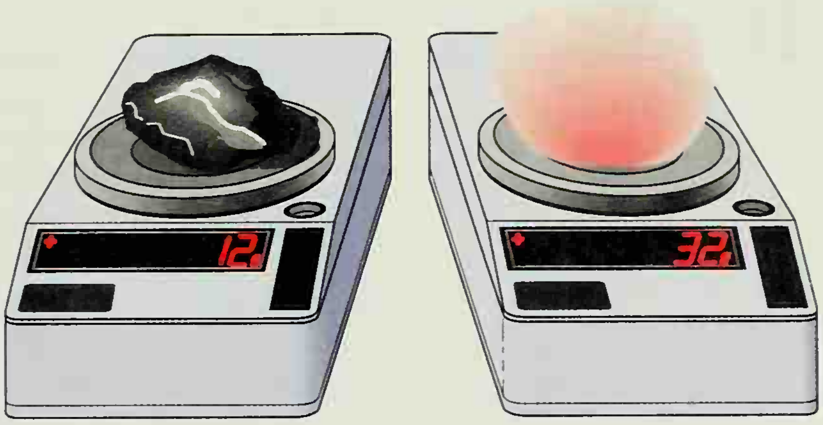


One carbon atom has a mass of 12 atomic mass units

One diatomic oxygen molecule has a mass of 32 atomic mass units

Figure 9.3

The mass of one carbon atom and of one diatomic oxygen molecule, expressed in atomic mass units. The scale is completely imaginary.



There are as many diatomic oxygen molecules in 32 grams of oxygen as there are carbon atoms in 12 grams of carbon

Figure 9.4

Equal numbers of carbon atoms and oxygen molecules.

real scales, one of which holds a piece of charcoal made up of 12 *grams* of carbon. Now we ask the question, "What weight of oxygen reacts with 12 *grams* of carbon to produce carbon dioxide?" To answer this question we don't have to know how many carbon atoms are on the scale in Figure 9.3. We need only weigh out 32 *g* of oxygen to have the same number of oxygen molecules on hand as we have carbon atoms, whatever that number may be. We know that's so because the ratio of the mass of a molecule of oxygen to the mass of an atom of carbon is 32:12.

What's important about all this is that *we have counted out atoms by weighing them*. In actual practice we could weigh out 12 g of carbon as charcoal. For 32 g of oxygen we could place a cylinder containing oxygen on a scale and open its valve until the weight of the cylinder and the oxygen it contains changes by 32 g.

We don't know (just yet) how many carbon atoms and how many oxygen molecules we are dealing with in Figure 9.3, but we do know that the two scales hold *equal numbers of the two chemical species*. And since carbon atoms and oxygen molecules react in a 1:1 ratio to produce carbon dioxide, all the oxygen atoms in 32 g of oxygen will react with all the carbon atoms in 12 g of carbon, with neither carbon nor oxygen left over.

Now we can answer our original question, "How many grams of oxygen does it take to convert one lump of charcoal that weighs 36 g completely into carbon dioxide?" We now know that one molecule of diatomic oxygen reacts with one atom of carbon, and we know that the ratio of the weight of a molecule of oxygen to the weight of an atom of carbon is 32:12, or 8:3. The weight of oxygen we need is 8/3rds of whatever weight of carbon we have. Since the charcoal weighs 36 g we need

$$36 \text{ g of carbon} \times \frac{8}{3} = 96 \text{ g of oxygen}$$

QUESTION

What weight of CO_2 results when 36 g of charcoal burns completely in air?

9.4 The Mole

As long as the ratio of weights of oxygen molecules and carbon atoms is 32:12 (8:3), the ratio of their respective molecular and atomic weights, we are dealing with equal numbers of carbon atoms and oxygen molecules. With this in mind, it doesn't matter in what units our scales are calibrated: grams, ounces, kilograms, pounds, tons, or some other units. All will do. Nor do we have to work with whole multiples of 12. With the simplest of algebra we can see that if we have x grams of carbon, then it takes 8/3 times x grams of oxygen to convert all the C to CO_2.

A **mole** is the number of atoms of carbon-12 in exactly 12 g of carbon-12. In practice, a *mole* of a substance is the number of chemical particles contained in its atomic, molecular, or ionic weight, expressed in grams.

As simple as the algebra is, it's far easier and much more convenient to handle the calculations of chemistry by defining a specific number of chemical particles in the same sort of way we define specific numbers of socks (a pair), soft drink cans (a six-pack), eggs (a dozen), and typing paper (a ream). The set of chemical particles chemists have worked out, the **mole,** has the same relation to atoms, molecules, and ions that a pair has to socks, a six-pack to cans of soda, and a dozen to eggs. That is, just as a pair, a six-pack, or a dozen represent specific numbers of items, a mole also represents a specific number of items, which happen to be chemical particles. *A mole is a specific number of chemical particles.*

By its precise, chemical definition, a mole (abbreviated *mol*) is the amount of any substance that contains the same number of chemical particles as there are atoms in exactly 12 g of carbon-12. Looked at from a different angle, the number of atoms of carbon-12 in exactly 12 g of this particular isotope of carbon defines the number of chemical particles in a mole. (Carbon-12 is the isotope of carbon with a mass of 12 amu; see Section 2.6.) In practice it amounts to this: Weigh out a quantity of an element or a compound equal to its atomic or molecular weight expressed *in grams*, and you have one mole of atoms or molecules of the substance.

As we weigh quantities of elements and compounds we are, in effect, actually counting out chemical particles, mole by mole (or fraction of a mole by fraction of a mole). The utility of this idea of a mole of particles doesn't depend on our knowing the actual number of particles that make up a mole, although we will learn the value of this number in Section 9.5. To use the mole successfully, we need only recognize the simplifying fact that *one mole of any chemical substance contains the same number of chemical particles as one mole of any other chemical substance.* One mole of carbon atoms (12 g of C) reacts completely with one mole of oxygen molecules (32 g of O_2) because one mole of carbon and one mole of molecular oxygen contain exactly the same numbers of carbon atoms and oxygen molecules.

One mole of carbon, of lead, of water and of sulfur.

Before continuing with the mole, we'll examine briefly the connection between the *number* of a group of objects or items and their *weight*. Suppose, for example, you had a dozen feathers and a dozen elephants. You would have the same number of each (12, a dozen), but would the two groups weigh the same? Then again, suppose you have 3 tons of feathers and 3 tons of elephants. You would have the same weight of each, 3 tons. But would you expect to have more elephants, more feathers, or the same number of each?

For another illustration, we'll use actual weights and values of U.S. coins.

Coin	Value	Weight (g)	Number of Coins in a Dozen	Value of a Dozen	Weight of a Dozen (g)
Quarter	25¢	5.6	12	$3.00	67
Dime	10	2.3	12	1.20	28
Nickel	5	5.0	12	.60	60
Penny	1	2.5	12	.12	30

Here the weight of a set of a dozen coins ranges from a high of 67 g for quarters to a low of 28 g for dimes, yet there are 12 coins in each set. Similarly, the value of a dozen coins ranges from a high of $3.00 for quarters to a low of 12 cents for pennies, yet there are still exactly 12 coins in each set.

Following are a few additional examples of these same principles.

EXAMPLE NICKLES BY THE DOZEN

How many nickels are there in 60 g of nickels?

Since a dozen nickels weigh 60 g, there must be 12 nickels in 60 g of nickels.

EXAMPLE MAKING SENSE OF GRAMS

How many pennies are there in 60 g of pennies?

Since a dozen pennies weigh 30 g, there must be two dozen pennies, 24 pennies, in 60 g of pennies.

EXAMPLE PENNIES AND DIMES

What weight of dimes do we need to equal the monetary value of 100 g of pennies?

We'll take this stepwise. First, we find the value of 100 g of pennies.

$$100\text{ g} \times \frac{\text{penny}}{2.5\text{ g}} \times \frac{1¢}{\text{penny}} = 40¢$$

Now that we know that 100 g of pennies are worth 40 cents we can find the weight of dimes we need to equal this same 40 cents:

$$40¢ \times \frac{\text{dime}}{10¢} \times \frac{2.3\text{ g}}{\text{dime}} = 9.2\text{ g}$$

We find that 9.2 g of dimes have the same financial value as 100 g of pennies.

EXAMPLE GOLDEN MOLES

Which has more atoms, one mole of gold or one mole of lead?

A mole is a specific number of chemical particles. One mole of gold contains just as many atoms as one mole of lead (just as there are as many socks in a pair of socks as there are shoes in a pair of shoes).

EXAMPLE ALUMINATING HELIUM

Compare the number of atoms in 27 g of aluminum and 4 g of helium.

The two contain the same number of atoms. Since 27 g of aluminum represents the atomic weight of aluminum, in grams, and 4 g of helium represents the atomic weight of helium, again in grams, the two contain the same number of atoms, one mole of each element.

EXAMPLE HYDROGEN OR OXYGEN?

Which has more atoms, one gram of hydrogen atoms or one gram of oxygen atoms?

Since the atomic weight of oxygen is 16, one gram of oxygen represents 1/16th of a mole of oxygen atoms. On the other hand, one gram of hydrogen, atomic weight 1.008, represents very nearly one mole of hydrogen atoms. Since one mole of any chemical substance must contain exactly the same number of chemical particles as one mole of any other chemical substance, there must be almost 16 times as many atoms of hydrogen in one gram of hydrogen as there are oxygen atoms in one gram of oxygen.

EXAMPLE MOLES OF METHANE

How many molecules of CH_4 are there in 8.02 g of methane (Section 7.2)?

A molecule of methane contains one carbon atom and four hydrogen atoms. Its molecular weight (Section 3.13) is the sum of the atomic weights of each of its atoms. The molecular weight of methane, then, is

$$\begin{array}{lrl}
\text{C:} & 1 \times 12.01\ \text{amu} = & 12.01\ \text{amu} \\
\text{H:} & 4 \times 1.008\ \text{amu} = & \underline{4.032\ \text{amu}} \\
 & & 16.04\ \text{amu}
\end{array}$$

Since one molecule of methane weighs 16.04 amu, one mole of methane weighs 16.04 g. Therefore, 8.02 g of methane must contain half a mole of CH_4 molecules.

EXAMPLE WATERY HYDROGEN

How many hydrogen atoms are there in 18.02 g of water?

The molecular weight of water is

$$\begin{array}{llll} \text{H:} & 2 \times 1.008 \text{ amu} & = & 2.016 \text{ amu} \\ \text{O:} & 1 \times 16.00 \text{ amu} & = & 16.00 \text{ amu} \\ \hline & & & 18.02 \text{ amu} \end{array}$$

This weight of water represents one mole of water. Since there are two hydrogen atoms for each water molecule, there must be twice as many hydrogen atoms as there are water molecules in *any* quantity of water molecules. In 18.02 g of water (one mole of H_2O) there must be *two* moles of hydrogen atoms.

QUESTION

(a) How many moles of carbon are in a charcoal briquette that weighs 36 g? Assume that the charcoal is pure carbon. (b) Assuming that the rounded tablespoon of salt of the opening demonstration weighed 23.4 g, how many moles of sodium chloride did it contain? Use 23.0 amu for the atomic weight of Na and 35.5 amu for the atomic weight of Cl. (c) Assuming that the rounded tablespoon of sugar in the second part of the opening demonstration weighed 17.1 g, how many moles of sugar did it contain? The molecular formula for sucrose is $C_{12}H_{22}O_{11}$ and its molecular weight is 342.

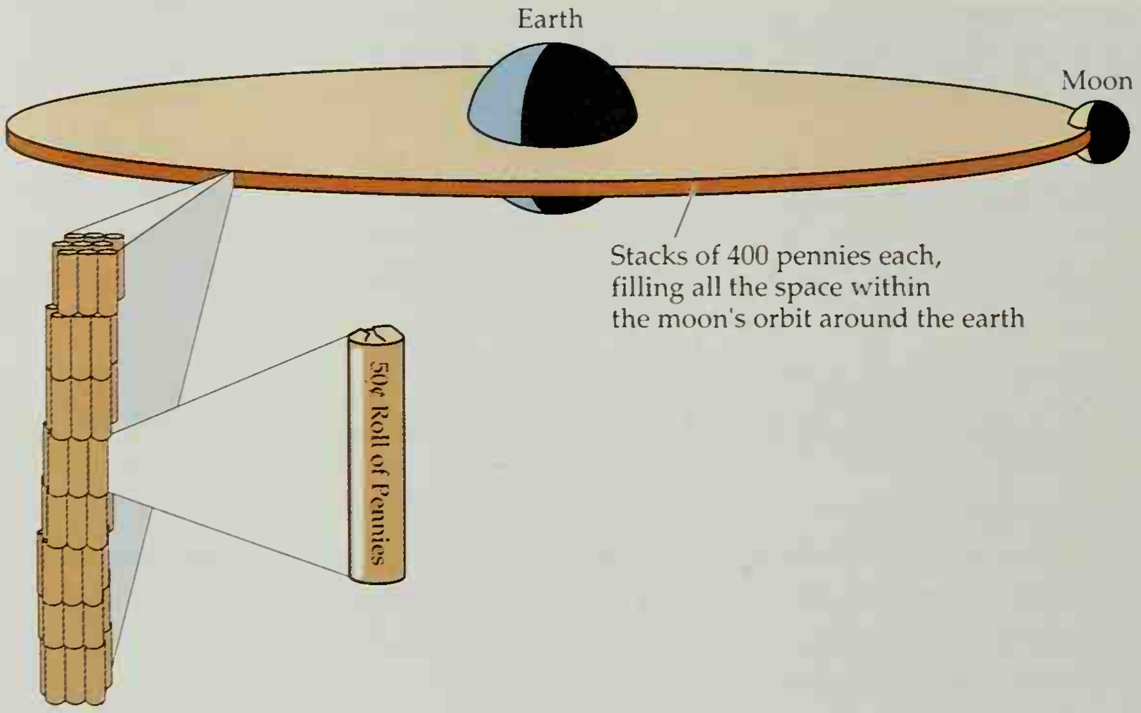
9.5 Avogadro's Number Wins!

Although knowing the exact number of particles in a mole isn't critical to using the whole idea successfully, chemists are never satisfied with ignorance. We know now that one mole of anything consists of 6.02×10^{23} chemical particles. This number is called **Avogadro's number** in honor of the Italian physicist Amedeo Avogadro, who was born in the year of the Declaration of Independence and whose pioneering work led to the way we now count chemical particles.

Avogadro's number, 6.02×10^{23}, is the experimentally determined number of chemical particles in a mole.

Avogadro's number is staggeringly large. In terms of time, Avogadro's number of seconds, 6.02×10^{23} seconds, stretches out to about 2×10^{14} centuries, which is roughly a million times the best current estimates of the age of the entire universe. In money, just one mole of pennies would fill all the space within the moon's orbit around the earth in stacks of about 400 pennies each (Fig. 9.5). Distributed equally to everyone in the earth's population of about five billion people, a mole of pennies would give each one of us a little over a trillion dollars.

Figure 9.5
A mole of pennies.



In terms of chemical particles, an aluminum soft drink can, which weighs about 16.5 g, contains about

$$16.5\text{ g} \times \frac{\text{mol Al}}{27.0\text{ g}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{\text{mol}} = 3.68 \times 10^{23}\text{ atoms of aluminum}$$

A 1-oz coin of pure silver contains

$$1\text{ oz} \times \frac{28.3\text{ g}}{\text{oz}} \times \frac{\text{mol Ag}}{108\text{ g}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{\text{mol}} = 1.58 \times 10^{23}\text{ atoms of silver}$$

Amadeo Avogadro, for whom the number of chemical particles in a mole is named.

As another illustration, an ordinary 8-oz glass of water contains about 13.1 mol of water, which amounts to 13.1 times Avogadro's number or just under 79×10^{23} molecules of water (Fig. 9.6). By any measure that's a lot of molecules.

Getting a good value for the number hasn't been simple. Our best estimate comes from X-ray measurements of various crystalline substances, including diamonds and a form of calcium carbonate, $CaCO_3$, known as calcite.

QUESTION

The sun is 150,000,000 km from the earth and the diameter of a penny is 1.9 cm. If Avogadro's number of pennies were used to build a road from the earth to the sun, and the road were just one layer of pennies deep, how many pennies wide would the road be? (This problem is worked in some detail in Appendix C.) __________

Figure 9.6

There are 3.68 × 10^{23} atoms of aluminum in the can, 1.58 × 10^{23} atoms of silver in the coin, and 79 × 10^{23} molecules of water in the glass.

9.6 Counting Atoms and Molecules: Part II

Now, by using the mole and understanding its connection to Avogadro's number, we can count out chemical particles in any reaction. The discharge of the automobile's lead–acid storage battery, for example, converts lead, lead oxide, and sulfuric acid into lead sulfate and water according to the chemical equation (Section 6.16)

$$\text{discharge:}\quad Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

This equation tells us, among other things, that *one* mole of lead reacts with *one* mole of lead dioxide and *two* moles of sulfuric acid to produce *two* moles of lead sulfate and *two* moles of water. (Naturally, other quantities of these chemicals react with each other as well, but always in that same ratio.) This must be the case since in this balanced equation every atom of every element that appears among the products also appears among the reactions. This, in turn, is required by the Law of Conservation of Mass (Section 4.12), which tells us that mass may be neither created nor destroyed in a chemical reaction.

We can summarize the logic of all this as follows: Since mass may be neither created nor destroyed, every atom appearing on one side of the arrow must appear on the other side as well. To obtain this condition, we balance equations. Balanced equations, in turn, tell us the ratios of the moles (or atoms or molecules or ions) of all the substances that make up the reactants and the products. From this information we can calculate the weight of each chemical involved in the reaction, given the weight of any one of them.

Here's an example based on our observation in Section 6.16 that the density of the fluid bathing the plates in the lead–acid battery drops as water replaces sulfuric acid during discharge.

EXAMPLE FIVE EASY STEPS

What weight of water appears for every gram of sulfuric acid that disappears during the discharge of the battery?

We can solve this problem in five simple steps, represented graphically as follows:

Step 2
Weight of
sulfuric acid

Step 5
Weight of
water

Step 1
Balanced
equation: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2\ H_2O$

Step 3
Moles of
sulfuric acid

Step 4
Moles of
water

Step 1: Write the balanced equation for the reaction. This gives us the relationship among the numbers of particles of each chemical among the reactants and of each chemical among the products.

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

Step 2: Identify the *known weight* of any of the chemicals taking part in the reaction. In this case we are told that one gram of sulfuric acid disappears. Since we want to know how much water appears for every gram of sulfuric acid that disappears, we'll start with 1.00 g of sulfuric acid.

$$Pb + PbO_2 + \overset{1.00\ g}{2H_2SO_4} \rightarrow 2PbSO_4 + 2H_2O$$

Step 3: Determine how many moles this corresponds to. For the molecular weight of sulfuric acid, we find

H: 2×1.008 amu = 2.016 amu
S: 1×32.06 amu = 32.06 amu
O: 4×16.00 amu = 64.00 amu

98.08 amu, which we
round off to 98.1 amu
to maintain 3 significant figures

Thus, there are 98.1 g of sulfuric acid (and 6.02×10^{23} molecules) of H_2SO_4 in every mole of sulfuric acid. Using units cancelation (Appendix C), we convert 1.00 g of sulfuric acid to

$$1.00\ \text{g}\ H_2SO_4 \times \frac{\text{mol}\ H_2SO_4}{98.1\ \text{g}\ H_2SO_4} = 0.0102\ \text{mol}\ H_2SO_4$$

$$Pb + PbO_2 + \underset{0.0102\ \text{mol}}{\overset{1.00\ \text{g}}{2H_2SO_4}} \rightarrow 2PbSO_4 + 2H_2O$$

Step 4: Convert this to the number of moles of the chemical whose weight we want. The balanced equation tells us that two molecules (or 2 mol) of sulfuric acid react to produce two molecules (or 2 mol) of water. This means, of course, that for every molecule (or mole) of sulfuric acid that disappears among the reactants, one molecule (or mole) of water appears among the products. (The ratio that appears in the balanced equation is 2:2 or 1:1.) Therefore the disappearance of 0.0102 mol of H_2SO_4 must be accompanied by the appearance of 0.0102 mol of H_2O.

$$Pb + PbO_2 + \underset{0.0102\ \text{mol}}{\overset{1.00\ \text{g}}{2H_2SO_4}} \rightarrow 2PbSO_4 + \underset{0.0102\ \text{mol}}{2H_2O}$$

Step 5: Calculate the weight of the substance we're interested in. We saw in the examples in Section 9.4 that the molecular weight of water is 18.02 amu. This means that there are 18.02 g of water in every mole of water. Thus 0.0102 mol of water weighs

$$0.0102\ \text{mol}\ H_2O \times \frac{18.02\ \text{g}\ H_2O}{\text{mol}\ H_2O} = 0.184\ \text{g}\ H_2O$$

$$Pb + PbO_2 + \underset{0.0102\ \text{mol}}{\overset{1.00\ \text{g}}{2H_2SO_4}} \rightarrow 2PbSO_4 + \underset{0.0102\ \text{mol}}{\overset{0.184\ \text{g}}{2H_2O}}$$

We have now answered the original question. Every 1.00 g of H_2SO_4 that disappears during the discharge of the battery is replaced by 0.184 g of H_2O.

Along with water's considerably smaller density, this decrease in the mass of fluid as the battery discharges helps explain why the density of the fluid bathing the plates of lead and lead dioxide drops during discharge.

We'll look at one more example, one involving a different reaction and a different ratio of moles.

EXAMPLE A DANGEROUS CALCULATION

In Section 9.2 we found that when charcoal burns in the presence of insufficient oxygen, lethal carbon monoxide forms. How much oxygen is consumed when one charcoal briquette, weighing 36 g, burns to form CO?

Step 1: Write the balanced equation for the reaction.

$$2C + O_2 \rightarrow 2CO$$

Step 2: Identify the *known weight* of any of the chemicals taking part in the reaction. The briquette weighs 36 g. As before, we'll assume it's pure carbon.

$$\overset{36\ g}{2C} + O_2 \rightarrow 2CO$$

Step 3: Determine how many moles this corresponds to. Since the atomic weight of carbon is 12.01 amu,

$$36\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 3.0\ \text{mol C}$$

$$\underset{3.0\ mol}{\overset{36\ g}{2C}} + O_2 \rightarrow 2CO$$

Step 4: Convert this to moles of the chemical whose weight we want. In this case, *two* carbon atoms react with *one* oxygen molecule. This means that for every *one mole* of carbon that reacts, only *half a mole* of oxygen is consumed. The 3.0 mol of carbon in the briquette need only 1.5 mol of O_2 to be converted completely to carbon monoxide.

$$\underset{3.0\ \text{mol}}{\overset{36\ \text{g}}{2C}} + \underset{1.5\ mol}{O_2} \rightarrow 2CO$$

Step 5: Determine how many grams of oxygen this corresponds to.

$$1.5\ \text{mol}\ O_2 \times \frac{32\ \text{g}\ O_2}{\text{mol}\ O_2} = 48\ \text{g}\ O_2$$

$$\underset{3.0\ mol}{\overset{36\ g}{2C}} + \underset{1.5\ mol}{\overset{48\ g}{O_2}} \rightarrow 2CO$$

The 36 g of carbon in the charcoal briquette react completely with 48 g of O_2 to form carbon monoxide.

QUESTION

Using the five-step approach described, determine how many grams of oxygen it takes to react completely with 36 g of carbon to form carbon dioxide, CO_2. Show that the combination of your result in this exercise and your result in the question at the end of Section 9.3 illustrates the Law of Conservation of Mass. ____________________

9.7 Getting to the Right Solution Takes Concentration

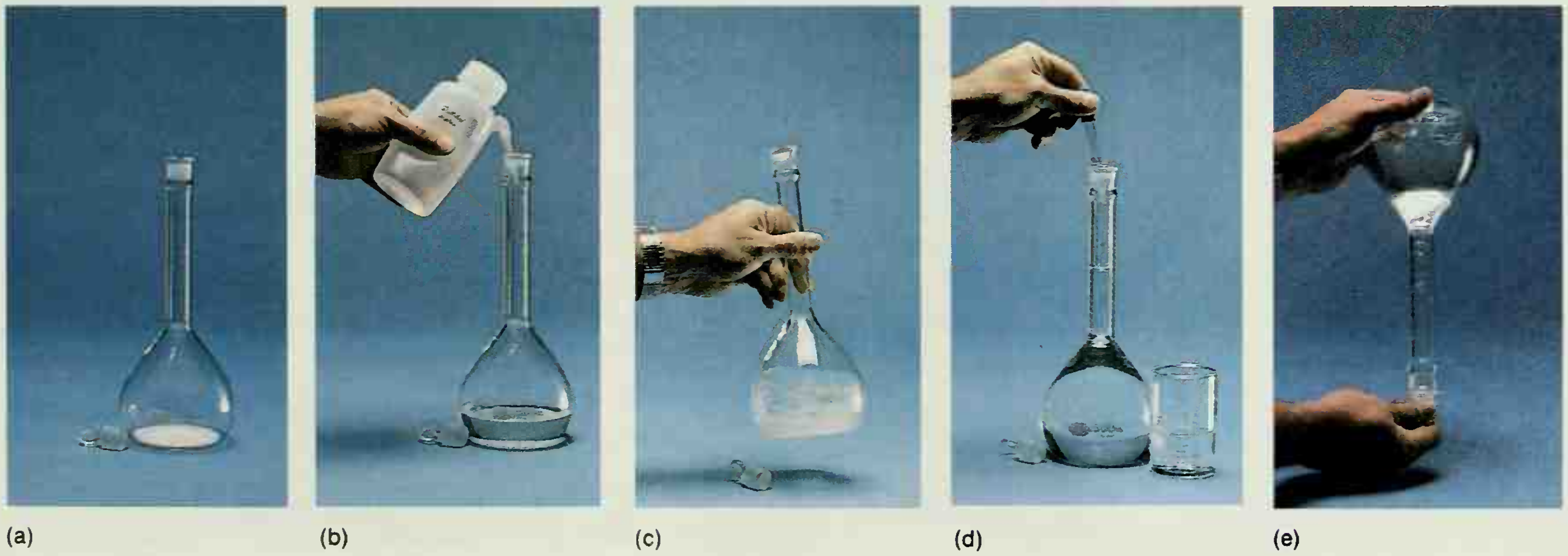
While weighing quantities of chemicals is a fine method for counting out atoms, molecules, and ions, we can often count chemical particles far more conveniently and easily by measuring volumes of liquid solutions. You make up a **solution** by dissolving one substance, the **solute,** in another substance, the **solvent.** The result is a solution of the solute in the solvent. Solutions are completely homogeneous mixtures of solutes and solvents. That is, the composition and properties of any solution are perfectly uniform throughout the entire solution. Sometimes it takes a bit of stirring or shaking to achieve this homogeneity, as when you dissolved the salt and sugar in water in the opening demonstration. With enough stirring, the sodium and chloride ions of the salt and the sucrose molecules of the sugar were distributed evenly throughout the water. The sodium chloride and the sucrose were the solutes, the water was the solvent, and the salt water and the sugar water were the solutions.

If we know how much of the solute is dissolved in a specific volume of the solution, we know the **concentration** of the solute. Knowing this value

A **solution** is a homogeneous mixture of one substance, the **solute**, dissolved in another, the **solvent.** The solute is present in a smaller proportion than the solvent.

The **concentration** of a solution expresses the quantity of solute dissolved in a specific quantity solution. The quantity of solution is usually stated as a volume.

The five steps in preparing a solution of a specific concentration. (a) Adding a known weight of solute to a flask etched with a mark to allow filling it to an accurately measured, predetermined volume. (b) Adding a portion of the solvent. (c) Swirling the mixture to dissolve the solute in the solvent. (d) Adding enough solvent to bring the surface of the solution exactly to the etched mark. This produces an accurately measured volume of solution, usually a multiple or simple fraction of a liter. (e) Shaking the stoppered flask to distribute the solute uniformly throughout the solution.



allows us to measure out an exact quantity of solute by measuring a volume of the solution itself. In effect we can count out chemical particles by measuring volumes of solutions.

In the demonstration that opened this chapter we saw examples of various concentrations of a solute (salt) in a solution (salt water). As we dissolved one tablespoon of sodium chloride in a glass of water we prepared a solution whose concentration was *one tablespoon per glass*. While we don't normally use units of this sort, our measurements with the standard glass of water in that demonstration make this a perfectly valid, if nonstandard and not very precise, description of the concentration of salt water in glass 1. Recall that we transferred 1/10th of the salt from the first glass into glass 2 by pouring out 1/10th of the solution. The concentration of the sodium chloride in glass 2 thus became 0.1 tablespoon per glass. In the next glass the concentration was 0.01 tablespoon per glass. The same principles and definitions of that demonstration apply equally to the much more accurate measurements carried out in scientific laboratories.

9.8 Molarity

The terms and units available for expressing concentrations are almost as varied as the kinds of solutions we can prepare. They range from the not-very-scientific and imprecise "tablespoon per glass" of our demonstration, through some of the terms that appear on the labels of our consumer products (which we'll examine in the next section), to well-defined units based on the concept of the mole. These latter make it particularly easy to get a quick count of chemical particles of solute by measuring the volume of a solution in an inexpensive, readily available, calibrated cup, beaker, flask, or cylinder. That beats carrying around a heavy, cumbersome, and expensive balance or scale.

The **molarity** of a solution refers to the number of moles of solute per liter of solution.

For counting chemical particles by measuring volumes of solutions we commonly use concentrations expressed in **molarity** (M). The molarity of a solution refers simply to *the number of moles of solute per liter of solution*. A 1 M (one molar) solution contains one mole of solute in each liter of solution, a 2 M solution contains two moles of solute per liter of solution, and so on.

Molarity provides an especially easy way to count chemical particles. Simply multiply the volume of a solution (in liters) by its concentration (in molarity) and you have the number of moles of solute in the volume of solution at hand. Two liters of a 1 M solution contain a total of 2 mol of the solute, but then so does 1 liter of a 2 M solution, or 0.5 liter of a 4 M solution:

Volume of Solution		**Concentration of Solution**		**Number of Moles of Solute**
2 liters	×	$\frac{1 \text{ mol}}{\text{liter}}$	=	2 mol of solute
1 liter	×	$\frac{2 \text{ mol}}{\text{liter}}$	=	2 mol of solute
0.5 liter	×	$\frac{4 \text{ mol}}{\text{liter}}$	=	2 mol of solute

EXAMPLE CLEANING UP

Solutions of ammonia are used as household cleaners. How many moles of ammonia, NH_3, are there in 1.2 liters of a solution that is 0.50 *M* in ammonia?

Using the definition of molarity as the number of moles of solute per liter of solution, we have

$$1.2\text{ liter} \times \frac{0.50\text{ mol } NH_3}{\text{liter}} = 0.60\text{ mol } NH_3$$

EXAMPLE MORE AMMONIA

We are still using this same 0.50 *M* solution of ammonia, but this time we need 1.8 mol of the solute. What volume of the solution do we use to get 1.8 mol of ammonia?

This time we start with the number of moles we need and we invert the value of the molarity to give us the answer in liters.

$$1.8\text{ mol } NH_3 \times \frac{\text{liters}}{0.50\text{ mol } NH_3} = 3.6\text{ liters}$$

EXAMPLE MIXING UP MORE

We have just run out of the 0.50 *M* solution of ammonia and must make up more. We prepare the solution 5 liters at a time. What weight of ammonia do we need to prepare 5.0 liters of 0.50 *M* ammonia? To convert between moles of ammonia and grams of ammonia we use the molecular weight of the ammonia:

$$\begin{array}{lrl} \text{N:} & 1 \times 14.01\text{ amu} = & 14.01\text{ amu} \\ \text{H:} & 3 \times 1.008\text{ amu} = & 3.024\text{ amu} \\ \hline & & 17.03\text{ amu} \end{array}$$

17.03 amu, which we round off
to 17 amu since we're using
only 2 significant figures
for volume and concentration

In this case we know we need 5.0 liters of solution, we know that the solution must contain 0.50 mol of ammonia per liter, and we know that there are 17 g of ammonia per mole. This knowledge gives us

$$5.0\text{ liters} \times \frac{0.50\text{ mol}}{\text{liter}} \times \frac{17\text{ g } NH_3}{\text{mol}} = 42\text{ g } NH_3$$

Our desired solution contains 42 g of ammonia in 5.0 liters of solution.

In a final example we stretch our definition of molarity just a bit to find the molarity of water molecules themselves in bulk water. It's a small stretch since molarity normally deals with the concentration of solute molecules in a solvent. In this case we're considering water to be both the solute and the solvent.

With a density of 1000 g per liter for bulk water and a molecular weight of 18.0 amu for the water molecule, we have

$$\frac{1000 \text{ g water}}{\text{liter of water}} \times \frac{\text{mol of water}}{18.0 \text{ g water}} = 55.6 \text{ mol of water per liter}$$

With 55.6 mol of water molecules per liter of bulk water, the molarity of water is 55.6 *M*. This gives water, of all our common liquids, the highest concentration of molecules in a given volume.

QUESTION

(a) Calculate the molarity of the salt water and the sugar water of glass 1 of the opening demonstration. Assume that the standard glass holds 400 mL of each solution and that the number of moles of sodium chloride and sucrose used in preparing the solutions were those you calculated in the question at the end of Section 9.4. (b) Calculate the molarity of the solution of glass 7. ____________________

9.9 Percentage Concentrations

Vinegar contains acetic acid at a concentration of 5% by weight.

Although molarity is a common measure of concentration in scientific studies, the solutions we prepare in our daily lives employ more common units. We use a teaspoon or two of sugar in our coffee or tea and a couple shakes of salt (if any at all) in our soup. A quarter-cup of detergent does the wash and a squeeze of the plastic bottle does the dishes. We take medicines a tablet or two or a teaspoon at a time. In all of these we're dealing with concentrations. A teaspoon of sugar in coffee or tea produces a concentration of one teaspoon per cup. The single teaspoon of sugar is the solute and the single cup of sweetened beverage is the solution. A quarter-cup of detergent gives us a concentration of 0.25 cup per laundry tub. A squeeze of dishwashing detergent into a sinkful of dishes gives us an imprecise concentration of one squeeze per sink. Even two aspirin tablets and a glass of water produce a certain concentration of *acetylsalicylic acid*, the active component of the tablet, per human body. We'll have more to say about that in Chapter 20. The unit of concentration of the salt water we prepared in our opening demonstration was "tablespoon per glass."

When we look at the labels on our commercial goods, we often find concentrations of solutes expressed as a percentage (%) of weight or volume. The acidity of vinegar, for example, results from a combination of simple organic acids, principally *acetic acid*, dissolved in water. The label of a typical bottle of ordinary table vinegar reveals that the product is "diluted with water to 5% acidity." Commercial vinegar, then, contains 5 g of simple organic acids, mostly acetic acid, in every 100 g of vinegar. A percentage concentration expressing the weight of solute for every 100 units of weight of the solution is a weight/weight percentage, or w/w %.

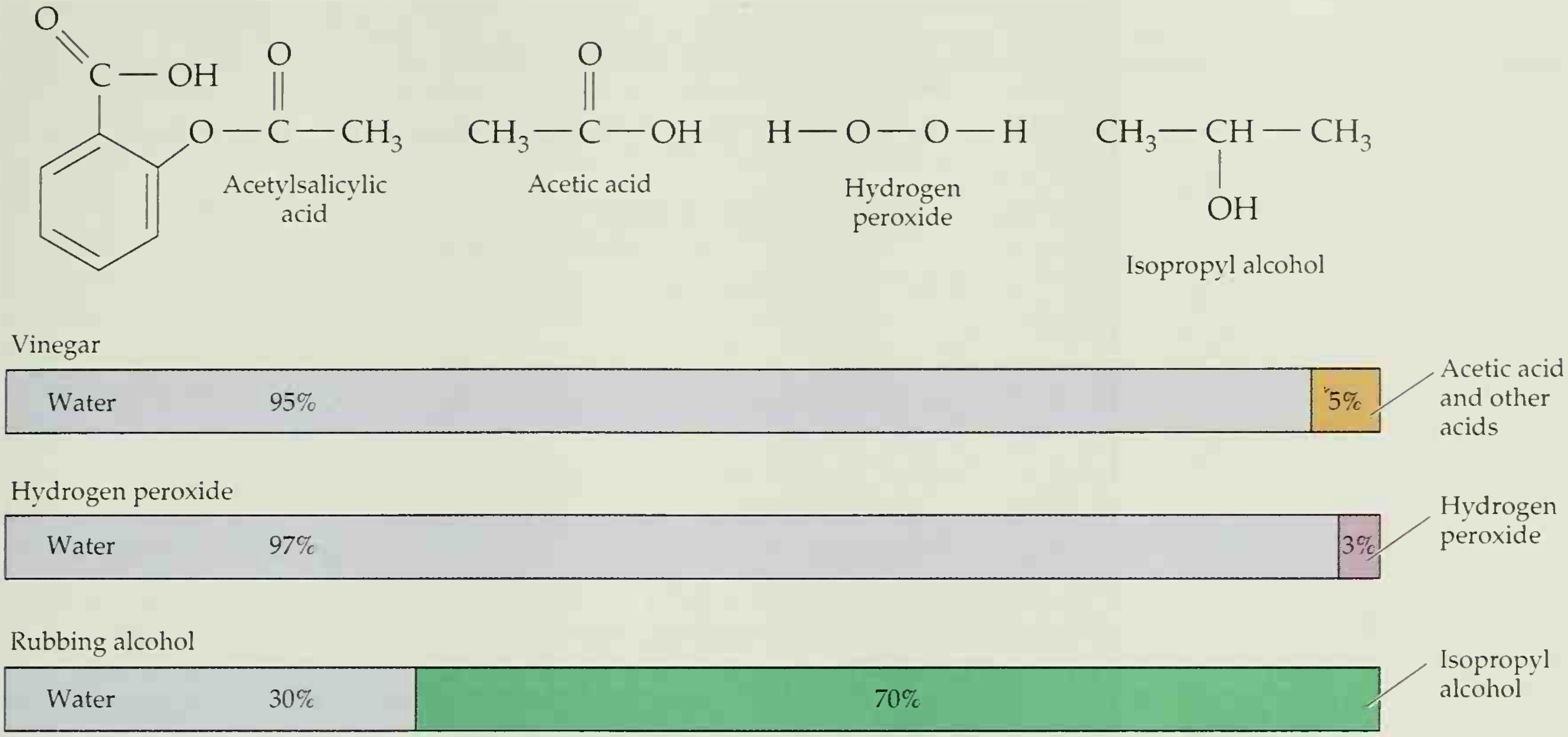


Figure 9.7
Commercial solutes, solvents, and solutions.

A 3% solution of H_2O_2 in water makes up the common antiseptic *hydrogen peroxide*, while rubbing alcohol is a solution of 70% *isopropyl alcohol* and 30% water. Here, as far as the language of chemistry is concerned, water is the solute since water is the minor component of the mixture. Isopropyl alcohol is the solvent in this case. In chemical usage the only difference between "solute" and "solvent" lies in the relative proportions of the two.

Figure 9.7 shows the structures of acetylsalicylic acid, acetic acid, hydrogen peroxide, and isopropyl alcohol, as well as the compositions of vinegar, commercial hydrogen peroxide, and rubbing alcohol.

QUESTION

A typical 8-fluid-ounce cup of coffee weighs about 240 g, while a teaspoon of sugar weighs about 5 g. What is the weight-percentage concentration of sugar in the coffee when you sweeten a typical cup of coffee with two teaspoons of sugar? (Don't forget to add the weight of the added sugar to the total weight of the solution.) ________

9.10 Vinegar and Sweet Coffee

The vinegar in Section 9.9 and the coffee in the question that followed give us a sense of the ranges of molarities we find in some ordinary solutions.

First, the vinegar. To simplify the calculation we'll assume that the density of vinegar occupies exactly 1 liter. An acetic acid concentration of 5% (w/w) means that each liter of vinegar weighs 1000 g and contains 50 g of acetic acid. We'll also assume that all of the acidity is due to acetic acid, $CH_3—CO_2H$, alone.

EXAMPLE A MOLAR MENU

With the assumptions made above, what is the molarity of acetic acid in vinegar?

The molecular weight of acetic acid is

$$\begin{array}{lrcl}
\text{C:} & 2 \times 12.01\ \text{amu} & = & 24.02\ \text{amu} \\
\text{H:} & 4 \times 1.008\ \text{amu} & = & 4.032\ \text{amu} \\
\text{O:} & 2 \times 16.00\ \text{amu} & = & 32.00\ \text{amu} \\
\hline
 & & & 60.05\ \text{amu}
\end{array}$$

60.05 amu, which we round off to 60 amu

At a concentration of 5% (w/w), and with the assumptions we've made, there are 5 g of acetic acid per 100 g of vinegar. Starting with this concentration we get

$$\frac{5\ \text{g}\ CH_3\text{–}CO_2H}{100\ \text{g vinegar}} \times \frac{1\ \text{mol}\ CH_3\text{–}CO_2H}{60\ \text{g}\ CH_3\text{–}CO_2H} \times \frac{1000\ \text{g vinegar}}{\text{liter vinegar}}$$

$$= \frac{0.8\ \text{moles}\ CH_3\text{–}CO_2H}{\text{liter vinegar}} = 0.8\ M$$

The concentration of acetic acid in vinegar is 0.8 *M*.

Now for the coffee. As you worked the question at the end of Section 9.9, you saw that adding two 5-g teaspoons of sugar to a 240-g cup of coffee gives you 250 g of sweetened coffee. As with vinegar, we'll assume that the sweetened coffee has a density of 1 g/ml, or 1000 g per liter. With a molecular formula of $C_{12}H_{22}O_{11}$, sucrose has a molecular weight of 342, so the 10 g of sucrose added to the coffee constitutes

$$\frac{10\ \text{g sucrose}}{250\ \text{g coffee}} \times \frac{1\ \text{mol sucrose}}{342\ \text{g sucrose}} \times \frac{1000\ \text{g coffee}}{\text{liter of coffee}} = \frac{0.12\ \text{mol sucrose}}{\text{liter of coffee}}$$

$$= 0.12\ M$$

Two teaspoons of table sugar in an 8-oz cup of coffee produces coffee that's about 0.12 *M* in sucrose.

QUESTION

As we saw in Section 9.9, the hydrogen peroxide sold as an antiseptic is a 3% (w/w) solution of H_2O_2 in water. If the density of 3% hydrogen peroxide is exactly 1 g/ml (so that 1 liter of the solution weighs exactly 1 kg), what is the molarity of the hydrogen peroxide solution? ______________________________

9.11 You're Two Hundred in a Trillion

The term *percent* means, literally, parts per hundred. A one percent solution contains one unit of solute in each 100 units of solution, whatever the units happen to be. We can also speak of concentrations in terms of parts per thousand, parts per million, parts per billion, and so on. The coffee in the question at the end of Section 9.9 contains 10 g of sugar in 250 g of the entire mixture. That amounts to 4% or 4 parts per hundred, which is the same as 40 parts per thousand.

It's useful to express exceedingly small concentrations, such as those of food contaminants and environmental pollutants, in terms of parts per million, parts per billion, and so on. One part per million is, in itself, a good reference concentration for all this. It's the concentration of one milligram of one substance distributed throughout one kilogram of another. A concentration of one part per million, then, is the same as a concentration of one milligram per kilogram, 1 mg/kg. One milligram is a thousandth part of a gram and a gram is a thousandth part of a kilogram. One-thousandth of one-thousandth is one-millionth

$$\underset{\text{one-thousandth}}{\frac{1}{1000}} \times \underset{\text{one-thousandth}}{\frac{1}{1000}} = \underset{\text{one-millionth}}{\frac{1}{1{,}000{,}000}}$$

The concentration term *parts per million* is often abbreviated as **ppm.** As an illustration, 35 mg of one substance in every kilogram of another would amount to a concentration of 35 mg/kg, or 35 parts per million, or 35 ppm.

The concentration term **ppm** refers to parts per million, or milligrams of solute per kilogram or liter of solution.

Plenty of examples of concentration terms occur in consumer products. Labels of canned fruit drinks, for example, often reveal the presence of 0.1% sodium benzoate, the sodium salt of benzoic acid (Chapter 10), as an added preservative. A tenth of one percent amounts to a concentration of one part per thousand.

Even smaller is the concentration of potassium iodide, KI, in iodized table salt. The presence of small quantities of iodide ion in the diet helps prevent the enlargement of the thyroid gland known as *goiter*. To provide this dietary iodide, KI is added to commercial table salt, NaCl, to the extent of about 7.6×10^{-5} g of KI per gram of NaCl.

EXAMPLE CONCENTRATE ON SALT

Translate the concentration of potassium iodide in table salt into ppm.

A million is 1,000,000 or 10^6. We know that the concentration of KI in salt is

$$\frac{7.6 \times 10^{-5}\text{ g KI}}{1\text{ g NaCl}}$$

and we want to know how many grams of KI there are in 10^6 g of NaCl. The quickest way to get the answer is to multiply both the numerator and the denominator by 10^6.

$$\frac{7.6 \times 10^{-5}\text{ g KI}}{1\text{ g NaCl}} \times \frac{10^6}{10^6} = \frac{7.6 \times 10}{10^6\text{ g NaCl}} = 7.6 \times 10\text{ ppm KI} = 76\text{ ppm KI}$$

The concentration of KI in table salt is 76 ppm.

Botulinum toxin, the virulent poison of spoiled food, provides us with another illustration of the importance of even very low concentrations of substances. As we'll see in Chapter 18, botulinum toxin is the most powerful biologically produced toxin known. A dose of as little as 1×10^{-9} g of this substance can kill a 20-g mouse. At that level the concentration of the poison in the mouse's body amounts to 1 g of toxin per 20×10^9 g of mouse. To state this more directly we can multiply both the weight of the toxin and the weight of the mouse by 50, which reveals that the toxin is lethal to the mouse at a concentration of only 50 parts per trillion!

For comparison, consider yourself as one individual person among all the people on earth. With the world's total population of about 5 billion humans, you yourself make up roughly one person in 5 billion, or 200 parts per trillion of all of those alive today on our planet. Remarkably, the lethal concentration of botulinum toxin in a mouse's body is even less than your own "concentration" among all those now living.

QUESTION

Zinc is important to human health. A deficiency of zinc leads to stunted growth, failure of the sexual organs to develop fully, and poor healing of wounds. Among foods richest in this element are liver, eggs, and shellfish, which contain zinc at levels ranging from about 2 to 6 mg per 100 g. Express this range of zinc concentrations in parts per million. (Note that an excess of zinc can be just as bad as a deficiency. Dietary excesses of this element can cause anemia, which is a deficiency of red blood cells, kidney failure, joint pain, and other medical problems. A balanced diet provides most of us with all the zinc we need.) ______________________________

9.12 The Very Purest Water on Earth

The presence of dissolved minerals and organic compounds in the water we drink provides a fine example of the significance of the concentrations of solutes. When we think of pure water we may imagine fresh rainwater falling from a crisp sky or clear water bubbling up from a mountain spring. The very purest water on earth isn't either of these. The very purest of all water comes from a chemist's laboratory. It's water that has passed through columns of specially prepared cleansing resins or water that has been distilled repeatedly under carefully controlled laboratory conditions to remove all traces of contaminants (opening demonstration in Chapter 8). All other water, including pristine rainwater and the very purest drinking water, carries a variety of chemical impurities in a range of concentrations.

To clarify the nature and origin of these impurities, we'll follow the rain as it drops to earth and becomes part of our water supply. As rain falls it absorbs, to varying degrees, the gases that make up our atmosphere. The nitrogen, oxygen, and carbon dioxide of air all dissolve to a very small extent in water. Near room temperature a maximum of about 0.01 g of nitrogen, 0.05 g of oxygen, and 3.4 g of carbon dioxide can dissolve in 1 liter of water. (The small bubbles that rise from heated tap water, just before it starts to boil, are bubbles of these very same dissolved gases. Almost all gases are much less soluble in hot water than in cold water. They tend to escape from their water solutions as the water warms up.)

Dissolved gases coming out of solution as water is heated.

Part of the carbon dioxide that enters rainwater reacts with the water itself to form carbonic acid:

$$\underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{carbonic acid}}{H_2CO_3}$$

As a result all rainwater is very slightly acidic. The absorption of still other atmospheric gases, especially industrial pollutants and automobile exhaust gases, can increase the acidity of rainwater sharply, well beyond its normal acidity, to produce what is known as *acid rain*. We'll have more to say about acids and about how acid rain affects our environment in Chapter 10.

Rain that falls onto land soaks into the earth, runs off to our rivers, lakes and other bodies of water, or simply evaporates and reenters the atmosphere. Even some of the rain that seeps into the ground finds its way, underground, to lakes and rivers. Much of it, though, enters layers of porous rock and earth lying just below the surface of the land, where it accumulates as large reservoirs of fresh water known as *groundwater*.

Even the very purest rain contains dissolved carbonic acid, H_2CO_3.

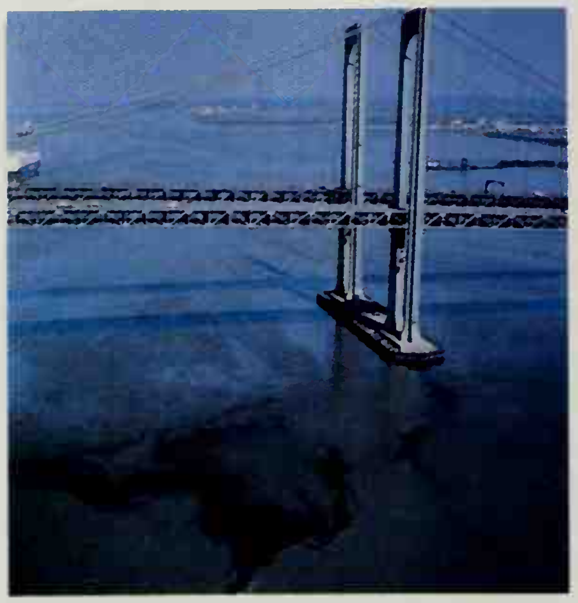
QUESTION

Name an acid found in *all* rainwater. ____________________

9.13 The Water We Drink

Despite the abundance of rivers, streams, and lakes throughout most of the populated land area, chances are that the water coming from your kitchen faucet or from a public water fountain was drawn up from the reservoir of groundwater. Reaching the surface through wells or springs, this source provides the drinking water for about half the people in the United States and about three-quarters of those of us who live in large cities. More water is present in this subsurface layer than in all of our rivers, streams, and lakes.

In chemical terms, groundwater and the water we draw from our rivers and other bodies of water are solutions of solutes in a solvent. Water is the solvent; the substances the water picks up in its travels from the clouds,


Water that is clearly polluted.

through the earth and into our faucets are the solutes. It's a combination of the chemistry of the solutes and their concentrations that determines whether the water is polluted.

Some of the solutes have been in earth's water since rain began to fall on the newly formed planet. Partly because of rainwater's normal acidity (resulting from the carbonic acid it contains) and partly because water itself is a very good solvent for many substances, the rainfall that passes through the soil picks up a variety of minerals from the earth itself. As a result, all the waters of the earth, including those that feed our public and private water supplies and those that furnish commercially bottled "natural" or "mineral" drinking water, contain a variety of minerals in a range of concentrations. Among these are calcium, iron, magnesium, potassium, and sodium cations

TABLE 9.1 Concentrations of Several Minerals in Natural Spring Water of the French Alps

Mineral	Concentration in mg/liter (ppm)
Calcium	78
Magnesium	24
Sodium	5
Potassium	1

TABLE 9.2 Maximum Contamination Levels of Minerals in Community Water Systems Permitted by the Safe Drinking Water Act of 1974

Contaminant	Maximum Permitted Level in mg/liter (ppm)
Arsenic	.05
Barium	1.
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Selenium	0.01
Silver	0.05
Sodium	160.

and fluoride anions. The concentrations of representative minerals found in natural spring water of the French Alps appear in Table 9.1. Minerals such as these are usually harmless or beneficial to most of us at their typical levels in natural and in commercially bottled drinking water, and at even higher levels as well. Some of us, for example, take mineral supplements that provide calcium, iron, or magnesium at levels far higher than those found in drinking water.

There are hazards, though. A few of the chemicals that can enter our water supplies are particularly toxic even at what may seem to be very low concentrations. Contamination by these substances comes as rainwater picks up residues of agricultural fertilizers and pesticides, known as agricultural runoff, and from industrial, urban, and household wastes dumped onto the surface or injected just below it. Any of these can be carried by the natural flow of rainwater into groundwater.

To ensure the safety and high quality of public drinking water, the U.S. Congress passed the Safe Drinking Water Act of 1974, which establishes, among other things, maximum drinking water levels for specific, potentially hazardous chemical contaminants. Some of the minerals controlled by the Act appear in Table 9.2, while representative organic compounds appear in Table 9.3. When present in concentrations greater than those shown in the tables, the minerals and the organic substances exceed the safety standards set by the Safe Drinking Water Act.

Curiously, the Act also applies to some kinds of commercially bottled water, but not to others. The federal standards for tap water apply as well to "bulk" or "commodity" water, the kind that comes in large jugs and can be dispensed through water coolers. "Mineral water," which we'd expect to be high in minerals anyway, is exempt from the standards of the Safe Drinking Water Act, as are both seltzer and club soda. These last two are considered soft drinks and are covered by regulations of the Food and Drug Administration (FDA, Chapter 18). In 1990 the sparkling drink Perrier was found to contain benzene at a concentration of 15 parts per billion, triple the FDA's permitted maximum of 5 parts per billion. The company withdrew 72 million bottles of the drink from store shelves and restaurants while it located and corrected the source of contamination.

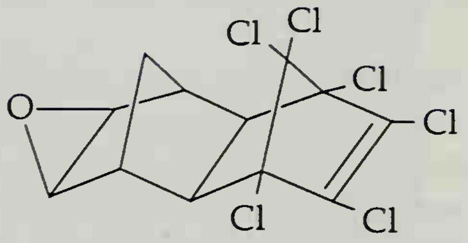
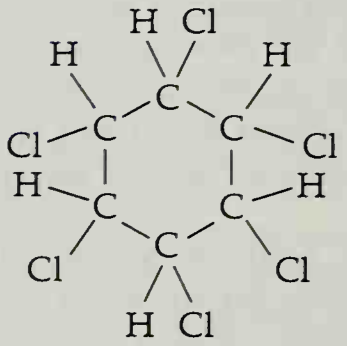
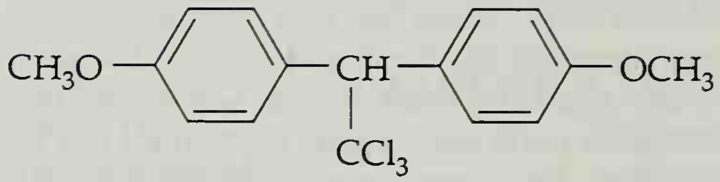
Of course, not all water pollution comes from accidents or the careless or deliberate dumping of waste chemicals or from agricultural runoff. Some results simply from the way our society operates. Just as the high concentration of cars in and near our cities, for example, contributes to air pollution (Section 8.9), the large number of gasoline stations that serve these cars are potential sources of pollution. Old and rusting underground tanks in these stations (some of which have been left abandoned in the ground as the stations closed) leak gasoline, which eventually travels into the groundwater. Whether this presents a major threat to our drinking water is still uncertain, but it does illustrate one of the many less visible sources of contamination.

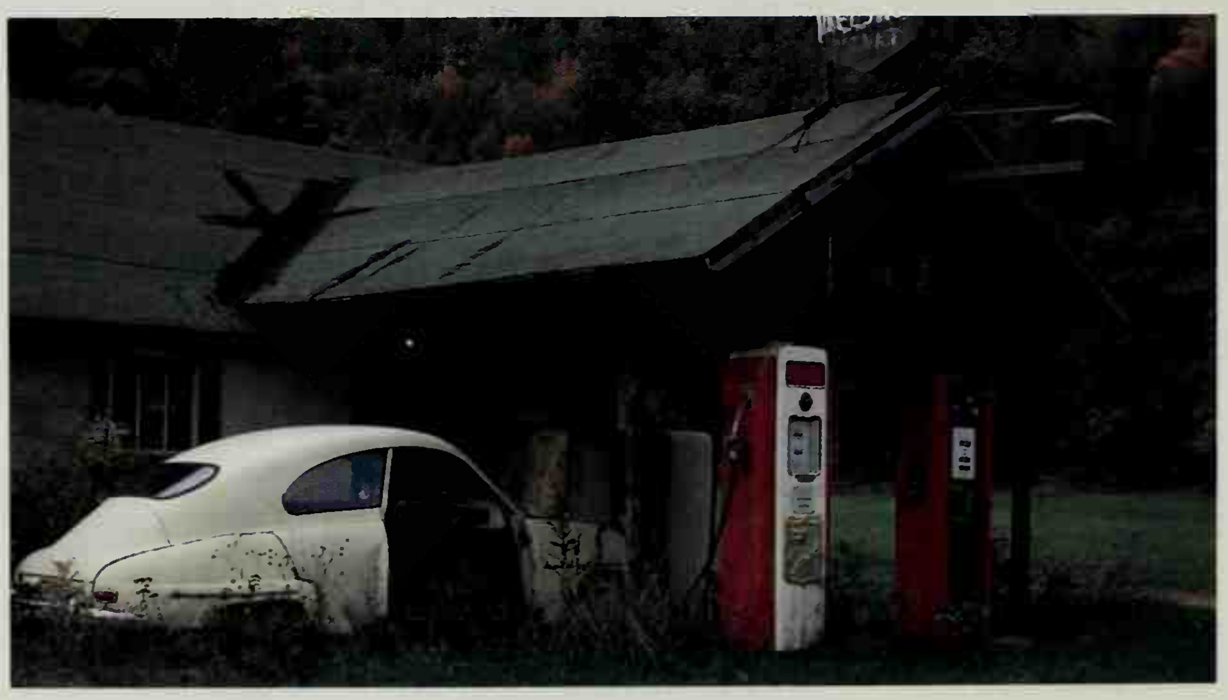
1,000,000,000
10,0000 100
1000 50

QUESTION

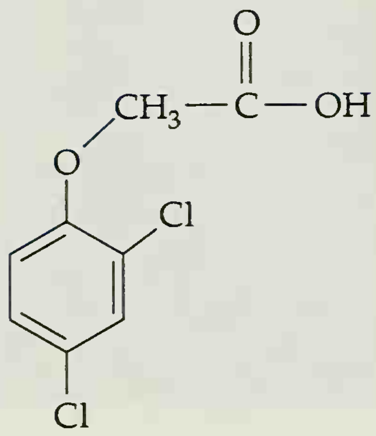
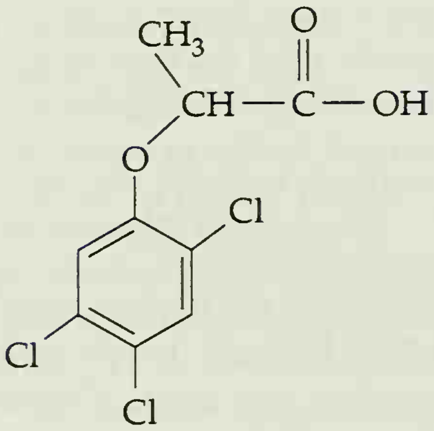
Which of the following, if any, exceed federally permitted levels in our public water supplies: (a) 0.1 mg lead per liter of water, (b) 0.10 part per thousand sodium, (c) 200 parts per billion barium, (d) 0.000002% mercury, (e) 0.1 part per million silver?

TABLE 9.3 Maximum Contamination Levels of Organic Compounds in Community Water Systems Permitted by the Safe Drinking Water Act of 1974

Compound and use	Structure of formula	Maximum permitted level (milligrams per liter)
Endrin (an insecticide no longer manufactured or used in the United States)	 (Carbons, hydrogens, and carbon-hydrogen bonds are omitted for clarity)	0.0002
Lindane (an insecticide)		0.004
Methoxychlor (an insecticide)		0.1



An abandoned gasoline station represents a potential source of groundwater pollution.

Compound and use	Structure of formula		Maximum permitted level (milligrams per liter)
2,4-D (an herbicide) Chemical name: (2, 4-dichlorophenoxy) acetic acid			0.1
Silvex (an herbicide) Chemical name: 2-(2, 4, 5-trichlorophenoxy) propionic acid			0.01
Trihalomethanes (solvents and other uses) bromodichloromethane dibromochloromethane bromoform chloroform	$CHBrCl_2$ $CHBr_2Cl$ $CHBr_3$ $CHCl_3$	combined total	0.10

9.14 Misplaced Matter and Other Forms of Pollution

Chemical pollutants, such as the contaminants of drinking water described in Section 9.13, have been called "misplaced matter." A chemical that might be tolerated, useful, or even vital when it's in an appropriate place can act as a pollutant when it's in another substance, even in very small quantities. The combination of water and gasoline provides a good example. Water itself is vital to life and health, while gasoline is essential to our transportation system. Yet it takes only a few milliliters of water per gallon to make gasoline unfit for use in an ordinary internal combustion engine, and even a single drop of gasoline renders a glass of water undrinkable.

Not all water pollution comes from dissolved chemicals. It can take other forms as well. Water pollution can come from soil, silt, and clays that are washed into lakes and rivers by rainwater running off the surface of the land.

Coagulation and sedimentation basin of a municipal water treatment plant. One stage in the purification of community drinking water.

The presence of infectious bacteria and viruses can produce biological pollution. Even the heat released by nuclear power plants (Section 5.2) and other forms of commercial power generation can raise the temperatures of nearby natural bodies of water beyond their normal ranges, generating a form of pollution known as *thermal pollution*.

To minimize contamination of all sorts, water that's distributed through municipal water systems, regardless of its source, as well as much of the water obtained from private wells and other sources, is treated in some way before it's used. It's processed, often by some combination of filtration, chlorination, and aeration (spraying through the air to induce oxidation of contaminants) to remove chemical and biological contaminants. Yet some polluting substances can survive commonly used purification methods, or they can pass through in quantities so small that they border on our ability to measure them.

Because of the great variety of potentially hazardous substances in agricultural runoff and in wastes—by some counts that are about 5000 different substances that pose threats to our water supplies—it's unlikely that we will ever be able to remove each and every one of them, completely, from our water. Instead it seems more practical to control their disposal so that we can keep them from getting into our water supplies in the first place. If we consider pollutants to be misplaced matter, one approach to controlling pollution is simply to keep our wastes out of our water.

QUESTION

Give an example, other than water and gasoline, of a substance that is useful or beneficial to us in one place but acts as a pollutant in another. ________________

LEAD

PERSPECTIVE: The Arithmetic of Pollution

Given the variety of sources of water pollution and the variety of the pollutants themselves, it's unrealistic to expect that our water can ever be made *completely* free of every foreign substance imaginable. Moreover, we'd have to understand what it would mean for water to be *completely* free of every other substance. As our means of chemical detection and measurement become increasingly sensitive and sophisticated, we become able to detect contaminants at concentrations far below those we could smell or taste or see, or that we might reasonably expect to be hazardous. We could imagine, for example, a method of detection that would reveal the presence of a single molecule of, say, pentane (from gasoline) or phenol (a typical industrial waste) or trichloroethylene (a chlorinated hydrocarbon) in an 8-oz glass of water. At that concentration, one molecule of contaminant per 79×10^{23} molecules of water (Fig. 9.6), our language provides no terms of reference equivalent to parts per million, parts per billion, or the like. Would we realistically call the water "polluted"? Surely not.

Nor would we consider a glass of water to be polluted if it contained two, three, or ten molecules of another substance. Yet at some higher level, some threshold concentration, we would just as surely call the water polluted and unfit to drink. We do, indeed, expect the concentrations of any contaminants in our drinking water to remain well below the levels at which they might be hazardous or might give the water an offensive taste, odor, or appearance, but we cannot realistically expect the total and complete absence of anything but molecules of H_2O in our drinking water.

When we consider the arithmetic of pollution we can better understand the questions of the opening demonstration. What must be asked is not "*Is* there any contaminant in our drinking water?" but rather "What are the *limits* of contamination we can reasonably accept?" Understanding the answer to this more critical question requires an understanding of how we count chemical particles and what their concentration terms mean.

QUESTION

Using a density of 1 g/mL (1000 g/liter) for water, rewrite the maximum permitted levels of contaminants in Table 9.3 in terms of (a) parts per million (ppm) and (b) parts per billion (ppb). ______________________________

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

One ______ of a substance is equal to its atomic or molecular weight expressed in ______ and contains 6.02×10^{23} chemical particles, which is also known as ______ of particles. Since one mole of any chemical substance contains the same number of ______ as one mole of any other chemical substance, we can calculate the weight of one chemical that will react completely with a given weight of another by using their ______ in our calculations. We can also use ______ of solutions rather than weights in these calculations as long as we know the ______ of the solution, which is a measure of the amount of ______ dissolved in a specific volume of the ______. A solution that contains one mole of solute per ______ of solution has a concentration of one ______.

- atomic or molecular weights
- Avogadro's number
- chemical particles
- concentration
- grams
- liter
- molar
- mole
- solute
- solution
- volumes

2. Explain, define, or describe the significance of each of the following:

a. groundwater
b. mineral water
c. ppm
d. The Safe Drinking Water Act of 1974
e. weight/weight percentage (w/w %) concentration

3. Write the chemical equation for the reaction that occurs as charcoal burns (a) in the open air; (b) in an enclosed space, with a limited supply of air.

4. (a) What is the danger in heating a closed room by burning charcoal briquettes in a grill placed in the room? (b) Why isn't this a hazard when the grill is used outdoors?

5. How do we measure out a mole of an element or compound?

6. Is it necessary to know the numerical value of Avogadro's number to carry out calculations using quantities of moles? Explain.

7. Is it necessary to use a *balanced* equation when calculating the amount of product that can be produced from a given weight of one of the reactants in a chemical reaction? Explain.

8. Why are concentrations expressed in *molarity* particularly useful to chemists?

9. Name three chemicals, in addition to water, that you can expect to find in raindrops.

10. What are two forms of contamination or pollution, in addition to chemical pollution, that can affect water?

11. What are two characteristics of a solute that determine whether water is contaminated?

12. Explain why a concentration of 1 mg of solute in 1 kg of solution is the same as a concentration of 1 ppm.

13. Name a gas that is hazardous to human health when it forms in the air we breathe, yet its presence in the stratosphere protects life on the surface of the earth from the harmful effects of solar radiation.

14. Name three processes used to purify groundwater before it is distributed through municipal water lines.

15. Describe three processes that remove freshly fallen rainwater from the ground.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

16. How many (a) months are in a decade? (b) musicians in a pair of string quartets? (c) cards in a dozen decks (not counting jokers)? (d) atoms in a half-dozen moles of an element?

17. What is the weight of

a. one mole of neon
b. two moles of zinc
c. one mole of diatomic nitrogen
d. three moles of diatomic hydrogen gas
e. half a mole of chloride ions
f. one mole of chlorine atoms
g. one mole of diatomic chlorine molecules
h. two moles of neutrons

18. How many moles of hydrogen atoms does it take to produce one mole of diatomic hydrogen molecules?

19. How many (a) *left* shoes are there in 15 *pairs* of shoes? (b) dozen yolks would you get from half a dozen eggs? (c) moles of sodium cations are there in half a mole of sodium chloride?

20. What weight of (a) sodium contains one mole of sodium atoms? (b) chlorine atoms contains one mole of chlorine atoms? (c) sodium chloride contains one mole of sodium ions? (d) sodium chloride contains one mole of chloride ions? (e) CO_2 is produced when one mole of carbon combines with one mole of diatomic oxygen molecules?

21. Assuming that rubbing alcohol is 70% (w/w) isopropyl alcohol, and that its density is 1 kg/liter,

a. How many moles of water and how many moles of isopropyl alcohol (molecular weight 60) are there in a liter of rubbing alcohol?
b. If we decide which is the solute on the basis of *weight*, is isopropyl alcohol the solute or the solvent?
c. If we decide on the basis of the *number of moles*, is isopropyl alcohol the solute or the solvent?

22. Which one of the following contains the greater number of moles of sucrose, (a) or (b), or do they contain the same number? (a) 4 liters of a 0.125 *M* sucrose solution, b) 0.375 liter of a 1.5 *M* sucrose solution?

23. A typical aspirin tablet contains 0.325 g of the active ingredient, *acetylsalicylic acid*. What is the average concentration, expressed as a percentage by weight (% w/w), of the acetylsalicylic acid in the body of a 165-pound (75-kg) person who has just taken two aspirin tablets?

24. Chlorine gas consists of diatomic molecules, Cl_2. The balanced chemical equation for the reaction of sodium metal with chlorine gas to produce sodium chloride is $2Na + Cl_2 \rightarrow 2NaCl$.

a. What weight of chlorine gas does it take to react completely with 4.6 g of sodium?
b. What weight of sodium does it take to react completely with 1.42 g of chlorine gas?

25. Sulfur trioxide, SO_3, is a gas that dissolves in water to form sulfuric acid, H_2SO_4, according to the chemical equation $SO_3 + H_2O \rightarrow H_2SO_4$. When sulfur trioxide is released as a pollutant into the atmosphere, or forms there through chemical reactions of other pollutants, it dissolves in rainwater, raises the acidity of the rainwater, and contributes to acid rain.

a. How many moles of SO_3 are there in 8 g of sulfur trioxide?
b. How many moles of sulfuric acid form when 8 g of sulfur trioxide dissolve in water?
c. What weight of sulfuric acid forms when 8 g of sulfur trioxide dissolve in rainwater?

26. Which of the following, if any, exceed federally permitted levels in our public water supplies: (a) 0.1 mg lead per liter of water, (b) 0.10 part per thousand sodium, (c) 200 parts per billion barium, (d) 0.000002% mercury, (e) 0.1 part per million silver?

27. You have 1 liter of a solution that contains selenium at a level of 15 parts per billion and 1 liter of another solution that contains barium at a level of 3 parts per million. You now mix the two solutions together to produce 2 liters of a single solution. Does the new solution produced by mixing the two original liters together meet federal drinking water standards for selenium? For barium?

28. Using a density of 1 g/mL (1000 g/liter) and a molecular weight of 18 for water, show that the presence of one molecule of a solute per liter of water amounts to a contamination level of one molecule per 334×10^{23} molecules of water.

29. The Safe Drinking Water Act of 1974 permits a maximum of 160 mg of sodium per liter of drinking water. (a) How many moles of sodium are there in 160 mg of sodium? (b) What is the molarity of the sodium ion in a solution that contains 160 ppm of Na^+ (which is the same as 160 mg of Na^+ per liter of water)? (c) How many moles of chloride anion does it take to balance exactly 160 mg of sodium cations? (d) How many moles of NaCl does 160 mg of sodium cation represent? (e) What is the maximum *molarity* of sodium chloride permitted in community drinking water by the Safe Drinking Water Act?

30. (a) Using your answer to the question at the end of Section 9.8, prepare a chart showing the molarity of the salt water in each of the seven glasses of the demonstration that opened this chapter. (b) Which glass contains sodium chloride at the highest concentration that would be permitted in community drinking water by the Safe Drinking Water Act? (c) Would you consider the water in this glass fit to drink?

31. How many sodium cations are there in all of the water in glass 7?

32. Prepare a chart showing the molarity of the sugar water in each of the seven glasses of the demonstration that opened this chapter. Which glass comes closest to the molarity of two teaspoons of sugar in a cup of coffee? Refer to the examples in Section 9.10.

33. (a) You have just prepared a cup of coffee for yourself and mistakenly add three teaspoons of sugar instead of your usual one teaspoon. The coffee is far too sweet and you cannot drink it. What can you do to decrease the sweetness of the coffee? That is, what can you do to decrease the concentration of the sugar? (Recalling the opening demonstration may help here.) (b) As we saw in Section 9.10, coffee sweetened with two teaspoons of sugar per cup is, in effect, a 0.12 *M* solution of sucrose in coffee. Exactly what would you do to reduce the molarity of this solution to 0.06? (c) You have a large volume of a solution that is 0.5 *M* in NaCl and you need exactly 250 mL of a solution that is 0.1 *M* in NaCl. Describe exactly how you would obtain the needed solution.

34. If you count all of the protons and all of the neutrons in the body of a person weighing 165 pounds and add the sum of all the protons you have counted to the sum of all the neutrons you have counted, what is the combined total? This is not a trick question and you don't have to perform tiresome or complex calculations. All that's required is a good understanding of the material in this chapter and a little thought. The solution appears in Appendix E, along with a discussion of the chemical principles involved.

THINK, SPECULATE, REFLECT, AND PONDER

35. Why is it not possible, either in theory or in practice, to calibrate a scale in units of *moles*?

36. Suppose you had a scale you knew to be accurate, but that doesn't show what *units* of weight it measures. You have a quantity of acetic acid and you want to measure a quantity of water that contains the same number of water molecules as there are acetic acid molecules. Could you use the scale to do that? Explain. Suppose you want to prepare a one molar solution of acetic acid in water. Could you use the scale to do that? Explain.

37. Arrange the following three types of water in order of increasing numbers of different chemical solutes you would expect to find dissolved in each. Place the water in which you would expect to find the smallest number of individual chemical solutes first: (a) distilled water, (b) groundwater, (c) rainwater. Explain your answer. What chemical solute might you expect to find in the tap water obtained from a municipal water system but probably not in distilled water, groundwater, or rainwater?

38. Suppose you have an analytical instrument that could tell you quickly exactly how many molecules of gasoline hydrocarbons there were in a glass of water. What standard(s)—the number of hydrocarbon molecules, odor, color, taste, or any other criterion—would you use to determine whether the water is fit to drink?

39. Regardless of any legal definition, which glasses in the opening demonstration would you consider to be polluted with salt? Which, if any, would you consider safe to drink?

40. Define "pollution" in your own words.

41. (a) Under what conditions would you consider water to be "polluted"? (b) Would you say that all "polluted" water is unfit to drink? (c) Can water that is unfit to drink not be "polluted"? (d) Can water that is "polluted" be safe to drink?

42. Do you believe the water in your neighborhood is safe to drink as it comes directly from the faucet? Explain you answer.

43. Describe three specific actions you would recommend to improve the purity of your drinking water. Which one would you want carried out first?

44. We normally think of community water purification processes as designed to *remove* impurities from water. Yet they can also *add* chemicals to water to benefit the public health and welfare. Many communities, for example, add chlorine to water to kill disease-causing microorganisms. Some add fluoride salts to retard tooth decay (Chapter 21). Do you favor the addition of chemicals to public drinking water to promote the public health and welfare? Do you think that small quantities of essential nutrients or vitamins ought to be added to drinking water? Do you think that nothing ought to be added to the water since everyone in the community must drink the same water and some may not wish to have anything added to their drinking water? Do you think the public welfare ought to be more important than individual wishes in making these decisions? Discuss your answers.

45. Flash! It's just been discovered that the value accepted for Avogadro's number is wrong! The value used for so long has just been shown to be off by at least 25%, although no one knows just yet exactly how much or in which direction. Which answers in these end-of-chapter exercises will have to be changed as soon as we learn the correct value of Avogadro's number, and which can we let stand as they are?

Acids and Bases

10

IF IT TASTES
SOUR IT MUST
BE AN ACID

It tastes sour. It's citric acid.

Figure 10.1

The red cabbage breath test. (a) Heating leaves of red cabbage in water to extract the acid-base indicator that give the cabbage its color.

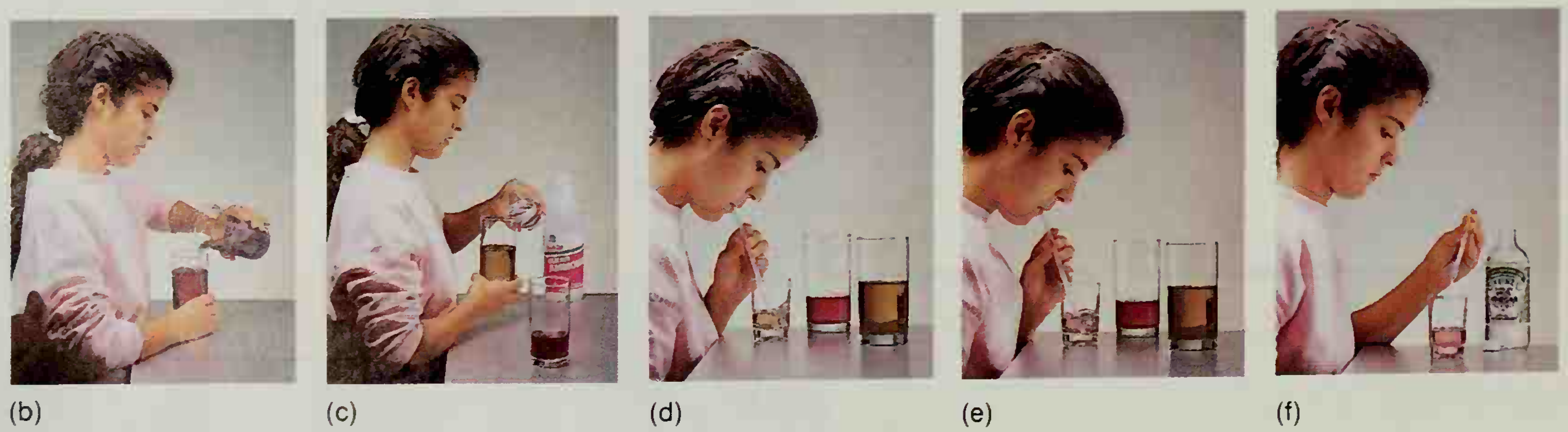
Breath with the Strength of Red Cabbage

Here's a bit of chemical magic you can use to entertain, impress, or embarrass your friends. You'll need a leaf of red cabbage, a little household ammonia, a little vinegar, some water, two glasses, and a drinking straw. Announce that you're about to perform a breath test. (Make it a breath test for anything you'd like: alcohol, bad breath, sweet breath, the residual odor of cabbage, or something of that sort. Use your imagination).

It works like this (Fig. 10.1). First, put a few drops of ordinary household ammonia into about half a glass of water. The exact amounts of ammonia and water don't matter much; what you need is a very dilute solution of ammonia in water. Identify the solution in some way so that no one mistakes it for plain water and then put it aside for a moment.

> **WARNING: Ammonia is a poison!** Be sure to mark clearly anything containing ammonia and place the marked container out of reach. Don't drink

(b) Pouring out the solution of the indicator. (c) Adding just enough dilute ammonia to turn the indicator solution green. (d), (e) Blowing into the slightly basic solution to make it slightly acidic and turn its color from green to blue. (f) Adding vinegar turns the blue solution pink.



or taste the ammonia and don't let any ammonia solutions get on your skin or clothes. Don't let anyone else come in contact with the ammonia.

Next, break into small pieces about half of a large leaf of red cabbage. A leaf with a deep purple color is best. Boil the pieces in just enough water to cover them. Keep the water boiling for about two minutes to extract the dye that gives the cabbage its color; then remove the mixture from the heat and set it aside to cool. Pour the cool, deep blue water extract of the cabbage into a clear, colorless glass (so you can see the coming color changes easily) and discard the boiled cabbage pieces. You've extracted the dye that makes the stunt work and don't need what remains of the leaves.

What you have now is a blue solution of cabbage leaf extract. Add *just* enough of the dilute ammonia solution you prepared earlier to this cabbage extract to turn it from deep blue to an emerald green. A few drops of the solution usually work nicely. Don't add more ammonia solution than just enough to give the green color. This is now your breath test solution.

Pour a bit of the test solution into another clear, colorless glass, enough to cover the bottom to a depth of a few centimeters (about an inch) and put the straw into the glass. Finally, have someone whose breath is to be "tested" blow a steady stream of bubbles through the straw into the green test solution and watch for a color change. (It's a good idea to try out this stunt yourself before going public with your claims.)

The total volume of breath that has to be blown into the solution depends on just how it was prepared. Several lungfulls might be necessary. In any case, with continuous blowing into the solution, its color soon turns from emerald green back to a distinct blue, close to the shade of the cabbage dye originally extracted by the boiling water. Having more of the green test solution nearby for comparison makes it easier to see the color change. So does looking at the solutions against a white background and with good lighting.

You can make up whatever stories you wish about what this color change says of the state of your friend's breath, but you ought to point out that things could be much worse. Pour a little vinegar into the (now blue) solution and its color changes to a brilliant pink!

The fact is that the color change from green to blue doesn't reflect sweet breath or bad breath or the odor of cabbage or any other food or drink. It reveals only one thing, something that is characteristic of all human breath and of the breath of all animals. It indicates that the exhaled breath is acidic, and that's something all of us can be thankful for.

Actually, what appears to be a clever stunt is no more than a chemical demonstration that you exhale plenty of carbon dioxide as you breathe and that the carbon dioxide dissolves in water to form an acid. This, in turn, takes us into the chemistry of acids and bases and, later, to an examination of how our bodies use the food we eat. [Incidentally, the color of the solution changes from blue to pink as you add the vinegar because the acetic acid in the vinegar (Section 9.9) is even more acidic than the solution of the carbon dioxide from your breath, and so the acetic acid causes an additional color change.]

Very briefly, here's how the "breath test" works. It uses two acids, one base and an **acid–base indicator**. The acids are the solution of carbon dioxide formed as your friend blows into the "test" solution and the acetic acid of the vinegar, the base is the ammonia of the solution you prepared, and the acid–base indicator is the dye you extracted from the cabbage leaf. Acid–base

An acid–base indicator is a dye that changes, loses, or acquires color as a solution containing the dye changes in acidity or basicity.

indicators are dyes that change color (or becomes either colored or colorless) as solutions containing them change in acidity or basicity.

When you add the dilute ammonia solution to the extracted cabbage dye, which is a member of a class of compounds known as *anthocyanins*, you make the test solution slightly basic and the molecular structure of the dye changes, turning the color of the entire solution to an emerald green. By blowing your exhaled breath into the test solution you add carbon dioxide, which forms carbonic acid, neutralizes the basic ammonia, and eventually turns the solution slightly acidic. With the change from basicity to acidity, the molecular structure of dye changes to one that appears blue. Adding the acetic acid makes the solution even more acidic and produces further molecular changes in the dye, changing its color to red. We'll examine some of these transformations and the chemistry behind them in more detail as this chapter unfolds.

QUESTION

Suppose you have a dilute solution of vinegar in water in one glass and a dilute solution of household ammonia in another, but you didn't label them and now you have forgotten which is which. How could you use red cabbage to determine which is which? ____

10.1 The Real Litmus Test

Before entering the world of acids and bases we'll spend a few moments with an indicator, *litmus*, that has added color to the English language as well as to chemistry. This oldest and best known of the acid–base indicators is a pink mixture of plant compounds extracted from certain lichens found principally in the Netherlands. Included in this mixture is a dye, *erythrolitmin*, that turns red in acid, blue in base. Small strips of paper impregnated with litmus serve as a highly convenient diagnostic tool, *litmus paper*, which is used to test liquids and moist solids for acidity and basicity.

Wetting a strip of litmus paper with a water solution of an acid produces a distinctly red spot; water solutions of bases turn the paper blue. This is the *litmus test* for acids and bases. To accentuate the color changes, commercial litmus paper is pretreated to produce blue litmus paper for use in testing acids, which give a red spot that shows up clearly against the blue background, and red litmus paper for testing bases, which give a blue spot against a red background (Fig 10.2).

The phrase "litmus test," first applied to the simple and definitive test that establishes beyond question the acidic or basic properties of substances, has entered our language to describe simple and definitive tests of political candidates, social issues, economic policies, and related matters. The "litmus test" of social issues is often a simple question whose answer determines the

Figure 10.2
Acids turn blue litmus red. Bases turn red litmus blue.

fate of an entire social or political issue, just as the chemical litmus test determines simply and quickly whether we are dealing with an acid or a base.

QUESTION

What is the color of litmus paper when it's moistened: (a) with ammonia? Blue (b) with vinegar? red

10.2 What Are Acids and Bases? Phenomenological Definitions and Other Bits of Erudition

In reply to the question "What are acids and bases?" there is only one honest and truly realistic answer: *It depends*. If you mean "How can I tell if a certain substance that I have here in a bottle is an acid or a base?" you'll need a phenomenological definition. That is, you'll need a definition that depends on phenomena, on activities or properties that you can sense. It's a definition that hinges on what you can see, taste, feel, or touch.

In this phenomenological sense, water solutions of all acids

- taste sour
- turn litmus red
- react with certain metals, such as iron and zinc, to liberate hydrogen gas

A sour taste may be the world's oldest indication of acidity. Our word acid comes from the Latin *acidus*, an adjective meaning "sour" or "having a sharp taste."

Water solutions of all bases, on the other hand,

- taste bitter
- turn litmus blue
- feel slippery

Acids and bases in common consumer products. Some are safe, others are hazardous and must be used with care.

WARNING: Of all these diagnostic tests, only the litmus test is safe enough for general use with a substance of uncertain identity. **Tasting any questionable material to learn whether it's sour or bitter or rubbing it between your fingers to determine whether it feels slippery is a dangerous activity.** Although many of our foods—lemons and vinegar, for example—contain acids and taste distinctly acidic, other substances may be composed of acids (or bases) powerful enough to destroy skin and mucous membranes and cause great harm. Some substances we may come in contact with are highly poisonous in ways that have nothing to do with acidity or basicity. Even many consumer products are toxic and/or corrosive and can cause much damage if used carelessly or in ways other than those specified by their labels. Never taste or touch any material you aren't sure of. It could be quite dangerous. We'll examine some of our ideas about safety in more detail in Chapter 18.

The remaining phenomenon, the reaction of acids with metals like iron and zinc, can also be hazardous. The product is hydrogen gas, which is dangerous in itself because of its flammability.

Neutralization occurs when an acid and a base react with each other to produce a solution that is neither acidic nor basic. A **salt** is a compound (other than water) produced by the reaction of an acid with a base.

In addition to the characteristics we've just described, another useful property that distinguishes acids from all other kinds of chemical substances is their ability to neutralize bases. Similarly, all bases can neutralize acids. In this acid–base **neutralization** an acid and a base react chemically with each other to produce a **salt**, a compound that has no (or much weaker) acidic or basic properties. *A salt is a compound (other than water) produced by the reaction of an acid and a base.*

A particularly simple acid–base neutralization occurs, for example, when hydrochloric acid (HCl, hydrogen chloride) reacts with sodium hydroxide (NaOH). Hydrochloric acid, usually available in hardware stores by its commercial name, *muriatic acid,* is a strong acid useful for cleaning metals, masonry, cement, and stucco. Sodium hydroxide, better known as household *lye,* is a powerful base often effective in clearing clogged drains. Both sodium hydroxide and hydrochloric acid are dangerous, corrosive chemicals that must be handled with great care.

Hydrochloric acid and sodium hydroxide react with each other to form sodium chloride (a salt) and water:

$$\underset{\text{hydrogen chloride}}{HCl} \underset{\text{and}}{+} \underset{\text{sodium hydroxide}}{NaOH} \underset{\text{react to produce}}{\longrightarrow} \underset{\text{sodium chloride, a salt}}{NaCl} \underset{\text{and}}{+} \underset{\text{water}}{H_2O}$$

Notice that the hydrogen of the HCl and the OH of the NaOH combine to form water, while a combination of the Cl of the HCl and the Na of the NaOH produces NaCl. This resulting sodium chloride is a salt in two closely related senses. It's not only the common table salt that we use on our food and that began our study of chemistry in Chapter 1, but it's also a salt in the generic sense. That is, sodium chloride is produced, along with water, by the reaction of HCl (an acid) with NaOH (a base). Sodium chloride is a perfectly neutral salt, neither acidic nor basic in any sense at all.

A strip of zinc metal reacts with hydrochloric acid to produce hydrogen gas.

Other salts include potassium iodide, KI, which provides the iodide of iodized salt (Section 9.11); magnesium sulfate, $MgSO_4$, better known as *epsom* *salts* and sometimes used as a laxative; monosodium glutamate; and $CaCO_3$, common chalk.

Acid		**Base**		**Salt**		
HI	+	KOH	→	KI	+	H_2O
hydrogen iodide		potassium hydroxide		potassium iodide		
H_2SO_4	+	$Mg(OH)_2$	→	$MgSO_4$	+	$2H_2O$
sulfuric acid		magnesium hydroxide		magnesium sulfate		
H_2CO_3	+	$Ca(OH)_2$	→	$CaCO_3$	+	$2H_2O$
carbonic acid		calcium hydroxide		calcium carbonate		

QUESTION

Hydrogen fluoride (HF), an acid, reacts with sodium hydroxide to produce a salt that's used in toothpaste to help prevent tooth decay. Write the chemical equation for the neutralization of hydrogen fluoride with sodium hydroxide. What is the name of the salt that forms in this reaction? ______________________________

10.3 Acids and Bases, from Arrhenius . . .

We don't have to know anything at all about the molecular structure of a substance, then, to decide whether it's an acid. All we need to do is dissolve a bit of it in water and test it with litmus, taste it (but only if we are absolutely certain of its safety), observe whether it reacts with zinc or similar metals to produce hydrogen gas, and determine whether it neutralizes bases. If it does all of these, it's an acid.

But chemistry is interested in more fundamental phenomena than color changes, tastes, and the like. In chemistry the question "What are acids and bases?" has a deeper meaning, more like: "What is the single characteristic of a molecule that gives it all the properties of an acid or of a base?"

The answer isn't simple and it isn't even a single, unequivocal answer. Attempts at answering this question start with the Swedish chemist and physicist Svante August Arrhenius. In 1887 he proposed what we now know as the *Arrhenius theory of acids and bases*. According to Arrhenius, an acid is anything that produces hydrogen ions, H^+, in water and a base is anything that generates hydroxide ions, OH^-, in water. By the Arrhenius definition hydrogen chloride (HCl) is an acid because it ionizes in water (Section 3.15) to produce H^+; it produces Cl^- as well. Sodium hydroxide (NaOH) is a base because it produces OH^- (and Na^+ as well) when it dissolves in water.

Svante August Arrhenius proposed that an acid is anything that produces hydrogen ions, H^+, in water and that a base is anything that produces hydroxide ions, OH^-, in water.

HCl is an acid because it ionizes in water to produce H^+, a proton.

$$HCl \rightarrow H^+ + Cl^-$$

NaOH is a base because it ionizes in water to produce OH^-, a hydroxide ion.

$$NaOH \rightarrow Na^+ + OH^-$$

This explains nicely the neutralization of HCl with NaOH. The hydrogen ion produced by the acid, HCl, and the hydroxide ion produced by the base, NaOH, combine to form water

$$H^+ + OH^- \rightarrow H_2O$$

while the Na^+ formed by ionization of NaOH and the Cl^- of the HCl give ionic, crystalline NaCl as the water evaporates.

QUESTION

Carbonic acid, H_2CO_3, ionizes in water to produce H^+ and HCO_3^-. Referring to Section 9.12 and using the Arrhenius definition, show why the solution containing the carbon dioxide of your breath is acidic. ________________________

10.4 . . . To Brønsted and Lowry . . .

Johannes Brønsted. He and Thomas Lowry extended Arrhenius's definition of an acid to anything that can transfer a proton to another chemical species. They defined a base as anything that can accept a proton.

Unfortunately, relying only on Arrhenius limits our world of acids and bases to their solutions in water. To expand our chemical horizons beyond aqueous solutions, and even beyond solutions in general, two chemists, the Dane Johannes Brønsted and the Englishman Thomas M. Lowry, in 1923 independently defined an **acid** as anything that can transfer a proton to another chemical species and a **base** as anything that can accept a proton. Water may be a solvent, but it needn't be.

You can literally see the importance of the step that Brønsted and Lowry took if you place an open bottle of ammonia next to a bottle of hydrochloric acid (Fig. 10.3). The liquid hydrochloric acid available commercially is actually a solution of hydrogen chloride in water; similarly, the ammonia is a solution of gaseous ammonia in water. As the open bottles stand next to each other, molecular HCl and molecular NH_3 both vaporize from their respective solutions and escape into the atmosphere as gases.

The fog that forms above the two open bottles results from a reaction of gaseous HCl with gaseous NH_3 to form the solid, crystalline salt *ammonium chloride*, NH_4Cl. Neither water nor any other solvent is present as the acid and the base combine in the open atmosphere.

$$HCl + NH_3 \rightarrow \underset{\substack{\text{ammonium chloride,}\\ \text{a salt}}}{NH_4Cl}$$

By the Brønsted–Lowry definition, an **acid** is any substance that can transfer a proton to another substance. A **base** is a substance that can accept a proton.

Here, in this gaseous neutralization reaction, Brønsted and Lowry give us our definition of choice. The HCl is an acid because it donates a proton to the ammonia molecule, and NH_3 is a base since it accepts a proton from the HCl. We can see what's happening more clearly if we write the ammonium chloride as an ionic compound, $NH_4^+Cl^-$. In this reaction a proton, H^+, is transferred from the HCl to the NH_3, forming NH_4^+, the *ammonium ion.*

Notice that acids and bases are intimately connected by the Brønsted–Lowry definition. For anything to act as an acid, a base *must* be present to accept a proton; for anything to act as a base, an acid *must* be present to provide the proton. In essence, the Brønsted–Lowry definition views an acid–base reaction as no more than the simple transfer of a proton (H^+) from one substance (the acid) to another (the base).

Figure 10.3

Vapors of ammonia and hydrogen chloride combine above the bottles to form ammonium chloride, which appears as a fog. Since this reactions takes place in the absence of water, the Brønsted-Lowry definition of acids and bases is superior to the Arrhenius definition in this case. The reaction that takes place is $NH_3 + HCl \rightarrow NH_4Cl$.

EXAMPLE A MOVABLE PROTON

In the reaction of ammonia with water to form the ammonium ion and the hydroxide ion,

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

what is the acid and what is the base?

Here a proton moves from the water molecule to the ammonia molecule. The water, which loses the proton, must be the acid; the ammonia molecule, which gains the proton, must be the base.

QUESTION

In the reaction

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

what is the acid and what is the base? ______________________

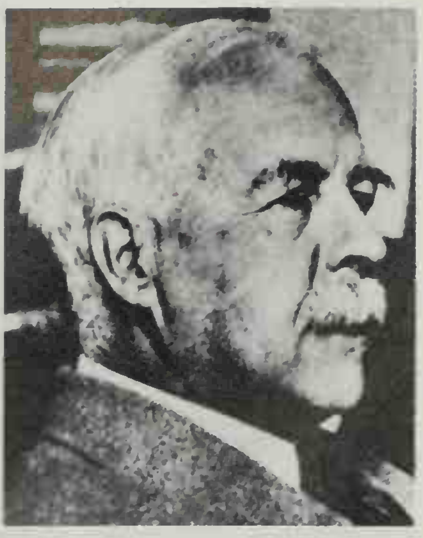
10.5 . . . To Gilbert Newton Lewis

Finally, even as Brønsted and Lowry were presenting their definition in 1923, the American chemist Gilbert Newton Lewis further broadened our ideas of acids and bases. He extended the definition to chemical systems that not only are free of any solvent, but that need not contain any hydrogen either. To Lewis, the ultimate test of acids and bases rests on pairs of electrons. Any chemical species capable of *donating* a pair of electrons to another species is a **base** according to the Lewis definition, while any chemical species capable of *accepting* a pair of electrons from another is an **acid**. A base, then, is an electron pair *donor* in bond formation, and an acid is an electron-pair *acceptor*.

By the Lewis definition, an **acid** is a chemical species capable of accepting a pair of electrons; a **base** is a chemical species capable of donating a pair of electrons.

Applying this definition to the neutralization of HCl by NaOH, we see that the hydroxide ion, OH^-, is a base by the Lewis definition since it donates a pair of electrons in covalent bond formation with the proton, while the proton is the acid since it accepts a pair of electrons from the OH^- (Fig. 10.4).

(As we saw in Section 3.10, the sodium and chloride ions do not bond to each other in water solution, but remain separated and serve as the electrolyte. They come together in the crystal lattice of sodium chloride only as the water evaporates. The sodium and chloride ions of this reaction, then, are not among the acids and bases of the Arrhenius, Brønsted–Lowry, or Lewis definitions.)



Gilbert Newton Lewis, who defined an acid as anything that accepts a pair of electrons and a base as anything that denotes a pair of electrons.

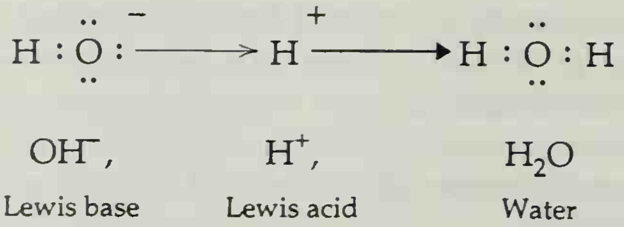


Figure 10.4

Lewis acids and bases: The Lewis base donates a pair of electrons; the Lewis acid accepts a pair of electrons.

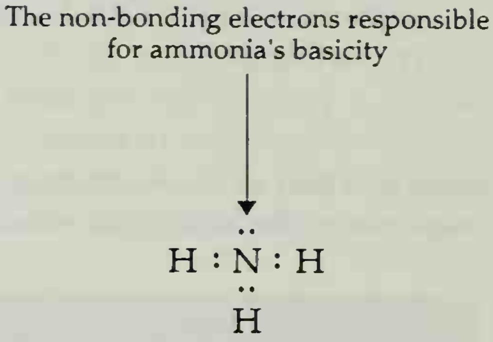


Figure 10.5

Nonbinding electrons of ammonia.

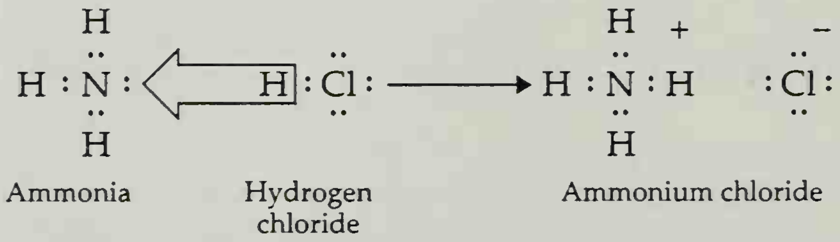


Figure 10.6

As ammonia reacts with HCl, nitrogen's nonbonding electrons become bonding electrons. They form a covalent bond between the nitrogen and the proton released by the HCl. The chlorine retains the pair of electrons from its covalent bond with the H and thus becomes a Cl^- anion.

Ammonia, too, is a base regardless of the presence or absence of water. Like the OH^- anion, the ammonia molecule (NH_3) donates a pair of electrons to any acid it neutralizes. In the electronic structure of the ammonia molecule three hydrogens bond to the central nitrogen through three shared pairs of electrons, while a fourth pair of electrons resides on the nitrogen but doesn't participate in any bonding. These two idle electrons are ammonia's *nonbonding* electrons (Fig 10.5) and are responsible for its basicity. When ammonia reacts with HCl, for example, these free electrons form a covalent bond to the proton donated by the HCl, forming the *ammonium* ion of the salt *ammonium chloride* (Fig. 10.6).

EXAMPLE **BYE-BYE IODIDE**

In the reaction

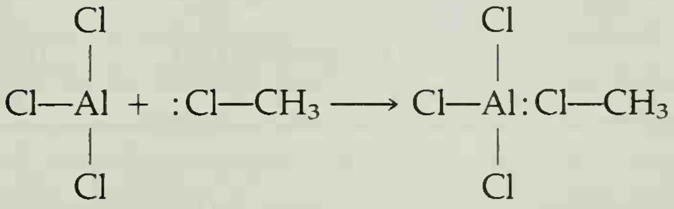
$$\underset{\substack{\text{lithium}\\ \text{hydroxide}}}{LiOH} + \underset{\substack{\text{hydrogen}\\ \text{iodide}}}{HI} \rightarrow \underset{\substack{\text{lithium}\\ \text{iodide}}}{LiI} + \underset{\text{water}}{H_2O}$$

which compound is the acid, which is the base, and which is the salt?

Since there's a proton present here, we can use it as a guide along with the Brønsted–Lowry definition that an acid releases a proton to a base and a base accepts a proton from an acid. The proton of the HI clearly leaves the HI and moves to the LiOH, forming H_2O. The HI, then, is the acid and the LiOH is the base. As the proton departs from the HI it leaves the iodine anion, I^-, behind and as the OH of LiOH becomes part of the water molecule it leaves the lithium cation, Li^+, behind. The combination of the lithium cation and the iodide anion produces the salt, lithium iodide, LiI.

EXAMPLE WHERE'S THE SALT?

In the reaction



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl—Al} \\ | \\ \mathrm{Cl} \end{array} + \mathrm{:Cl—CH_3} \longrightarrow \begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl—Al:Cl—CH_3} \\ | \\ \mathrm{Cl} \end{array}$$

aluminum chloride · methyl chloride · aluminum chloride–methyl chloride complex

which is the acid, which is the base, and which is the salt?

There are hydrogens present, but there's no transfer of a proton from one species to another. Here we're better off using the Lewis definition: an acid is an acceptor of an electron pair and a base is a donor of an electron pair. With this in mind, we can see that the $:Cl—CH_3$ (methyl chloride) donates a pair of electrons to the $AlCl_3$ (aluminum chloride). Since the methyl chloride is the donor, it's the base; since the aluminum chloride is the acceptor, it's the acid. The product formed by the combination of the aluminum chloride and the methyl chloride is the salt.

QUESTION

Identify each ion or compound in the following reaction (other than water) as an acid, a base, or a salt.

$$CH_3—CO_2H + NaOH \longrightarrow CH_3—CO_2^-\ Na^+ + H_2O$$

10.6 Which is the Right Choice?

All three definitions of acids and bases are useful and each is our best choice under different conditions. In water, the Arrhenius definition (acids generate H^+ in water, bases generate OH^-) is the simplest. Outside water, and with

TABLE 10.1 Definitions of Acids and Bases

Method	Acids	Bases
By Physical Phenomena		
Taste	Sour	Bitter
Feel	Not applicable	Slippery
Effect on metals	Liberates H_2 on reaction with iron, zinc, and tin	Not applicable
Effect on indicators		
Litmus	Red	Blue
Phenolphthalein	Colorless	Red
By Chemical Structure		
Arrhenius	Generates protons in water	Generates hydroxide ions in water
Brønsted–Lowry	Transfers a proton to a base	Accepts a proton from an acid
Lewis	Accepts an electron pair from a base	Transfers an electron pair to an acid

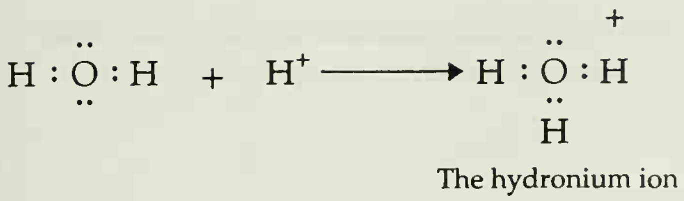
acid–base reactions proceeding by proton transfer, the Brønsted–Lowry definition (a proton, H^+, transfers from an acid to a base) is our choice. If neither water nor transferable protons are present, then we choose the Lewis definition: bases donate electron pairs and acids accept electron pairs in bond formation. Generally, since almost all common consumer products that involve acids and bases contain water as a solvent, we'll use H^+ formation in water in discussing acids and OH^- formation in discussing bases. That won't stop us, though, from applying the Brønsted–Lowry or Lewis definitions whenever one of them is more appropriate.

At this point, we have examined some of the phenomena that identify acids and bases experimentally and some of the definitions that focus on molecular structures. We'll summarize what we now know of acids and bases in Table 10.1. The table includes two acid–base indicators, litmus (Section 10.1) and *phenolphthalein*, a useful indicator that's red in base and colorless in acid.

Recall that litmus is red in acid and blue in base. It's impossible to predict what colors any particular indicator will show in acid and in base. Each turns its own, characteristic colors. In fact some show various colors, depending on the strength of the acid or base. The anthocyanins of red cabbage, for example, don't appear in the table because of the multitude of colors and hues they produce with acids and bases of various strengths. We'll have more to say about the strengths of acids and bases shortly.

Phenolphthalein is useful both as an acid-base indicator and as the active ingredient of laxatives. Swirling a piece of a chocolate-flavored laxative with rubbing alcohol extracts some of the phenolphthalein. Adding a small amount of household ammonia to the solution causes the phenolphthalein to turn red.

In addition to its value as an acid–base indicator, phenolphthalein is also a relatively mild laxative. It's listed as the active ingredient of commercial, chocolate-flavored candylike laxatives, such as Ex-Lax. You can make your own phenolphthalein acid–base test solution by swirling some of the chocolate laxative in a little rubbing alcohol. The isopropyl alcohol of the solution extracts the phenolphthalein from the laxative and turns red when you add a drop or two of dilute household ammonia. Pour off a bit of the solution and add a few drops of lemon juice to the red solution. The solution loses its red color and turns clear and colorless as it becomes acidic. The red color



$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H} + \mathrm{H}^+ \longrightarrow \overset{+}{\mathrm{H}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}}$$

Figure 10.7
The hydronium ion. One of the oxygen's two pairs of nonbonding electrons forms a covalent bond with a proton.

returns as you again add a drop or two of dilute ammonia, which once again makes the solution basic.

Now that we have summarized the properties and definitions of acids and bases, we'll turn for a moment to the acid–base properties of water. By far, water is the one compound we consume in the greatest quantities. Depending on our age and the amount of fat in our bodies, water makes up half to three-quarters of our weight. Through the food and drink we consume, about 2.5 liters of water enters our bodies directly each day. About another quarter of a liter comes from the chemical oxidation of food inside our bodies. By one route or another, some 75,000 liters of water pass through our bodies in just over 75 years. Question: Is all this water we consume an acid, a base, neither, or both? Answer: It's both an acid and a base, in equal measure and at the same time.

In Figure 3.15, we saw that water ionizes reversibly to provide both protons and hydroxide ions. To show that ionization and recombination are going on at the same time we write the overall reaction with two arrows, showing reactions proceeding simultaneously forward and backward:

$$H_2O \rightleftarrows H^+ + OH^-$$

Water, then, is both an acid and a base by the Arrhenius definition since it provides both hydrogen ions and hydroxide ions (in water, of course).

It's both an acid and a base by the Brønsted–Lowry definition as well, since one water molecule can transfer a proton from itself, acting as an acid, to another water molecule, which acts as a base. As we saw in Figure 3.15 the oxygen atom of water holds eight electrons in its valence shell. Two pairs of these electrons form the two covalent bonds to the hydrogens of the molecule, while the remaining two pairs serve as nonbonding electrons. Each pair of these nonbonding electrons is available for covalent bond formation to a proton. The resulting species, H_3O^+ (Fig. 10.7), is the **hydronium ion**.

The **hydronium ion**, H_3O^+, forms when a proton is bonded to a water molecule.

$$2H_2O \rightleftarrows \underset{\substack{\text{the}\\ \text{hydronium}\\ \text{ion}}}{H_3O^+} + OH^-$$

Substances that, like water, can behave as either acids or bases are called *amphoteric* from the Greek *amphoteros*, meaning "either of two."

Actually, protons themselves don't exist as identifiable species in water. Partly because of the proton's enormous affinity for any base and partly because of the very high concentration of water molecules in the body of the water itself (Section 9.8), any and all protons that might form in water bond firmly to a free electron pair of a water molecule to produce the hydronium ion.

$$H^+ + H_2O \rightarrow H_3O^+$$

In a more modern statement of the Arrhenius definition, then, an acid is anything that generates hydronium ions in water.

QUESTION

Recognizing that free hydrogen ions do not exist in water, complete the chemical equation for the ionization of HCl in water:

$$HCl + H_2O \rightarrow Cl^- + ?$$

10.7 Cabbage Chemistry

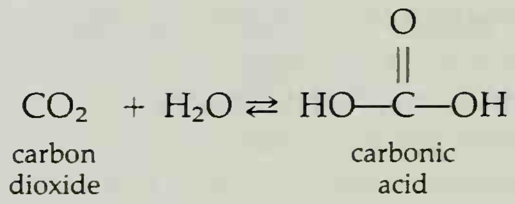
Now we can examine more closely the red cabbage stunt that starts this chapter. It works because the dilute ammonia that's added to the deep blue solution of cabbage extract makes the solution slightly basic and turns the color of the indicator solution to an emerald green. As someone blows into the test solution, the carbon dioxide of the exhaled breath dissolves in the water to form carbonic acid, which first neutralizes the ammonia. Then, after all the ammonia has been converted to ammonium carbonate, the excess carbonic acid ionizes and produces hydronium cations and *bicarbonate* anions, and the indicator turns to a light blue color as the test solution becomes slightly acidic. At the end, adding the vinegar introduces acetic acid into the solution. The acetic acid is a much stronger acid than carbonic acid. Adding the acetic acid makes the test solution far more acidic than the carbon dioxide of breath does. With the marked increase in acidity, the indicator turns a vivid pink or red.

Here's the chemistry:

Ammonia as a base:

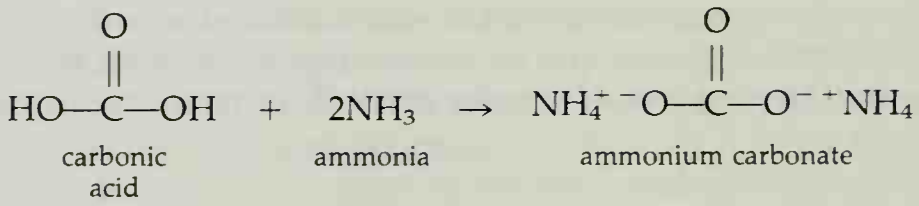
$$NH_3 + H_2O \rightarrow NH_4OH$$

Formation of carbonic acid as carbon dioxide dissolves in water:



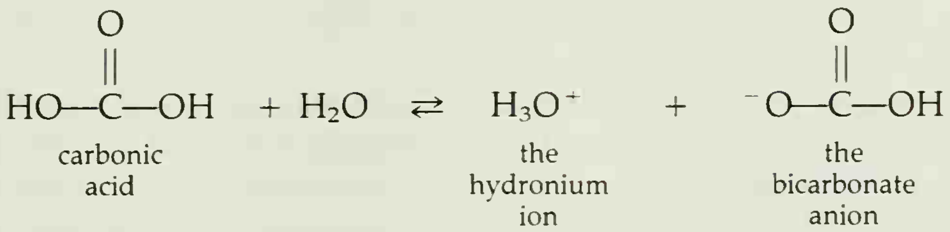
$$\underset{\text{carbon dioxide}}{CO_2} + H_2O \rightleftharpoons \underset{\text{carbonic acid}}{HO{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

Neutralization of ammonia by carbonic acid to form the salt, ammonium carbonate:



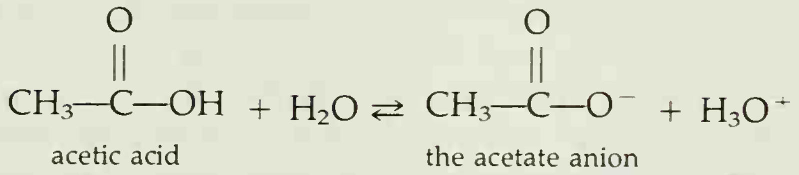
$$\underset{\text{carbonic acid}}{HO{-}\overset{\overset{O}{\|}}{C}{-}OH} + \underset{\text{ammonia}}{2NH_3} \rightarrow \underset{\text{ammonium carbonate}}{NH_4^+\ {}^-O{-}\overset{\overset{O}{\|}}{C}{-}O^-\ {}^+NH_4}$$

Ionization of excess carbonic acid, with water acting as a base as it accepts the proton released by the carbonic acid and forms the hydronium ion:



$$HO-\overset{\overset{\large O}{\|}}{C}-OH + H_2O \rightleftarrows H_3O^+ + {}^-O-\overset{\overset{\large O}{\|}}{C}-OH$$

Ionization of acetic acid to form a hydronium ion and an acetate anion:



$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH + H_2O \rightleftarrows CH_3-\overset{\overset{\large O}{\|}}{C}-O^- + H_3O^+$$

(The *bi-* of *bi*carbonate, HCO_3^-, refers to the hydrogen. The compound $NaHCO_3$ can be called either sodium bicarbonate or sodium hydrogen carbonate.)

QUESTION

What would you observe if you added the dilute ammonia solution, drop by drop, to the pink mixture you obtained after adding the vinegar? ____________________

10.8 Dynamic Equilibrium: Hurly-burly in Pure Water

Pure water is perfectly neutral, neither the slightest bit acidic nor the slightest bit basic. Yet a measurable concentration of hydronium ions does exist even in the very purest water. Although this may seem paradoxical, we've already seen that water molecules ionize to produce hydrogen ions, which proceed immediately to form hydronium ions as they combine with water molecules that haven't ionized.

$$H_2O \rightarrow H^+ + OH^-$$

$$H^+ + H_2O \rightarrow H_3O^+$$

Water's ionization is reversible. Even as some water molecules are ionizing, previously formed hydrogen ions leave their hydronium ions and recombine with hydroxide ions to form new, covalent water molecules:

$$H^+ + OH^- \rightarrow H_2O$$

As we saw in Section 10.6, we can combine the reaction showing the ionization of water with the reverse reaction, the recombination of the ions to regenerate covalent water molecules. For simplicity we'll show only the free proton, H^+, rather than the hydronium ion (H_3O^+, the combination of the proton with a water molecule).

$$H_2O \rightleftarrows H^+ + OH^-$$

This is a dynamic process. At any moment, countless water molecules are decomposing into hydrogen ions and hydroxide ions, and equally countless numbers of hydrogen and hydroxide ions are recombining to regenerate covalent water molecules. When the rate of ionization equals the rate of recombination—when the rates of the forward reaction and the reverse reaction are equal—there is a *dynamic equilibrium*. Water molecules forever ionize and ions forever recombine to regenerate water molecules. Yet with all the hurly-burly of random ionizations and recombinations at equilibrium, the actual concentrations of both the hydronium and hydroxide ions in pure water are fixed and measurable values and are constants at any given temperature.

The molar concentrations of all the transient hydronium and hydroxide ions that exist at equilibrium are fixed at any given temperature and, in chemically pure water, are always equal to each other. They *must* equal each other in pure water since the ionization of each water molecule produces an equal number of the two, one hydronium ion and one hydroxide ion. Experimental measurements show that each of these ions is present in pure, neutral water at a concentration of almost exactly 0.0000001 mol per liter at 25°C. For brevity, we write $[H_3O^+]$ for "the molar concentration of H_3O^+" and we express the value of the molar concentration in exponential notation (Appendix A), with the capital M as the symbol for moles/liter.

$$\underset{\text{The molar concentration of the hydronium ion}}{[H_3O^+]} \underset{\text{is}}{=} \underset{0.0000001\,M}{1 \times 10^{-7}\,M}$$

Equally, $[OH^-] = 10^{-7}\,M$. Thus pure water, which is perfectly neutral and neither the slightest bit acidic or basic, contains both OH^- anions and H_3O^+ cations, each at a concentration of 10^{-7} M.

QUESTION

There *are* ions in pure water, after all. In the demonstration that opened Chapter 1, why didn't the light bulb with the wires dipping into the pure water glow as brightly as the one with leads dipping into the sodium chloride solution? (*Hint:* Assume that the salt-water of that demonstration contained sodium chloride at the same molar concentration as glass 1 of the opening demonstration to Chapter 9.) ____________

10.9 pH, The Measure of Acidity

Chemically, an increase in the acidity of an aqueous solution is brought about by increasing the concentration of its hydronium ion, H_3O^+. As long as we stay with water solutions, we can use the concentration of the hydronium ion as a direct measure of a solution's acidity. Formation of the hydronium ion is, after all, the mark of an acid in water. To measure a solution's acidity, then, we measure the molar concentration of the hydronium ion.

While we can increase the H_3O^+ concentration by adding acid, such as HCl, or increase the OH^- concentration by adding base, such as NaOH, the numerical *product* obtained by multiplying $[H_3O^+]$ by $[OH^-]$ is always constant, regardless of the addition of acid or base to the water. Since the value of this product remains fixed at any specific temperature, adding acid not only increases $[H_3O^+]$, but lowers $[OH^-]$ as well. Similarly, adding a base to water increases the hydroxide concentration and lowers the hydronium ion concentration. In pure water at 25°C, this *ion product constant* of water, K_w, equals the product of the two molar concentrations:

K_w	$=$	$[H_3O^+] \times [OH^-]$	$=$	$10^{-7} \times 10^{-7} = 10^{-14}$
The ion product constant of water	is	the product of the hydronium ion concentration times the hydroxide ion concentration	and,	at 25°C, equals 0.00000000000001, which is a constant at this temperature.

Thus at 25°C the product of the hydronium ion concentration times the hydroxide ion concentration, $[H_3O^+] \times [OH^-]$, is always 10^{-14}.

Only when $[H_3O^+]$ equals 10^{-7} (and $[OH^-]$ also equals 10^{-7}) is water perfectly neutral. Any increase in the hydronium ion concentration above 10^{-7} (with an associated decrease in hydroxide ion concentration) produces an acidic solution; any decrease in $[H_3O^+]$ (and increase in $[OH^-]$) renders the solution basic.

The variations in hydronium ion concentrations can be enormous. In 0.1 M HCl, which ionizes completely in water, $[H_3O^+]$ is 0.1, or 10^{-1}. In 0.1 *M* NaOH, which also ionizes completely in water, $[OH^-]$ is 0.1, or 10^{-1}. Since $[H_3O^+] \times [OH^-]$ equals 10^{-14}, the hydronium ion concentration in 0.1 M NaOH solutions must be 10^{-13} as shown:

$$[H_3O^+] \times [OH^-] = 10^{-14}$$

$$[H_3O^+] \times 10^{-1} = 10^{-14}$$

$$[H_3O^+] = \frac{10^{-14}}{10^{-1}}$$

$$[H_3O^+] = 10^{-13}$$

The hydronium ion concentration in 0.1 *M* HCl is one trillion times (10^{12}) as great as it is in 0.1 *M* NaOH.

Largely to simplify the discussion of acidities and to accommodate the enormous variations in the values of acidities, the Danish biochemist S. P. L. Sørensen proposed in 1909 that concentrations of H^+ be treated as exponential values. Following Sørensen's recommendation, we now consider $[H_3O^+]$ in terms of **pH**, which is defined as *the negative logarithm of the hydronium ion concentration*. This simply means that to find the pH we

- write the concentration of $[H_3O^+]$ as a power of 10 and

The **pH** of a solution is a measure of the solution's acidity. The pH is the negative logarithm of its hydronium ion concentration.

- use the exponent of 10, but
- reverse its sign.

The letters *pH* represent the *p*ower of the *H*ydrogen (or *H*ydronium) ion. As a symbol for acidity, pH reflects nicely the international character of chemistry. The letter *p* begins the English word *power* as well as its French and German equivalents, *puissance* and *Potenz*. At the time of Sørensen's suggestion, English, French, and German were the world's dominant scientific languages.

The following mathematical expression of pH uses exponential notation. You may want to review the topic, which is discussed in Appendix A.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

For neutral water,

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 10^{-7},\\ \text{pH} &= -\log\,[\text{H}_3\text{O}^+]\\ &= -\log 10^{-7}\\ &= -\ (-7)\\ \text{pH} &= +7\end{aligned}$$

The pH of neutral water, then, is 7.

In acidic solutions the H_3O^+ concentration is greater than 10^{-7} *M* and so the exponent of 10 must be *less negative* than -7. That is, it falls in a range between -7 and zero. In acidic solutions, then, the pH (which is the negative of the exponent) must be less than 7. If a particular acidic solution had a hydronium ion concentration of, for example, 10^{-6} *M*, the *negative* of the logarithm (-6) would be $+6$, and so the pH of this particular solution would be 6.

In basic solutions the reverse is true; with the hydronium ion concentration less than 10^{-7}, the exponent of 10 must be *more negative* than -7 and the pH must be greater than 7. In a particular basic solution the $[H_3O^+]$ might be, for example, 10^{-8} *M*. For this solution the pH would be 8. Because of the way pH is defined, the pH of an acidic solution must be less than 7 and the pH of a basic solution must be greater than 7.

To summarize, at 25°C

- The pH of an acidic solution is less than 7.
- The pH of a neutral solution equals 7.
- The pH of a basic solution is greater than 7.

What's more, the definition of pH requires that for every *tenfold* increase in the $[H_3O^+]$ concentration there is a decrease of *one unit* in the pH; for every *tenfold* decrease in the acidity there is an increase of *one unit* in the pH. Table 10.2 summarizes the relation between acidity and pH.

Let's look at a few illustrations of the connection among pH, $[H_3O^+]$, and acidity.

TABLE 10.2 Acidity and pH

	pH		$[H_3O^+]$
Strongly acidic	1	10^{-1}	0.1
	2	10^{-2}	0.01
	3	10^{-3}	0.001
	4	10^{-4}	0.0001
	5	10^{-5}	0.00001
Weakly acidic	6	10^{-6}	0.000001
Neutral	7	10^{-7}	0.0000001
Weakly basic	8	10^{-8}	0.00000001
	9	10^{-9}	0.000000001
	10	10^{-10}	0.0000000001
	11	10^{-11}	0.00000000001
	12	10^{-12}	0.000000000001
	13	10^{-13}	0.0000000000001
Strongly basic	14	10^{-14}	0.00000000000001

EXAMPLE THE BASIC EGG

A hydronium ion concentration of 10^{-8} is common for fresh eggs. What is the pH of a fresh egg?

Here, the hydronium ion concentration is given to us as a power of 10. All we need to do is write the exponent of 10 (which is -8), but with its sign reversed: $+8$. A common pH for a fresh egg is 8.

EXAMPLE HOW ACIDIC IS A SOpHT DRINK?

A typical pH of a soft drink is 3.0. What's the value of $[H_3O^+]$ for a typical soft drink?

In this case we reverse the process. Since the pH is 3, the exponent of 10 must be the negative of $+3$, which is -3. Using this value as the power of 10 that corresponds to the $[H_3O^+]$, we get $[H_3O^+] = 10^{-3}$.

EXAMPLE BLOOD AND SEAWATER

Which is more acidic, human blood, with a pH of 7.3–7.5, or seawater, with a pH in the range 7.8–8.3?

In Table 10.2 we see that the *lower* or less positive the value of pH, the *higher* the value of $[H_3O^+]$ and the *higher* the acidity of the solution. Since human blood has a lower pH than seawater, the hydronium ion concentration in blood must be higher than it is in seawater.

QUESTION

(a) A typical pH for household ammonia is 11. To what value of $[H_3O^+]$ does this correspond? (b) What is the value of $[OH^-]$ in household ammonia? (c) The hydronium ion concentration of an average tomato is about 0.001 *M*. What's the pH of the average tomato? ____________________

10.10 Strong Acids and Weak Acids

Now that we understand that pH is a measure of the acidity of a solution, a measure of the molarity of the hydronium ion, and that the larger the value of pH, the less acidic the solution, let's go back for a moment to our red cabbage demonstration. As you blow into the green (basic) solution, the CO_2 of your breath changes the color of the indicator from a shade of green to a shade of blue. But no matter how long you blow into the solution, the color won't depart much from that particular shade of blue. When you add the vinegar, though, the color changes to a pink or red.

The reason is that the acetic acid of the vinegar ($CH_3—CO_2H$) is a stronger acid than the carbonic acid (H_2CO_3) that the carbon dioxide of your breath forms as it reacts with water. Adding the acetic acid produces a larger value of $[H_3O^+]$ and therefore a lower pH than you can get by blowing into the indicator solution.

The value of $[H_3O^+]$ produced by any particular concentration of an acid depends on the extent to which the acid ionizes. We've already seen that the very slight ionization of water generates a very small concentration of hydronium ions in pure water. Similarly, the ionization of an acid in water produces hydronium ions, as we saw in the question at the end of Section 10.6 for the ionization of HCl:

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

As we might expect, the higher the fraction of the molecules that ionize, the greater the concentration of the hydronium ions it produces (for any particular concentration of the acid itself). Since hydrogen chloride ionizes completely and irreversibly in water, every HCl molecule that enters water produces one Cl^- ion and one H_3O^+ ion. Since *all* of the HCl molecules ionize instantaneously and irreversibly to produce these ions, once the HCl molecules enter the water, the hydronium ion concentration of the HCl solution exactly equals the concentration of the HCl. (More precisely, the hydronium ion concentration is the same that the concentration of the HCl molecules would have been if they had remained intact. There are no HCl molecules left since all of them have ionized to H^+ and Cl^-.)

EXAMPLE SPLITTING UP

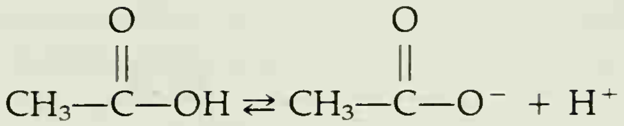
What is the pH of a solution prepared by dissolving 0.01 mol of pure HCl in 1 liter of water?

Here we have a solution that would be 0.01 molar in HCl if the molecule didn't ionize. But each HCl molecule ionizes irreversibly to produce one cation and one anion.

HCl	$\rightarrow$	H^+	$+$	Cl^-
0.01 mol		0.01 mol (which reacts with the water present to form 0.01 mol of H_3O^+)		0.01 mol

Since the HCl ionizes to form 0.01 mol of hydronium ions in water, the value of $[H_3O^+]$ is 0.01 *M*, or 10^{-2} *M*. The pH is 2.

Like water molecules (and unlike HCl molecules), acetic acid molecules ionize reversibly.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightleftarrows CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H^+$$

As a result, not all of the acetic acid molecules in solution are ionized at the same time. Since only a fraction of these molecules are producing H^+ at any given moment, the concentration of H^+ at any instant is less than the concentration of acetic acid molecules introduced into the solution. Naturally, the greater the fraction of the acetic acid molecules ionized at any moment, the greater the concentration of the hydronium ions would be and the more acidic the solution. We saw in the previous example that the pH of a 0.01 M solution of HCl in water is 2. For the same molar concentration of acetic acid in water the pH is 3.4. The 0.01 *M* acetic acid solution is thus less acidic than the 0.01 *M* HCl solution.

Since a particular concentration of hydrogen chloride renders a solution more acidic than does the same concentration of acetic acid, we consider hydrogen chloride to be a stronger acid than acetic acid. In fact, any acid that ionizes completely and irreversibly in water (like hydrogen chloride) is considered to be a *strong acid*, while an acid that ionizes reversibly and therefore only partially (like acetic acid) is a *weak* acid.

Typical strong acids are hydrochloric acid (HCl, the muriatic acid of Section 10.2), sulfuric acid (H_2SO_4, the acid of the lead–acid storage battery in Chapter 6), and nitric acid (HNO_3). Nitric acid is seldom, if ever, used in consumer products. Typical weak acids are the acetic acid and the carbonic acid of our red cabbage demonstration.

QUESTION

What is the concentration of Cl^- in a solution of HCl that has a pH of 2? ______

10.11 The Strength of Acids: K_a

Since, for any given concentration, the value of $[H_3O^+]$ produced by the ionization of an acid depends on the extent to which the acid ionizes, we can determine the strength of any acid by determining the fraction of its molecules ionized at any particular instant. We determine this fraction of the acid that's ionized by allowing a solution of the acid to come to equilibrium (Section 10.8) and measuring experimentally the concentrations of all the ions it produces and of the intact acid itself. For acetic acid we have

$$\underset{\text{acetic acid}}{CH_3\text{—}CO_2H} \rightleftarrows \underset{\textit{acetate}\text{ anion}}{CH_3\text{—}CO_2^-} + \underset{\text{proton}}{H^+}$$

We measure the concentrations of the acetate anion and the hydronium ion (which represents the concentration of protons) and of the acetic acid.

In reasonably dilute solutions, about 0.1 *M* or less, and at any fixed temperature, the ratio

$$\frac{[CH_3\text{—}CO_2^-] \times [H^+]}{[CH_3\text{—}CO_2H]}$$

The **acidity constant** or **ionization constant**, K_a, is the ratio of the concentrations of the ionization products of the acid to the concentration of the un-ionized acid. It is a measure of the strength of the acid since it reflects the fraction of the acid that ionizes.

is constant and is represented by the symbol K_a. This is the **acidity constant** or the *ionization constant* of the acid.

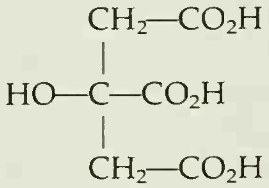
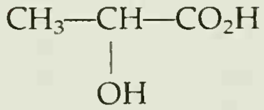
$$K_a = \frac{[CH_3\text{—}CO_2^-] \times [H^+]}{[CH_3\text{—}CO_2H]}$$

The higher K_a, the stronger the acid. For acetic acid, $K_a = 1.8 \times 10^{-5}$ at 25°C.

The strength of an acid, then, is directly related to its degree of ionization, as expressed by K_a. The acidity constants of several acids appear in Table 10.3. For easier comparison the same exponential notation, 10^{-5}, is used throughout the table. Some acids, such as carbonic acid and citric acid, can release more than one proton in water. For these the table shows K_a for the proton that's released first, the most acidic of those present.

The values in Table 10.3 explain very nicely the color changes in the breath test solution of the opening demonstration. In adding the dilute ammonia to the cabbage extract you made the solution basic and raised the pH above 7, to a region where the indicator dye is green. By blowing through the straw you first neutralized the ammonia with carbonic acid, a weak acid with a K_a of 0.04×10^{-5}. Adding more carbonic acid as you continued to blow through the straw lowered the pH to a range in which the dye is blue. Finally you added vinegar, which is a solution about 0.83 *M* in acetic acid (Section 9.10). With a K_a of 1.8×10^{-5}, acetic acid is over 40 times as strong an acid as carbonic acid ($K_a = 0.04 \times 10^{-5}$). Addition of the acetic acid lowered the pH

TABLE 10.3 Strengths of Some Common Acids (at 25°C)

Acid	Occurrence	Structure	K_a
Acetic acid	Vinegar	$CH_3{-}CO_2H$	1.8×10^{-5}
Boric acid	Mild antiseptic; eye drops and rectal suppositories	H_3BO_3	0.00006×10^{-5}
Carbonic acid	Solution of carbon dioxide in water	H_2CO_3	0.04×10^{-5}
Citric acid	Acid of citrus fruit	 $\begin{array}{l} \quad\; CH_2{-}CO_2H \\ \qquad\vert \\ HO{-}C{-}CO_2H \\ \qquad\vert \\ \quad\; CH_2{-}CO_2H \end{array}$	74.5×10^{-5}
Formic acid	Sting of red ants	$H{-}CO_2H$	17.7×10^{-5}
Lactic acid	Sour milk	 $\begin{array}{l} CH_3{-}CH{-}CO_2H \\ \qquad\;\vert \\ \qquad OH \end{array}$	13.7×10^{-5}

of the test solution even further, to a region where the anthocyanin dye turns from the blue of a weakly acidic solution to the pink of a stronger acid.

QUESTION

Would the data in Table 10.3 lead you to you expect (a) lemon juice, (b) sour milk, or (c) eye drops to have the same effect on the test solution as vinegar? Explain your answer. ______________________________

10.12 Acidities of Some Common Substances

Usually pH is measured with either a strip of test paper or an instrument called a *pH meter* (Fig. 10.8). While the red and blue colors of litmus paper show the presence of acidity and basicity very clearly, they give no indication of the strength of the acid or base. Other, more sensitive types of test strips are impregnated with combinations of acid–base indicators that turn various colors as the pH changes. While these "universal" test strips offer fast, convenient, and cheap indications of pH, they give only approximate values. For more precise measurements the pH meter is the instrument of choice. It's essentially a specially designed voltmeter connected to a pair of electrodes that are dipped into the solution being examined. Most common pH meters provide values accurate to about 0.1 pH unit.

Table 10.4 presents the pH of some common substances. Notice that our stomach's digestive juices (sometimes called *gastric* juices and rich in hydrochloric acid) are quite acidic and that our food and drink range from the very high acidity of citrus fruits, such as lemons, to neutral or weakly basic substan-

Figure 10.8
A pH meter, an instrument used for the very accurate measurement of hydrogen ion concentrations.

TABLE 10.4 pH of Some Common Substances

	pH	Material
Acidic	1.0–3.0	Gastric juices
	2.2–2.4	Lemons
	2.4–3.4	Vinegar
	2.5–3.5	Soft drinks
	3.0–3.4	Sour pickles
	3.0–3.8	Wine
	3.0–4.0	Oranges
	4.0–4.4	Tomatoes
	4.8–7.5	Human urine (usually 6.0)
	5.6	Carbonated water, rainwater
	6.3–6.6	Cow's milk
	6.4–6.9	Human saliva (during rest)
	6.6–7.6	Human milk
	6.5–8.0	Drinking water
Neutral	7.0	Pure water
Basic	7.0–7.3	Human saliva (while eating)
	7.3–7.5	Human blood
	7.6–8.0	Fresh eggs
	7.8–8.3	Seawater
	8.4	Sodium bicarbonate, saturated
	9.4	Calcium carbonate, saturated
	10.5	Milk of magnesia
	10.5–11.9	Household Ammonia

ces like drinking water, fresh eggs, and crackers. The stomach's acidity, which comes from HCl secreted by the cells of its lining, promotes the digestion of food proteins by the enzymes of the gastric juices. *Pepsin,* for example, is a stomach enzyme that cleaves the very large molecules of proteins into smaller, more easily handled fragments. Pepsin does its chemical work best at a pH of 1.5–2.5 and quits functioning when the pH rises to between 4.0 and 5.0. Both good health and the digestion of proteins require an acidic stomach.

QUESTION

Acids and bases react with each other to produce neutral solutions. Could you obtain a neutral aqueous solution by mixing, in the proper proportions: (a) vinegar and sodium bicarbonate; (b) the juice of sour pickles and carbonated water; (c) seawater and milk of magnesia? ______________________

10.13 Antacids: Palliatives for Cannibalism

An acid stomach can bring us problems as well as good health. Excess acid sometimes produces the discomforts commonly called "acid indigestion" and "heartburn," as well as the pain of gastric ulcers. Like much of our food, our body tissues and organs, including the walls of the stomach itself, are made of protein. The enzymes of the stomach fluids can't discriminate between the protein of food and the protein of the stomach walls and would digest the stomach itself as easily as a steak if it weren't for special protective devices, such as an alkaline mucous lining that resists the action of the stomach's acid and its enzymes. This barrier keeps the stomach from being eaten away by its own juices. Sometimes, though, things get out of hand. When the body's defenses fail, a combination of stomach acid and pepsin can attack the stomach wall in an act of chemical cannibalism. The result is a gastric ulcer (Fig. 10.9).

Among the best palliatives for the discomforts of excess stomach acid, which can include the pain of ulcers, are OTC antacids such as Alka-Seltzer, Milk of Magnesia, Rolaids, Titralac, and Tums, or simply some baking soda (sodium bicarbonate) in water. (*OTC* describes medicines sold in drugstores "over the counter," without a physician's prescription. Medications generally fall into either of two categories, "OTC" and "prescription.") Each year Americans buy about a quarter of a billion dollars worth of these and other OTC antacid products simply for the relief of pain brought on by maverick hydronium ions of the stomach.

The antacid's function isn't to bring the stomach's fluids to a complete acid–base neutrality of pH 7. Such an action would shut down digestion completely and could shock the walls into flooding the stomach with fresh acid in what's called "acid rebound." Instead, a good antacid neutralizes enough of the HCl in the gastric juices to alleviate the pain and discomfort, yet allows normal stomach action to proceed. Even if as much as 90% of the stomach's HCl were to be neutralized, the pH would still be a healthy 2.3.

The bases most widely used in antacids, providing an inexpensive combination of safety, effectiveness, and efficiency, include

Aluminum hydroxide, $Al(OH)_3$	Magnesium hydroxide, $Mg(OH)_2$
Calcium carbonate, $CaCO_3$	Sodium bicarbonate, $NaHCO_3$
Magnesium carbonate, $MgCO_3$	Potassium bicarbonate, $KHCO_3$

Magnesium oxide, MgO, is sometimes used as an antacid ingredient since it reacts with water to form magnesium hydroxide:

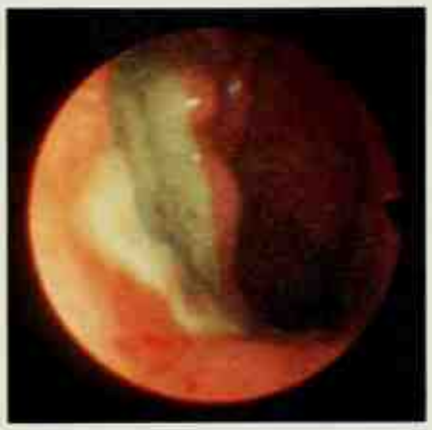
$$MgO + H_2O \rightarrow Mg(OH)_2$$

The active ingredients of several of the more popular antacid preparations appear in Table 10.5. On reaction with HCl, the sodium bicarbonate of Alka-Seltzer and of other commercial antacids forms carbonic acid, which is a much weaker acid than HCl and which decomposes readily (and reversibly) to carbon dioxide and water:

$$NaHCO_3 + HCl \rightarrow NaCl + \underset{\text{carbonic acid}}{H_2CO_3}$$

$$H_2CO_3 \rightleftarrows CO_2 + H_2O$$

Each Alka-Seltzer tablet contains 1.0 g of sodium bicarbonate, 0.3 g of potassium bicarbonate, and 0.8 g of citric acid. When you drop the tablet into



A gastric ulcer forms when the alkaline mucous lining protecting the stomach erodes and a combination of stomach acids and enzymes begins digesting the stomach wall itself.

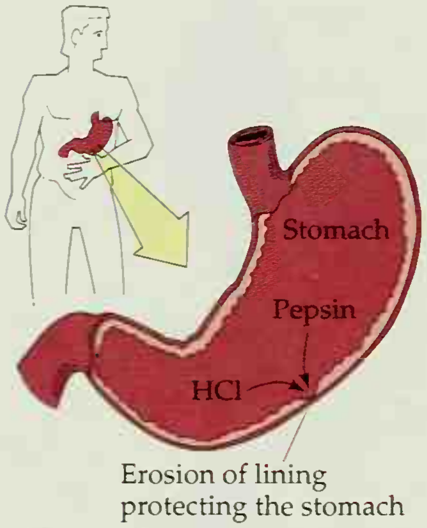


Figure 10.9

Formation of a gastric ulcer. The gastric juices begin digesting the protein of the stomach wall if its protective lining erodes.

Antacids available for the relief of discomfort due to excessive stomach acidity. These contain weak bases that neutralize a portion of the stomach's hydrochloric acid.

TABLE 10.5 Common Antacids

Principal Active Ingredient	Representative Antacid	Neutralization Reaction
Sodium bicarbonate Potassium bicarbonate	Alka-Seltzer	$NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3$ $(H_2CO_3 \rightarrow H_2O + CO_2)$
Magnesium hydroxide	Phillips' Milk of Magnesia	$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$
Dihydroxyaluminum sodium carbonate	Rolaids	$Al(OH)_2NaCO_3 + 4\,HCl \rightarrow AlCl_3 + NaCl + 2H_2O + H_2CO_3$
Calcium carbonate	Titralac Tums	$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2CO_3$
Aluminum hydroxide Magnesium carbonate Magnesium hydroxide	Di-Gel	$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$ $MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2CO_3$ $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

water, the citric acid and the sodium and potassium bicarbonates dissolve. They react with each other to produce carbonic acid, which decomposes to carbon dioxide by the very same sort of reactions shown above for the neutralization of HCl. The fizz of the Alka-Seltzer tablet comes from this chemical release of the carbon dioxide. You can produce the very same effervescence by squeezing a little lemon juice onto some household baking soda, which is a commercial form of sodium bicarbonate. The citric acid of the lemon juice reacts with the sodium bicarbonate to produce carbon dioxide just as it does when you drop an Alka-Seltzer tablet into water.

There's considerable choice among the various brands and formulations of antacid tablets. The selection could be made, for example, on the basis of the particular base used. People with hypertension (high blood pressure) who have been advised to avoid sodium might wish to choose an antacid that doesn't contain sodium bicarbonate ($NaHCO_3$). On the other hand, those who are concerned about the possible bone degeneration resulting from a loss of calcium, a condition known as *osteoporosis*, might choose an antacid formulated with calcium carbonate ($CaCO_3$).

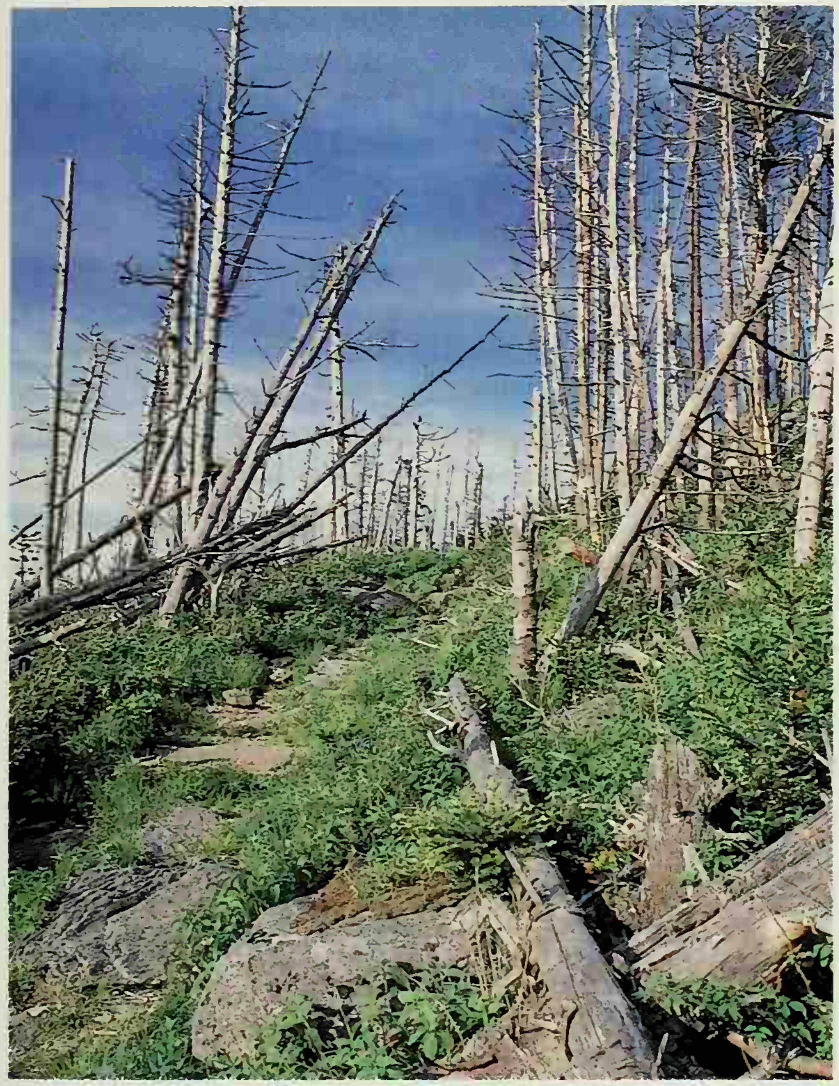
QUESTION

Acid deposits around a car's battery terminals can be cleaned with a solution of sodium bicarbonate. Assuming that the acid is sulfuric acid, complete and balance the equation for the neutralization reaction:

$$NaHCO_3 + H_2SO_4 \rightarrow ?$$

10.14 Acid Rain

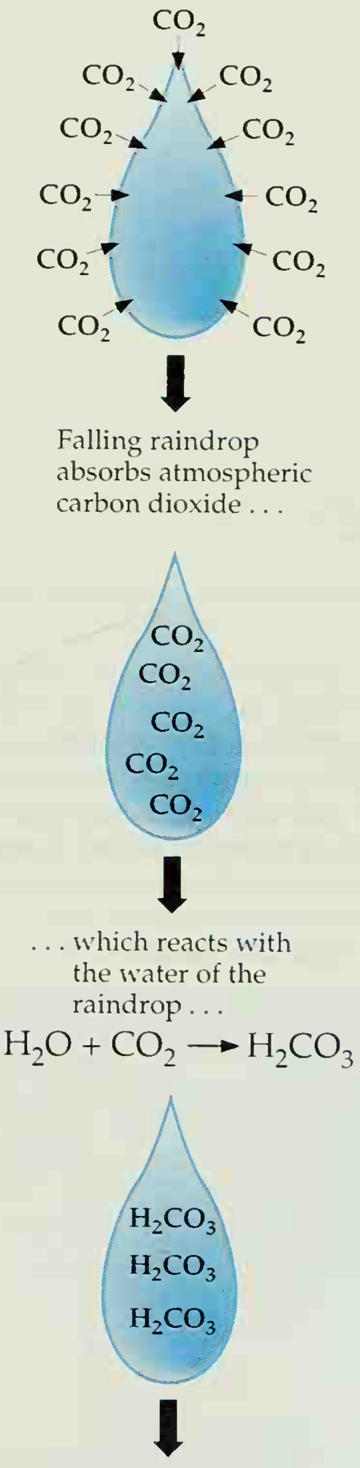
Rain and blood, one acidic, the other basic, provide two final examples of the importance of pH to the fluids of the environment and of life. We'll begin with a phenomenon known as *acid rain*, one of the products of our industrialized society. The rain's acidity comes ultimately from small quantities of or-



The destructive effect of acid rain on trees.

Figure 10.10

The natural acidity of rain.



ganic compounds of sulfur and nitrogen that occur in fossil fuels. As the fuels burn in our cars and in our factories, oxides of sulfur and nitrogen are disgorged into the atmosphere as pollutants. Once in the atmosphere these oxides undergo complex reactions that transform them into the strong acids sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These acids dissolve in the rain as it forms in clouds. As the rain falls they reach the ground as acid rain.

The term *acid rain* was first used in 1852 to describe the results of the atmospheric pollution produced by the beginnings of the Industrial Revolution in the midlands of England. (Industry in that region and at that time derived its energy from nearby deposits of coal, a fossil fuel.) By now the term has come to describe all forms of rain and snow whose excessive acidity causes environmental mischief, including the destruction of vegetation and marine life and the etching and corrosion of buildings and works of art that are exposed to the weather.

In a real sense all rain is acid rain, with or without air pollution, simply because of the natural presence of carbon dioxide in the earth's atmosphere. Like the carbon dioxide of breath that turns the cabbage water acidic, the carbon dioxide of the atmosphere dissolves in raindrops as they form and fall to the ground, and it reacts with the rainwater to form carbonic acid (Fig. 10.10). The chemical reaction is the same as the one that produces the change of color in the cabbage water demonstration.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Through this reaction we can dissolve carbon dioxide in the purest distilled water until the solution is saturated. The result is an acidic solution of pH 5.6. Similarly, the purest rain, falling through an unpolluted sky, can reach earth as an acidic solution of pH 5.6. Rainfall would still be acidic, then, even if all factories were to be shut down and all cars were to remain parked. (At this pH, the acidity of rainfall stands somewhere between that of milk and fresh tomatoes; see Table 10.4.)

Since the pH of pure rainwater can be as low as 5.6, we might consider rain whose pH is *lower* than 5.6 to be acid rain. Indeed many scientists did just that until about 1980. We know now, though, that other phenomena, not at all related to human activities, also work to decrease the pH of rainwater. Volcanic eruptions, for example, release gaseous sulfur dioxide and hydrogen sulfide, both of which are converted eventually to atmospheric sulfuric acid. Even the action of the bacteria of the soil contributes to the presence of sulfuric and nitric acids. As a result, even rain that falls far from inhabited or industrialized areas, through apparently uncontaminated air, shows a pH lower than 5.6 and generally about 5.0.

Yet it's clear that the great majority of the air pollutants that eventually form acids—as much as 90% of all the atmospheric sulfur, for example—result from human activity, primarily the burning of fossil fuels. It's also clear that this activity is the source of the rainfall and atmospheric moisture that show remarkably low pH values. Much of the rain that falls in the western regions of New York State, for example, carries a pH of 4.1; during the summer the bottoms of clouds above the eastern United States generally show a pH of about 3.6 (and occasionally as low as 2.6); a storm in Scotland in 1974 produced rainfall of pH 2.4; a recent fog in Los Angeles generated a pH of 2.0. For comparison, the pH of vinegar falls in the range 2.4–3.4 (Table 10.4). All of these very low pH values appear to trace back to the nitrogen- and sulfur-containing impurities of fossil fuels. As winds carry these across national borders acid rain becomes an international issue. Air pollutants pro-

Graphic damage done to outdoor artwork by the action of acid rain and air pollution over a period of 60 years. The sandstone statue is located at the Herten Castle in Westphalia, Germany.

duced in one country end up in the rainfall of another. Canada, in particular, appears to suffer from acid rain coming from pollutants released in the United States.

The effects of acid rain seem to result from a subtle complex of factors rather than from a direct, corrosive destruction of vegetation and marine life by the acids themselves. It seems that changes in the pH of fresh water and resulting changes in the balance of its minerals can affect the reproduction and survival of many species of fish and other marine life, and that changes produced in soils can place a biological stress on trees, decrease the soil nutrients that are available to them, and make the trees more susceptible to lethal diseases.

Acid rain and perhaps other forms of corrosive air pollution appear to be responsible for still other forms of environmental decay. In several European cities, statues and other works of art exposed to the weather show signs of severe erosion. While this form of destruction can't be repaired easily, at least some of the biological results of acid rain do appear to be reversible. With tighter regulation of emissions from automobiles and factories, the acidities of some lakes in the northeastern United States and in eastern Canada seem to be dropping and the variety of marine life in them seems to be increasing.

QUESTION

The oxidation of sulfur, carried out through several chemical steps, eventually produces sulfur trioxide, SO_3. Write a balanced chemical equation showing the reaction of SO_3 with water to produce sulfuric acid, H_2SO_4. ____________________

10.15 Le Châtelier's Principle

In previous sections we've looked at some of the chemistry of carbon dioxide and carbonic acid. We've seen, for example, that carbon dioxide dissolves in rainwater to form carbonic acid, and that carbonic acid decomposes to form carbon dioxide when we drop an Alka-Seltzer tablet into a glass of water. We'll look now at a subtle but important connection between the chemistry that goes on as a raindrop falls through the sky and the chemistry of an Alka-Seltzer tablet dropping into a glass of water.

The carbon dioxide of our breath and the carbon dioxide of the atmosphere both dissolve in water to produce carbonic acid.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

We've also seen (Section 10.13) that adding an acid to a solution of sodium bicarbonate ($NaHCO_3$) converts it to carbonic acid, which fizzes as it decomposes to carbon dioxide and water.

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

Each of these reactions is the reverse of the other. Taken together they represent an equilibrium reaction, which we can represent as

$$H_2CO_3 \rightleftarrows CO_2 + H_2O$$

Carbon dioxide is released when an Alka-Seltzer tablet is dropped into water. As the sodium bicarbonate and citric acid of the tablet react in water, they form carbonic acid. With increasing concentration, the carbonic acid decomposes to carbon dioxide and water.

Taken in the forward direction, as it's written in the second of the three preceding equations, this chemical reaction represents part of the chemistry of the Alka-Seltzer tablet: carbonic acid decomposes into carbon dioxide and water. Taken in the reverse direction, as it's written in the first of the three equations, it represents the formation of carbonic acid in a raindrop.

What determines the direction of the equilibrium reaction? What determines whether carbonic acid is converted to carbon dioxide and water, or carbon dioxide and water are converted to carbonic acid? The answer depends on the rules of chemistry, on the conditions at hand, and on a chemical principle known as **Le Châtelier's principle**, which states that *placing a stress on an equilibrium causes the equilibrium to shift so as to relieve the stress.* It's a principle that operates in all chemical equilibria, as well as in many situations in our personal lives that have nothing whatever to do with chemistry. Henri Louis Le Châtelier, the French chemist who first proposed this principle, lived from 1850 to 1936 and worked primarily on the chemistry of industrial processes and products.

Le Châtelier's principle states that when a stress is placed on a system in equilibrium, the system tends to change in a way that relieves the stress.

Le Châtelier's principle explains nicely why carbonic acid forms in a raindrop as it falls through the air, and why an Alka-Seltzer tablet produces a fizz when its dropped into water. The key lies in a simple bit of chemistry: in any equilibrium reaction, the ratio of the concentrations of the products to the concentrations of the reactants tends to remain constant. In the equilibrium of carbonic acid, carbon dioxide and water, for example,

$$H_2CO_3 \rightleftarrows CO_2 + H_2O$$

the ratio

$$\frac{[CO_2] \times [H_2O]}{[H_2CO_3]}$$

tends to remain at a constant value. Thus anything that might act to increase the concentration of carbon dioxide would also produce an increase in the concentration of the carbonic acid so as to keep the numerical value of the ratio constant. Similarly, anything acting to increase the concentration of carbonic acid would also act to increase the concentration of carbon dioxide.

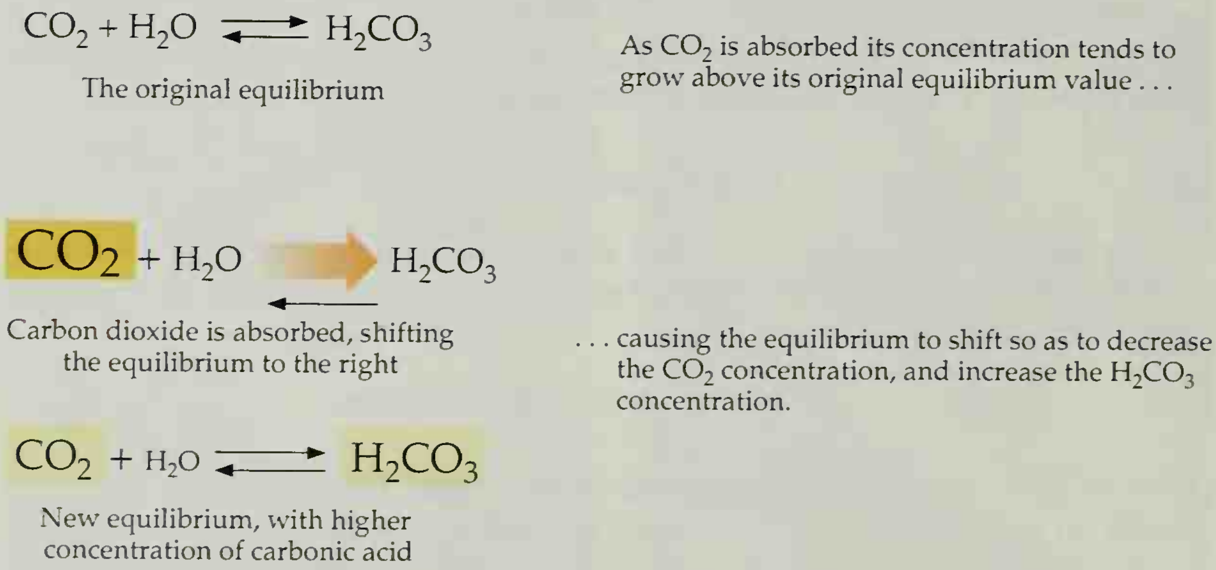
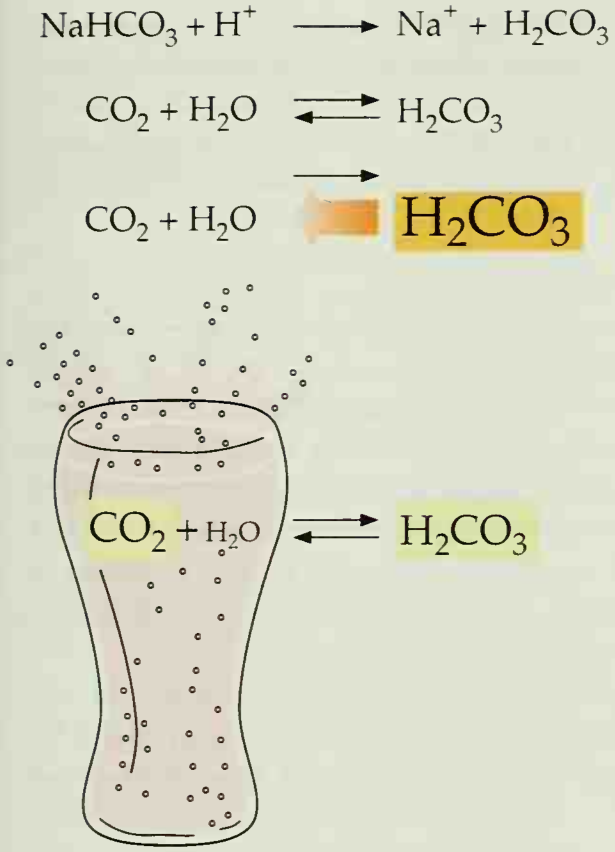


Figure 10.11
How a shifting equilibrium maintains a constant K_e.



Sodium bicarbonate reacts with citric acid producing carbonic acid . . .

. . . which equilibrates with carbon dioxide and water.

As the concentration of carbonic acid grows, through continuing reaction of sodium bicarbonate and acid, the equilibrium shifts toward carbon dioxide . . .

. . . which grows in concentration and escapes from the water as bubbles fizz.

Figure 10.12
The chemistry of the fizz.

We'll see now how Le Châtelier's principle applies to both rain and Alka-Seltzer. As a raindrop falls through the sky it absorbs CO_2, which reacts with the water to form H_2CO_3. The continuing absorption of additional carbon dioxide as the drop falls continually increases the concentration of the CO_2 and places a stress on the equilibrium. To relieve this stress and to maintain a constant value of the ratio described above, the equilibrium shifts to convert the additional carbon dioxide into a higher concentration of carbonic acid (Fig. 10.11). This process continues until the raindrop is saturated with carbon dioxide.

The reverse of this process occurs when we dissolve an Alka-Seltzer tablet in water or add the citric acid of lemon juice (or the acetic acid of vinegar) to a sodium bicarbonate solution. The acid reacts with the bicarbonate ion to produce carbonic acid.

$$H^+ + HCO_3^- \rightleftarrows H_2CO_3$$

As the concentration of carbonic acid grows, the equilibrium shifts to convert carbonic acid to water and carbon dioxide, which escapes as a gas. Once again the numerical value of the ratio is held constant. In this case the very large quantity of carbonic acid that is produced puts a stress on the system, which is relieved as carbonic acid decomposes into carbon dioxide and water (Fig. 10.12).

QUESTION

Consider a solution of carbonic acid in water, with the equilibrium mixture consisting of carbonic acid, the bicarbonate anion, and the proton:

$$H_2CO_3 \rightleftarrows HCO_3^- + H^+$$

In which direction, forward or reverse, would this equilibrium shift if a small amount of acid (which would act to increase [H^+]) were added to the solution? In which direction would the equilibrium shift if a small amount of a strong base such as NaOH (which would act to decrease [H^+] through the reaction $OH^- + H^+ \rightarrow H_2O$) were added? ____

10.16 Buffers and Blood

A **buffer** is a combination of a weak acid or a weak base and one of its salts.

Blood is slightly basic. Its pH, normally 7.4, doesn't vary by more than about one tenth of a pH unit in a healthy person. In maintaining this narrow range of pH through all the stresses of a normal life, the body uses a chemical system known as a **buffer**, which is simply a combination of a weak acid or a weak base and one of its salts. (A salt, you'll recall, is produced by the reaction of an acid and a base.) Le Châtelier's principle, operating through a combination of this sort, effectively keeps the pH within a very narrow range.

The major buffer system of the blood is a combination of carbonic acid and sodium bicarbonate. The presence of a mixture of carbonic acid and the bicarbonate anion, in a stable equilibrium, buffers the blood against changes in pH.

$$H_2CO_3 + H_2O \rightleftarrows H_3O^+ + HCO_3^-$$

It works like this. If the pH of the blood begins to drop, because of disease or some other factor, the concentration of the hydronium ion rises. This places a stress on the equilibrium and brings Le Châtelier's principle into action. In response to the stress, the bicarbonate anion combines with the acid and shifts the equilibrium to the left, thereby decreasing the concentration of the hydronium ion and maintaining a pH of 7.4.

If the reverse occurs and the pH begins to rise, the concentration of the hydronium ion tends to drop and so the equilibrium shifts to the right. Carbonic acid ionizes to restore the pH to its desirable level of pH 7.4.

All this, of course, depends on the body having some means for regulating the blood's supply of carbonic acid. With the blood's carbonic acid concentration rising as the equilibrium shifts to the left and dropping as it shifts to the right, quantities of carbonic acid must be moved into and out of the body. This particular piece of work, the regulation of carbonic acid concentrations, takes place as the blood passes through the lungs, and it operates through an equilibrium we've seen before.

$$H_2CO_3 \rightleftarrows CO_2 + H_2O$$

With an excess of carbonic acid, carbon dioxide passes from the blood into the lungs; with a deficiency the reverse occurs. Once again Le Châtelier's principle comes into play.

The kidneys are also important in regulating pH. They dispose of hydronium ions and maintain the blood's concentration of bicarbonate ions, which should exceed the concentration of carbonic acid in a ratio of about 20:1 for the most effective operation of the buffer.

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 20$$

The story of how the kidneys work, though, lies beyond the scope of this examination of the extraordinary chemistry of ordinary things.

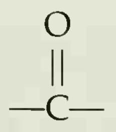
QUESTION

Hyperventilation, which occurs with very rapid and very deep breathing, results in a rapid loss of carbon dioxide from the body through the lungs. What happens to the pH of the blood as the direct result of hyperventilation? Does the pH immediately rise or drop, or does it remain unchanged? Explain your answer. ________________

10.17 Common and Uncommon Acids

Although the lead–acid storage battery (Chapter 6) is the only consumer product containing substantial amounts of sulfuric acid (H_2SO_4), this acid is by far our leading industrial chemical. In terms of raw tonnage produced, about 45 million tons in 1991, it swamps any of its rivals, whether they are acids, bases, or any other kind of chemical. Only a small fraction of all this sulfuric acid goes into storage batteries, though. Most of it ends up as a reactant or a catalyst (Section 8.9) in the manufacture of various consumer products, including pharmaceuticals, plastics, synthetic fibers, and synthetic detergents. More ammonia (over 16 million tons in 1991) is produced than any other base. Much of it goes into the production of agricultural fertilizers and synthetic fibers.

While most of the major industrial acids and bases lack the element carbon, many of the acids that are important to us as individuals and as consumers, and to our environment as well, are organic acids. That is, they are carbon-containing acids (Section 7.1). Of these, a major group consists of the *carboxylic acids*, which are acids characterized by the *carboxyl* structural unit. The carboxyl group itself is a combination of a *carbonyl group* (a carbon doubly bonded to an oxygen) and a *hydroxyl group* (an —OH group). The carboxyl group is often written as —CO_2H for brevity.

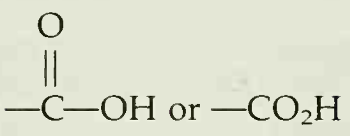


$$-\overset{\overset{\displaystyle O}{\|}}{C}-$$

carbonyl group

—OH

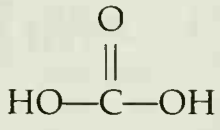
hydroxyl group



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH \text{ or } -CO_2H$$

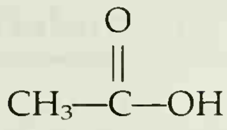
carboxyl group, the structural unit of a carboxylic acid

We've already discussed several carboxylic acids, including carbonic acid, acetic acid, and citric acid:



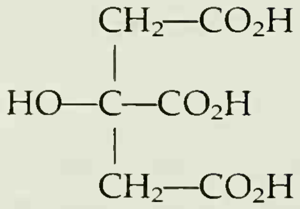
$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

carbonic acid



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

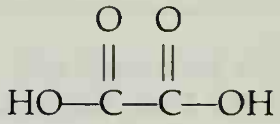
acetic acid



$$\begin{array}{c} CH_2-CO_2H \\ | \\ HO-C-CO_2H \\ | \\ CH_2-CO_2H \end{array}$$

citric acid

Other important carboxylic acids include oxalic acid, propionic acid, butyric acid, benzoic acid, and lactic acid. Oxalic acid is a toxic *dicarboxylic* acid (two carboxyl groups per molecule) that occurs widely in plants, including rhubarb, spinach and sorrel:



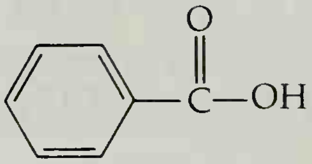
$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

oxalic acid

Although eating pure oxalic acid can be fatal, its concentration in most edible plants is probably too low to present a serious hazard. It's been estimated that an average person would have to eat about 4 kg of spinach at one meal, almost 9 lb of the vegetable, to consume the lowest dose of oxalic acid known to be fatal to a human. Not all parts of all food plants, though, are as innocuous as spinach. For example, only the cooked stalks of rhubarb are ordinarily eaten. The plant's leaves contain such high concentrations of the acid and its salts that even small portions of them can be poisonous, especially to children. Oxalic acid itself is a good rust and stain remover and is used in various commercial cleaning preparations.

Propionic acid, $CH_3{-}CH_2{-}CO_2H$, and butyric acid, $CH_3{-}CH_2{-}CH_2{-}CO_2H$, are important partly for their odors. The characteristic odor of propionic acid contributes to the flavor of Swiss cheese; butyric acid, whose name comes from the Latin *butyrum*, for "butter," gives rancid butter its peculiar odor. Salts of propionic acid, especially the sodium and calcium salts, are added to cheeses and to bread and other baked goods to retard the growth of mold and help preserve freshness.

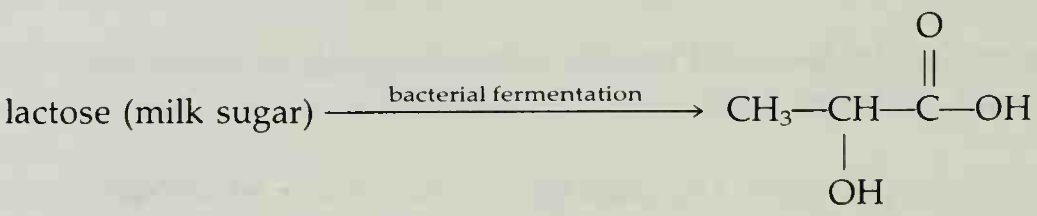
Benzoic acid consists of a carboxyl group bonded directly to a benzene ring:



benzoic acid

To consumers, benzoic acid is less important in itself than as its sodium salt, sodium benzoate (also known as benzoate of soda). This salt is used as a preservative in canned and bottled fruit drinks and also in baked goods.

Lactic acid is the acid that gives sour milk its sharp taste. Bacterial fermentation of *lactose*, the principal sugar of milk, produces the acid:



$$\text{lactose (milk sugar)} \xrightarrow{\text{bacterial fermentation}} \mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{C}H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

lactic acid,
the acid of sour milk

Lactic acid is also important to us in another, more immediate way, in our own bodies. As we'll see in later chapters, our biological energy comes from chemical oxidation of the food we eat. We obtain energy from our nutrients

Figure 10.13

Common acids include the citric acid of limes, lemons, oranges, grapefruit, and citrus juices, the propionic acid of Swiss cheese, and the oxalic acid of rhubarb.

by oxidizing them to carbon dioxide and water, much as we derive energy from the hydrocarbons of gasoline (Chapter 8). Our bodies are far more complex than the internal combustion engine, though. Converting the chemicals of our foods to carbon dioxide and water requires an enormous variety of steps involving a huge assortment of intermediate compounds. For example, as we metabolize glucose (a sugar) through muscular activity, lactic acid is generated in our muscles and is then decomposed into CO_2 and H_2O. With heavy exercise lactic acid forms more rapidly than it can be disposed of. It's this transient accumulation of lactic acid within our muscles that causes an aching, tired sensation of muscles when we use them vigorously. As our body disposes of the lactic acid, the discomfort disappears and we sense a recovery from fatigue.

Figure 10.13 summarizes the occurrences of some representative carboxylic acids and their salts.

QUESTION

Give a specific example of a *tricarboxylic* acid. ______________________________

PERSPECTIVE: The Balancing Act of Health

We began our examination of acids and bases with a demonstration of the effect of the acid we exhale, CO_2, on the dye of red cabbage. Throughout this chapter we have expanded our view to other acids and to bases and to their effects on the world around us. We've examined some of the acids of our foods and the bases of our antacids, and we've seen how the concentrations of acids and bases, expressed as pH, affect our bodies and the planet we live on.

We've seen the importance of the pH range of our stomach fluids to the digestion of protein, and we've seen how the buffer system of our blood regulates its pH. Similarly, we've seen that the health of our planet also depends on a balance between the acids and bases of the environment. Rain, although naturally acidic because of the CO_2 in the atmosphere, can be turned into corrosive acid rain by our societal pollutants, destroying not only our outdoor statues, facades of buildings, and other artwork, but our forests and marine life as well.

Clearly, many of our societal concerns and our activities focus on the chemistry of acids and bases. On the one hand, burning fossil fuels produces the pollution that leads to acid rain. On the other hand, sulfuric acid, our leading industrial chemical, is vital to the production of many of our consumer goods.

The chemistry of our bodies and the chemistry of our society hinge on the reactions of acids and bases. Maintaining and preserving the health of both the internal environment of our bodies and the external environment of the world we live in depend on the chemistry of acids and bases and the preservation of a healthy balance between the two. Understanding our environment and our own bodies requires that we understand the chemistry of acids and bases and their interactions.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

All acids have certain properties in common. When dissolved in water they produce a _______ taste, they turn _______ from blue to red, and they react with metals such as iron and _______ to liberate _______ . Water solutions of _______ , on the other hand, taste _______ , turn litmus from _______ to _______ , and produce a _______ sensation when rubbed between the fingers. As long as we are dealing with water solutions of these substances, we can use the _______ definition of an acid and a base, which states that an acid is anything that releases a _______ in water, while a base is anything that releases a _______ . The _______ definition eliminates the need for water in the definition by defining acid–base reactions in terms of a _______ from an acid to a base, regardless of solvent. A third definition, the _______ definition, treats an acid–base reaction in terms of the donation of an _______ from a base to an acid.

Regardless of definitions, any and all protons released by acids in water react rapidly with water molecules to generate _______ ions. The concentration of these ions is a measure of the acidic strength of the solution. One convenient measure of this concentration is the _______ of the solution, which has a value of 7 at neutrality, is _______ than 7 in acidic solutions, and is _______ than 7 in basic solutions.

Arrhenius
bases
bitter
blue
Brønsted–Lowry
electron pair
greater
hydrogen gas
hydronium
hydroxide ion
Lewis
litmus
pH
proton
proton transfer
red
slippery
smaller
sour
zinc

2. Define or identify each of the following:

a. acid–base buffer
b. antacid
c. anthocyanin
d. carboxylic acid
e. Le Châtelier's principle
f. neutralization
g. pepsin
h. a salt

3. What are the acids of the cabbage breath test demonstration that opened this chapter? What base is used in that demonstration?

4. What is indicated by (a) a red color of litmus? (b) a red color of phenolphthalein?

5. What color, red or blue, would you expect each of the following to produce when added to litmus: (a) milk of magnesia, (b) wine, (c) seawater, (d) a soft drink, (e) tomato juice?

6. Match the following:

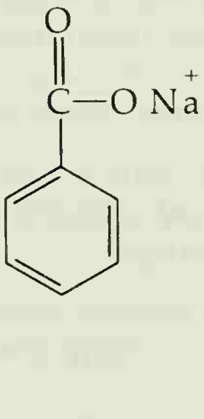
7 a. acetic acid
8 b. benzoic acid
3 c. butyric acid
9 d. carbonic acid
5 e. citric acid
4 f. hydrochloric acid
2 g. lactic acid
6 h. oxalic acid
11 i. propionic acid
10 j. sodium bicarbonate
1 k. water

1. amphoteric
2. formed as milk turns sour
3. found in rancid butter
4. ionizes completely in water
5. gives lemons a sour taste
6. occurs in spinach and rhubarb
7. the major acid of vinegar
8. contains a carboxyl group bonded directly to a benzene ring
9. decomposes to carbon dioxide and water
10. the basic component of the major buffer system in blood
11. forms in cheese; its calcium salt is used as a preservative in baked goods

7. Identify each of the following as an acid, a base, or a salt, give its chemical name (if it is shown as a chemical formula or structure); name a consumer product in which it occurs; and, if possible, describe its function in that product:

a. $Al(OH)_3$
b. $CaCO_3$
c. CH_3CO_2H
d. H_2SO_4
e. HCl
f. KI
g. $Mg(OH)_2$
h. $MgSO_4$
i. NaF
j. $NaHCO_3$
k. NaOH

l. NH_3
m. phenolphthalein
n.



8. Define a *salt* in terms of acids and bases.

9. Suppose the nucleus of a hydrogen atom enters a quantity of water. What is the nucleus of the hydrogen atom transformed into by the water?

10. What do we mean when we say that water is *amphoteric*?

11. What human activity is the principal cause of "acid rain"?

12. Assuming that the activity in Exercise 11 were to end, explain (a) why rainfall would still be acidic and (b) why rainfall would still be found with a pH *below* 5.6.

13. Give the names and molecular formulas of *three* acids found in acid rain.

14. *Phenolphthalein* is useful as an acid–base indicator. What is another use for this chemical?

15. What gas is formed when you drop an Alka-Seltzer tablet into water? Write the chemical reaction that takes place.

16. Name six acids that occur, as the acids themselves or as their salts, in substances we normally eat or drink and the name the food or drink that contains each.

17. What connection is there between sour milk and tired muscles?

18. What characteristic of molecular structure is common to all carboxylic acids?

19. Give the names of two carboxylic acids that can be found in the human body.

20. What's the difference between a weak acid and a strong acid? Give an example of each.

21. Write the chemical reaction for the generation of fizz or foam when you squeeze lemon juice into water containing dissolved baking soda.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

22. Suppose you prepare a solution by dissolving 1 mol of pure HCl gas in 100 liters of water. (Recall that HCl ionizes completely in water.) What is (a) the molarity of H_3O^+ in this solution? (b) The pH of this solution?

23. Suppose you prepare a solution by dissolving 1 mol of pure NaOH in 100 liters of water. (NaOH ionizes completely in water.) What is (a) the molarity of OH^- in this solution? (b) The molarity of H_3O^+ in this solution? (c) The pH of this solution?

24. What is (a) the pH of a solution in which $[H_3O^+]$ is 0.0001 *M*? (b) The pH of a solution in which $[H_3O^+]$ is 0.0000000001 *M*? (c) The pH of neutral water? (d) The molarity of $[H_3O^+]$ in a solution whose pH is 3?

25. Can the pH of water be: (a) greater than 14? (b) Negative? Explain.

26. K_a for acetic acid is 1.8×10^{-5}. If the pH of a solution of acetic acid and sodium acetate in water is 4, and the concentration of the acetic acid is 1.0 *M*, what is the concentration of the sodium acetate in equilibrium with the acetic acid?

27. The value of the ionization constant, for an acid, K_a can be determined experimentally by preparing a solution in which the molar concentration of the anion generated by the ionization of the acid and the concentration of the molecular, unionized acid itself are equal to each other. With these two concentrations equal, the numerical value of $[H_3O^+]$ is the same as K_a. Using the ionization of acetic acid show that this is true. You may wish to use actual values, such as 0.1 *M*, for the concentrations of the un-ionized acetic acid and the acetate anion.

28. When HCl dissolves in water, all of the HCl molecules ionize to produce H^+ and Cl^-. There are no covalent molecules of HCl in the solution. Given this situation and the definition of the K_a of an acid, what can you say about the value of K_a for HCl?

29. How many liters of 0.1 *M* NaOH solution does it take to neutralize (a) 1 liter of 0.1 *M* HCl? (b) 0.5 liter of 0.2 *M* HCl? (c) 3 liters of 0.01 *M* HCl?

30. How many liters of 0.5 M HCl solution does it take to neutralize (a) 0.5 liter of 0.1 *M* NaOH? (b) 1 liter of 0.5 *M* NaOH? (c) 0.1 liter of 2 *M* NaOH?

THINK, SPECULATE, REFLECT AND PONDER

31. Why is it so much more convenient to express acidities in terms of pH rather than in terms of the molarity of the hydrogen ion?

32. Sodium cyanide, NaCN, is a highly toxic salt that's handled in the form of pellets. It is sometimes used to generate the lethal gas hydrogen cyanide, HCN, in exterminating rats and insects in large buildings. Write a reaction for the production of HCN by dropping pellets of NaCN into a solution of hydrochloric acid.

33. For each of the following sets, pick the single compound that doesn't belong with the others. Explain your choice in each case.

1. (a) HCl, (b) $CH_3—CO_2H$, (c) H_2CO_3, (d) NH_3, (e) H_2SO_4
2. (a) acetic acid, (b) benzoic acid, (c) nitric acid, (d) lactic acid, (e) propionic acid

34. If you cover several galvanized nails with vinegar you will soon see small bubbles of gas forming on the nails and rising to the surface of the vinegar. Why? (See Chapter 6 for a discussion of galvanized nails.) Describe the chemical reactions taking place. Why could this be a hazardous thing to do? Would you expect the same result if you used iron nails that are not galvanized? Would you expect the same result if you used lemon juice instead of vinegar? Explain your answers.

35. Describe how you might prepare strips of acid–base indicator paper (which could be used in much the same way as litmus paper) from a common material available to you in drugstores and supermarkets.

36. Many acid–base indicators change color as a result of changes in their molecular structure as the pH of a solution changes. Some change color as a result of structural changes brought on as the molecule acquires a proton, H^+, with a drop in pH. To what general class of compounds do such indicators belong?

37. What would happen if someone used an antacid that *completely* neutralized the acid of stomach fluids?

38. Write the reaction of the carbonic acid–sodium bicarbonate buffer that is responsible for maintaining the pH at 7.4 when (a) an excess of *base* enters the blood and (b) an excess of *acid* enters the blood.

39. In addition to the $H_2CO_3/NaHCO_3$ buffer system, another buffer exists in the blood, the NaH_2PO_4/Na_2HPO_4 system. Recognizing that NaH_2PO_4 is the more acidic of these two components, and that Na_2HPO_4 is the more basic component, write a chemical reaction that shows how this system changes as the blood becomes more acidic than pH 7.4. Write a reaction that shows how it changes as the blood becomes more basic.

40. *Malonic acid*, with a molecular formula $C_3H_4O_4$, is a *dicarboxylic* acid containing three carbons. Draw its structural formula.

41. Natural gas consists almost entirely of pure hydrocarbons. Explain why the use of natural gas as

a fuel is less likely to lead to acid rain than the use of other fossil fuels, such as petroleum.

42. How would you respond to the suggestion that we spray solutions of concentrated ammonia into the atmosphere to counteract the effects of acid rain?

43. Some people claim that since *all* rain is acidic, the use of the term *acid rain* is misleading. What is your response to this?

44. Some chemical principles have their counterparts in social activities as well as in the chemical laboratory. Describe the operation of Le Châtelier's principle (or something closely resembling it) in a social situation.

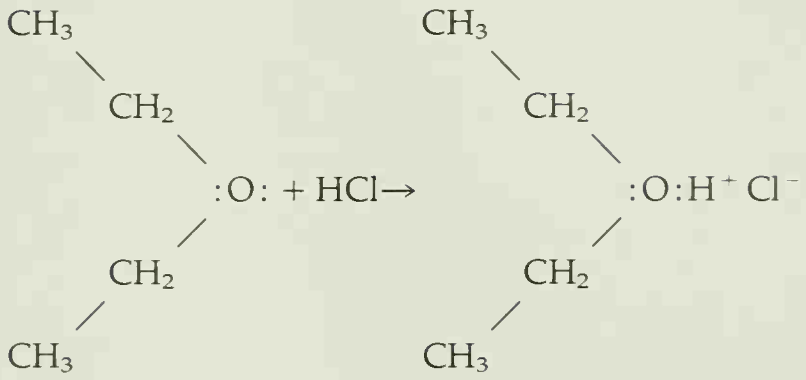
45. "An acid cannot exist in the absence of a base." Is this statement true or false? Explain your answer.

46. The term *litmus test* is sometimes used in describing a political issue that, in itself alone, can determine a voter's support for a candidate. Give several examples of "litmus test" issues that can, in themselves, determine a voter's choice of candidates.

47. Give a phenomenological definition of something you are familiar with outside the realm of chemistry.

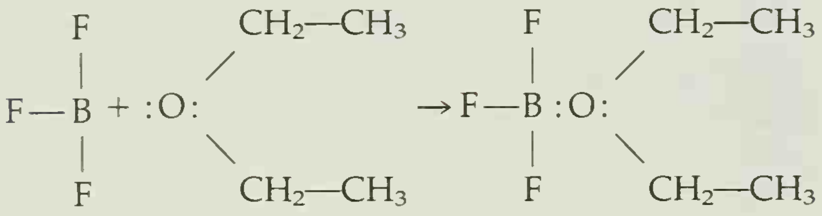
48. Which definition of an acid *cannot* be used to explain the formation of NH_4Cl when ammonia gas and hydrogen chloride gas react in dry air to form ammonium chloride?

49. Hydrochloric acid dissolves in *diethyl ether* according to the equation



Would you classify diethyl ether as an Arrhenius base, a Brønsted–Lowry base, or a Lewis base? Justify your choice.

50. The following is the chemical equation for the reaction of boron trifluoride with diethyl ether to form a complex of the two molecules. The reaction can be considered to be an acid–base neutralization. Identify both the acid and the base in the equation. Which definition of acids and bases is the best to use for this reaction?

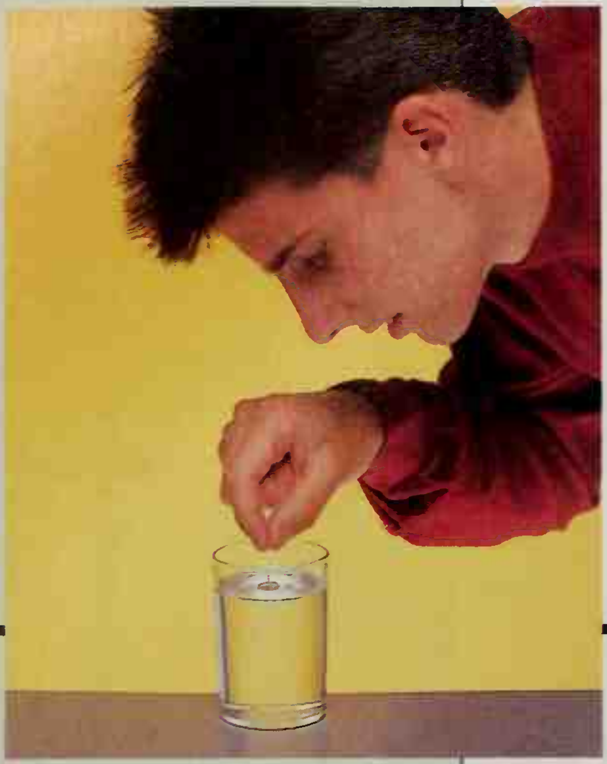


Solids, Liquids, and Surfaces

11

DETERGENTS: CLEANING UP WITH CHEMISTRY

An insect supported by the surface tension of water.



With Nerves as Steady as a Chemical Bond

Here's another piece of chemical magic. Unlike the cabbage breath test, this one requires a little advance preparation. You begin by "floating" a thumbtack on the surface of a glass of cold water. We know, of course, that thumbtacks don't actually float on water, but there's an old parlor stunt in which you place a thumbtack, or some other small metal object like a needle or a paper clip, *very gently* on the surface of a glass of water. Instead of sinking, it seems to float. Actually the metal isn't floating at all; it's resting on the water's surface, held up by a chemical phenomenon known as *surface tension*. We'll have more to say about surface tension later, but for now the key to this feat lies in placing the thumbtack *gently* onto the surface. If you have trouble with this step you can use a loop of fine wire shaped as shown in Figure 11.1.

Now challenge someone to duplicate what you're about to do next. Announce that you are about to poke the end of a toothpick into the water so

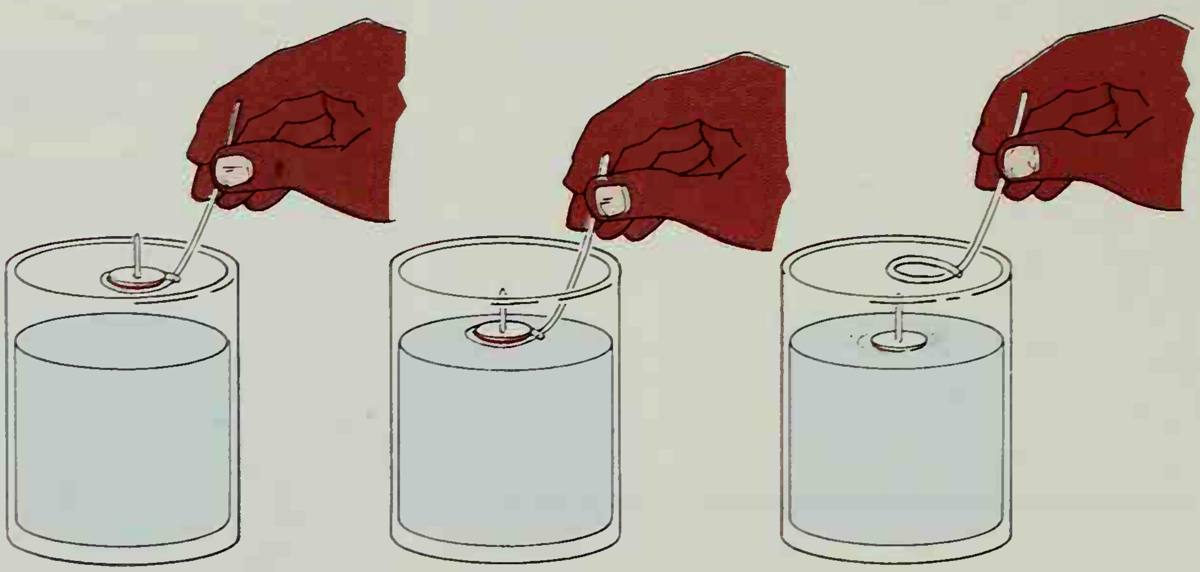


Figure 11.1
"Floating" a tack on water.

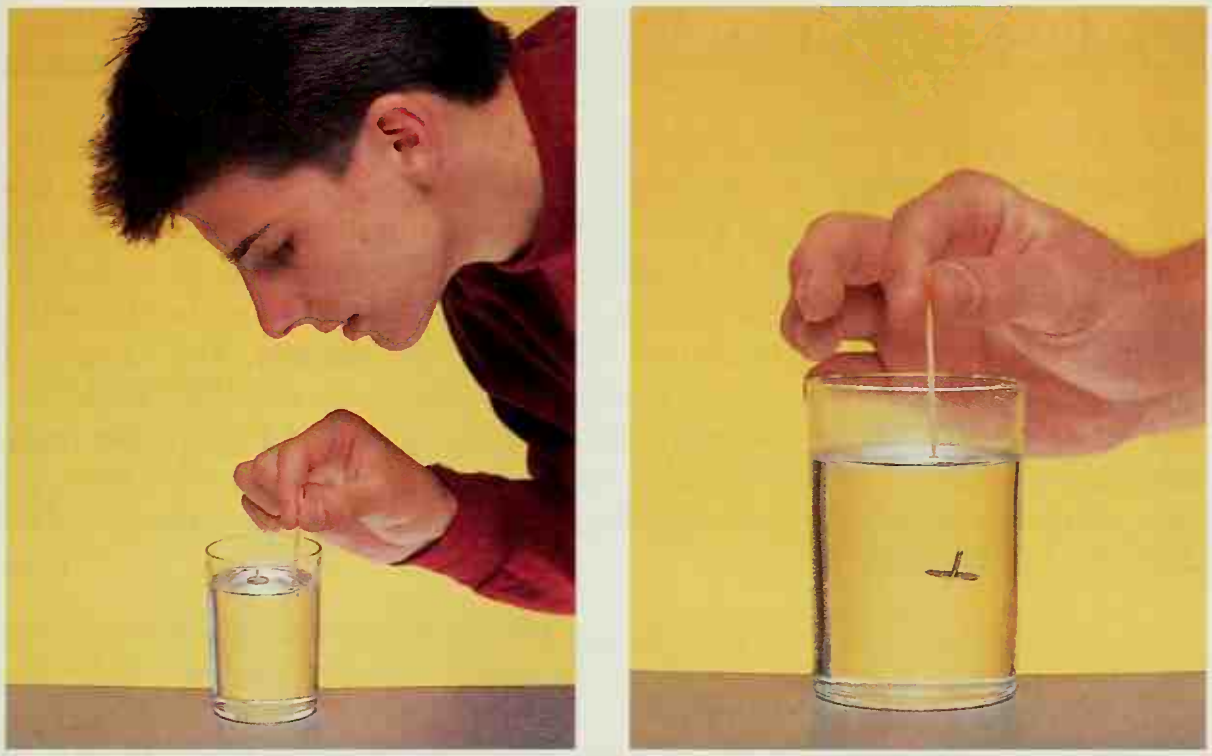


Figure 11.2

Place a tack on the surface of a glass of water. The tack remains on the water's surface as you gently push a toothpick into the water. The tack drops as soon as someone else pushes the toothpick through the water's surface, no matter how gently. The secret lies in the chemistry of liquids, surfaces, and detergents.

incredibly carefully—with nerves as steady as a chemical bond—that the thumbtack will remain undisturbed on the surface. The challenge is to push the toothpick into the water repeatedly, but so gently that the tack doesn't plummet to the bottom.

Push the toothpick ever so gently through the surface about midway between the tack and the edge of the glass. With a little practice you'll be able to do this easily without sinking the tack. A cylindrical toothpick, tapered to a point at each end, is better for this stunt than one of those flat toothpicks, broad at one end and narrow at the other.

Now give the toothpick to your friend. With the first stab into the water, no matter how gentle, the tack plummets to the bottom of the glass. The secret of the stunt lies in a twist of chemistry. Better yet, it lies in a twist of the toothpick.

To make the magic work, secretly coat one end of the toothpick with a drop of a colorless liquid detergent just before you begin the proceedings. *You* poke the *dry* end of the toothpick into the water, but as you hand it to your challenger you invert the toothpick (unobserved) so that your friend sticks the detergent-coated end into the water.

Rotating the toothpick as you pass it over takes a little sleight of hand and a bit of practice, but it's really the chemistry that does the job. Just as soon as the detergent touches the water, the tack drops sharply to the bottom of the glass. Figure 11.2 describes it all. (Using a toothpick whose ends have identical shapes decreases very slightly the likelihood of discovery. That's why the symmetrical toothpicks are a bit better for this stunt.)

11.1 Density, and How Insects Walk on Water

The **density** of a substance is its mass per unit volume. Density is stated in units of grams per milliliter or grams per cubic centimeter.

The real magic lies in the chemistry of surface tension and in the chemistry of soaps and detergents. If you've ever seen an insect skimming across the surface of a puddle or pond, you've seen surface tension in action. To understand the effects of surface tension—how it allows insects to walk over water and tacks to rest on its surface—we'll look first at a few fundamental definitions and properties of matter. We begin with **density**. The density of any substance is simply its mass per unit of volume. In scientific work, the accepted units of density are grams per milliliter (g/mL) and grams per cubic centimeter (g/cm^3). Since a milliliter is the same as a cubic centimeter, the two measures of density are equivalent and interchangeable. We calculate densities by the formula

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

(An easy way to determine the volume of an irregularly shaped object is to immerse it in water and determine the volume of water it displaces. Naturally, if the object can be damaged by water some other technique must be used.)

EXAMPLE STATUESQUE DENSITY

A small statue has a mass of 99 g and a volume of 45 cm^3. What is the density of the statue?

To find density, we divide mass by volume. In this case

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

$$\text{density} = \frac{99\ \text{g}}{45\ \text{cm}^3} = 2.2\ \text{g/cm}^3$$

The density of the statue is 2.2 g/cm^3.

Be sure that you recognize the difference between the *weight* of an object and its *density*. We sometimes think of lead, for example, as a heavy metal. But what we really mean is that it's dense. A single lead fishing sinker weighs only a few grams and is small enough to be held in your hand. A huge tree, though, can be heavy enough to crush a house if the tree falls in a storm. While the single tree is certainly much heavier than the sinker, the tree is nonetheless far less dense than the sinker. The key here is that one cubic centimeter of the sinker (lead) is heavier than the same volume, one cubic centimeter, of the tree (wood). Lead is more dense than wood, but small things made of lead can weigh less than large things made of wood. Densities of some typical solid substances appear in Table 11.1.

TABLE 11.1 Average Densities of Typical Solids

Substance	Density (g/mL or g/cm^3)
Aluminum	2.7
Cork	0.2
Diamond	3.5
Glass (common)	2.6
Gold	19.3
Ice	0.9
Lead	11.4
Pyrite, a worthless mineral called "fool's gold" and easily mistaken for gold	5.0
Quartz	2.6
Sodium chloride (as rock salt)	2.2
Sucrose	1.6
Wax (candles, paraffin)	0.9
Wood (average values)	
Balsa	0.1
Birch	0.6
Maple	0.7
Oak	0.8
Teak	0.9

Our standard for density is water, which we define as having a density of exactly 1 g/mL. Anything that's less dense than water—wood for example—floats; anything that's more dense—lead—sinks. That's why trees float in water but lead weights sink. Drop a nickel into a glass of water or a concrete block into Lake Erie and it sinks to the bottom. Metals and concrete are more dense than water—they weigh more than the volume of water they displace—and so they sink. Anything that weighs less than the volume of the water it displaces floats. Fats and oils float because they're intrinsically less dense than water. Boats float because the air trapped inside their hulls gives them an average density less than water's. Empty buckets float for the same reason. Some brands of bar soap, Ivory for example, float because of an enormous number of microscopic bubbles of air whipped into them as they're manufactured. Ducks float because a film of oil on the surface of their feathers traps plenty of air next to their bodies (Fig. 11.3).

But the tack you've been using *doesn't* float. The metal tack is denser than water and there's no trapped air to give it buoyancy. The tack is supported in a small dent on the water's surface, held up by the same phenomenon that supports an insect's feet as it walks across a pond: surface tension (see Chapter Opener photo). Surface tension supports the insect and the tack because water's surface—the surface of any liquid for that matter—behaves

Figure 11.3
Ducks float on water, supported by the buoyancy of air trapped by their feathers. Water's surface tension prevents it from penetrating the oily layer of their feathers and displacing the air.

a little differently from the bulk of its interior. To understand what this difference is and why it exists, we'll examine briefly some of the properties of solids, liquids and gases.

QUESTION

While exploring a remote area, you find a large, yellow nugget lying on the ground. The nugget looks like gold, yet you suspect it may be *pyrite*, a virtually worthless yellow mineral sometimes called "fool's gold" because it's so often mistaken for the real thing. You find that the nugget weighs 50 g and displaces 2.6 mL of water. Is it more likely to be fool's gold or the real thing? (Refer to Table 11.1 in your answer.)

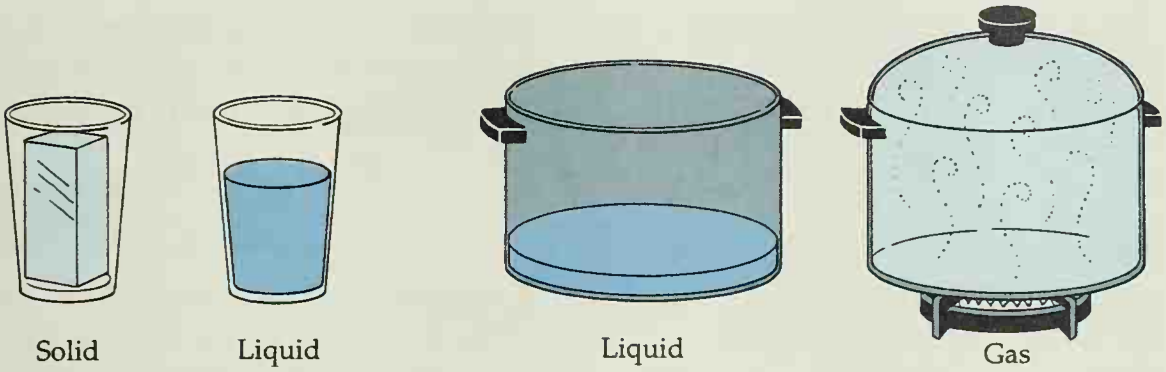
11.2 Solids, Liquids, and Gases

Solids, liquids and gases are three states or phases of matter. **Solids** maintain their own volumes and shapes. **Liquids** maintain their own volumes but takes the shapes of their containers. **Gases** take both the volumes and shapes of their containers.

All material substances of our everyday world exist in one of three states or phases of matter: **solids, liquids, and gases**. Solids have distinct, fixed volumes and well defined shapes. A piece of ice is a solid. It occupies a specific amount of space and it holds its own shape. It might have the form of an ice cube we get from a freezer tray, or it might be one of the irregular chunks of ice we find in bags of ice from supermarkets or convenience stores.

Liquids, too, occupy fixed volumes, but liquids have no shapes of their own. Except for small droplets that tend to become spheres, liquids always take the shape of whatever container they're held in. When a piece of ice melts, the liquid water that forms takes the shape of the container. Gases, on the other hand, always acquire both the shape and the volume of their container (Fig. 11.4). When we boil water the liquid water becomes a gas, which we call steam if it's freshly formed from the boiling water. More generally it's known as water vapor, especially if it is cooler than steam and part of a humid atmosphere. Steam or water vapor has no shape or size of its own, but it takes both the shape and size of whatever container holds it.

We can change a substance from a solid to a liquid and then to a gas simply by heating it. Heat an ice cube and it melts. Heat water and it boils. In the reverse direction, cooling converts a gas to a liquid and then to a solid. Steam condenses to liquid water as it cools, as we saw in the demonstration that



An ice cube in a glass retains its own shape and volume. When the ice cube melts, the liquid water retains its own volume, but takes the shape of the glass.

Poured into a pot, the water retains its volume, but now takes the shape of the pot. As it is boiled, the steam acquires both the shape and the volume of the pot.

Figure 11.4
Solid, liquid, gas.

opened Chapter 8. Place trays filled with liquid water in a freezer and you get ice cubes. Whether an element or a compound exists as a solid, a liquid, or a gas depends principally on its temperature.

(Often substances become transformed from one state to another when we heat them because they decompose or take part in chemical reactions with other elements or compounds, rather than because of melting or boiling. Hold a match to the bottom of a wax candle and you'll find that the solid hydrocarbons of the paraffin wax melt to a liquid, then harden again when you remove the match and allow them to cool. They have melted and then resolidified, remaining the same compounds throughout. But hold the match to the wick, as we did in the opening demonstration for Chapter 7, and the hydrocarbons vaporize, mix with the atmosphere, and react chemically with oxygen to produce carbon dioxide and water. When we refer to the effects of heat in this chapter we're assuming that no chemical reaction takes place and that subsequent cooling gives us the same substance we started with.)

QUESTION

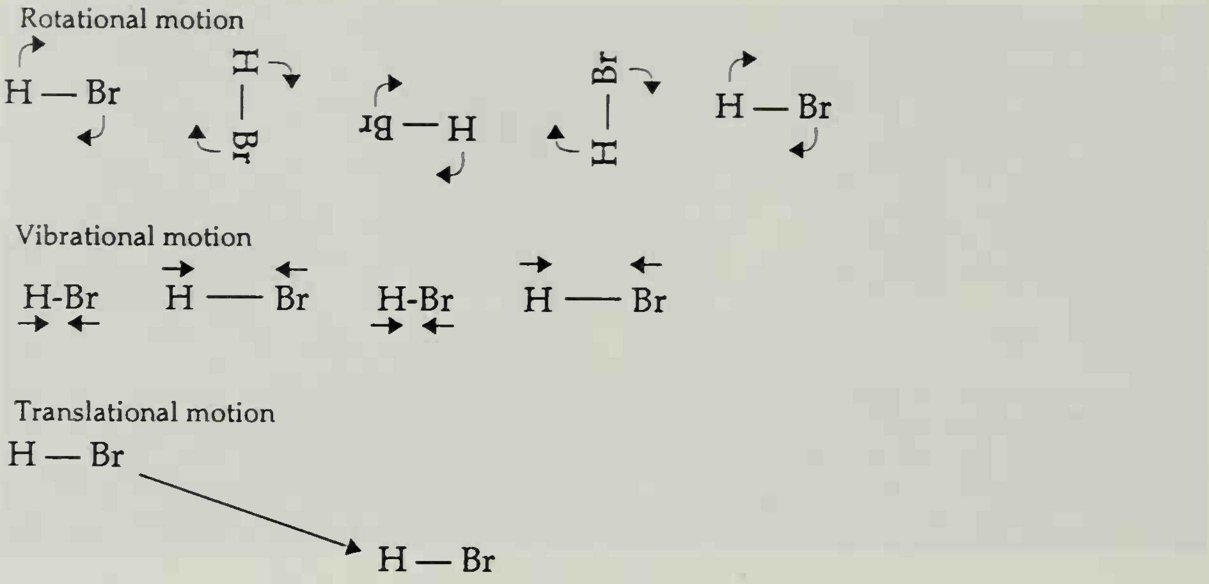
Which of the three states of matter—solids, liquids or gases— (a) maintain their own volumes, no matter what container holds them? (b) Maintain their own shapes, no matter what container holds them? ______________________________

11.3 What Happens When Liquids Boil

We can melt ice and boil water by heating each of them. Heat is a form of energy. When we heat anything we add energy to it, increasing the average kinetic energy (Section 8.4) of all of its chemical particles. Heating an ice cube or a pot of water, or even steam, for example, increases the average kinetic energy of all of its H_2O molecules. This illustrates one of the more fundamental rules of chemistry and physics: *The average kinetic energy of the chemical particles of any substance depends directly on its temperature.* The higher the temperature of anything, the greater the average energy of its atoms, ions, or molecules.

Each ion or molecule made up of two or more atoms expresses its energy in several different ways simultaneously by

Figure 11.5
Three modes of molecular motion.

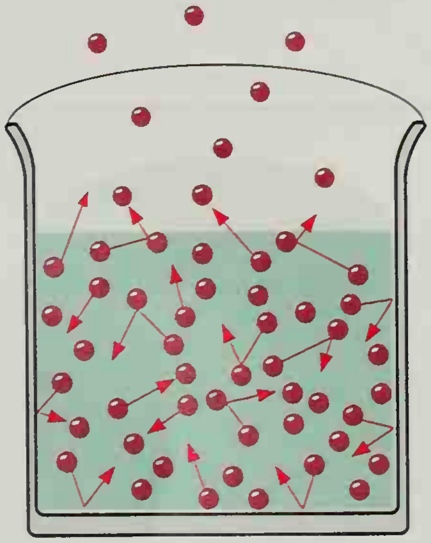


- rotating around its center of mass (equivalent to a body's center of gravity) with an energy called *rotational energy,*
- vibrating, with no change in the location of its center of mass, with an energy called *vibrational energy,* and
- moving from one location to another with an energy known as *translational energy.*

Figure 11.5 illustrates these three processes. The higher the temperature, the higher the average kinetic energy of the particle and the more vigorous are its rotational, vibrational, and translational motions.

In the range of energies of interest to us in this chapter, the average translational energy of a liquid's molecules is relatively small. It's smaller, at any rate, than the energy of the cohesive forces, the forces of attraction that hold the molecules close to each other and that keep them in the liquid state. If those cohesive forces were to disappear completely, the translational forces would tear the molecules away from each other and we would have a gas instead of a liquid.

Figure 11.6
Liquids evaporate as molecules with high translational energies escape from the liquid into the vapor.



As the particles move about in the liquid mass, then, they remain near enough to their neighbors to persist as a liquid. With a relatively low translational energy (which tends, however weakly, to tear them away from each other) and a relatively high energy of cohesion (which succeeds in holding them close together), the molecules remain trapped, for the most part, in the form of a liquid.

We say "for the most part" because while the *average* translational energy is too low to convert the entire bulk of the liquid into a gas, a few of the particles have energies far lower than average and a few have energies far higher than average. These few with the exceptionally high translational energies overcome the cohesive forces and escape into the vapor state in the process we call *evaporation* (Fig. 11.6).

When the temperature of the entire liquid reaches the boiling point, *all* the chemical species have translational energies high enough to escape the pull of their neighbors and so all the particles escape into the vapor phase. As this happens simultaneously throughout the entire bulk of the liquid, we see it boil. Chemical particles in the gaseous state have translational energies far higher than the forces that would bind them to their neighbors and so they move about freely, virtually independent of each other.

QUESTION

What are the three kinds of kinetic energy a molecule can exhibit? Which one of these three resembles a ballet dancer twirling about in one spot on the stage? Which one resembles the energy of a sprinting runner? Which one is analogous to the energy you expend while your chest expands and contracts as you breathe, yet you remain standing in one place? ____________________

11.4 What Happens When Solids Melt

Solids melt to liquids by a similar process, also involving an increase in the translational energies of their atoms, ions, or molecules. Solids keep their own shapes because the translational energies of their particles are especially small, too small to tear them out of a rigid order fixed by the cohesive forces. In crystalline solids, such as sodium chloride, sucrose, and ice, the particles remain firmly fixed next to each other in the orderly arrangement of the crystalline lattice, unable to move about within the bulk of the material. In crystals of sodium chloride and of sucrose, the movements of the particles are limited to small vibrations about their fixed positions in the crystalline lattice (Fig. 3.4).

When you heat a solid, though, it absorbs energy. Heat it to a temperature that's high enough and the movements of its particles become sufficiently vigorous to tear them away from their neighbors and out of their lattice positions. As they move out of the lattice and begin to move about freely within the bulk of the material, we observe that the solid begins to melt to a liquid.

As a pure, crystalline solid melts, all the added energy goes toward giving the particles greater freedom of movement rather than toward increasing the temperature. This specific temperature at which a pure solid melts to a liquid, or a liquid becomes a solid as it cools, is the substance's **melting point** (Fig. 11.7). Substances like fats and some plastics aren't crystalline materials. Instead of melting at sharply defined temperatures, they soften gradually to liquids. Without the rigor of fixed positions in a crystal lattice, the molecules of these *amorphous* solids (meaning "without form or shape") can move about more and more freely as the temperature increases.

A **melting point** is the temperature at which a solid becomes a liquid. The liquid returns to the solid state at this same temperature.

The temperature at which a liquid is transformed into a gas, or a gas into a liquid, is the material's **boiling point**. Since boiling points are particularly sensitive to changes in the external pressure, they're usually reported as temperatures at normal atmospheric pressure. Table 11.2 presents the melting points and boiling points of some common chemicals.

A **boiling point** is the temperature at which a liquid becomes a gas, and the gas becomes a liquid, usually at normal atmospheric pressure.

(The particles of some substances move directly from the solid state to the gaseous state without passing through a liquid state in a process called **sublimation**. At normal atmospheric pressure solid carbon dioxide, Dry Ice, sublimes directly to gaseous carbon dioxide.)

Sublimation occurs when a solid becomes a gas without first passing through the liquid state.

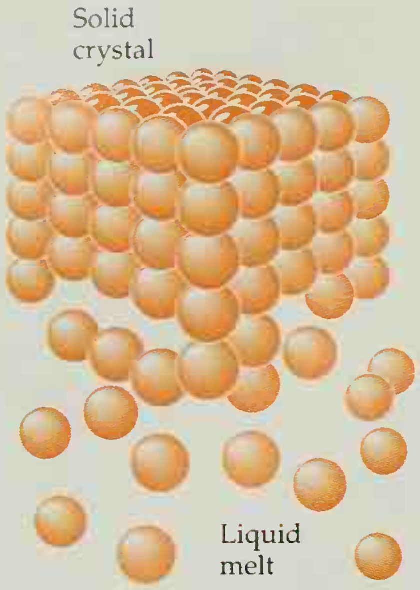


Figure 11.7
At its melting point, the chemical particles of a crystalline solid leave the orderly lattice and achieve a greater freedom of movement in the liquid melt.

C 0° - 100°
F 32° 212°
Melt Boiling

TABLE 11.2 Melting Points and Boiling Points of Typical Substances

Substance	Common Source or Use	Melting Point (°C)	Boiling Point (°C, atmospheric pressure)
Acetic acid	Vinegar	16.6	118
Ammonia	Household cleaner	−78	−33
Benzene	Gasoline hydrocarbon	5.5	80
Citric acid	Citrus fruit	153	(Decomposes)
Ethyl acetate	Food flavoring, solvent	−83.6	77
Ethyl alcohol	Beer, wine, liquors	−117	78.5
Gold	Coins, jewelry	1064	3080
Hydrogen chloride	Muriatic acid	−115	−85
Oxygen	Atmosphere	−218	−183
Potassium iodide	Iodized salt	681	1330
Propane	Fuel for grills	−190	−42
Sodium chloride	Table salt	801	1413
Sodium hydroxide	Lye	318	1390
Sucrose	Table sugar	185	(Decomposes)
Toluene	Paint remover	−95	110.6
Water	Water	0	100

QUESTION

As shown in Table 11.2, sodium chloride and potassium iodide boil at much higher temperatures than do water, ethyl alcohol, and propane. What kind of bonding, covalent or ionic, occurs in each of these compounds? What do these boiling points indicate about the relative strengths of the forces of attraction between ions of ionic compounds and between molecules of covalent compounds? ______________

11.5 Surface Tension

Now, with a knowledge of some of the forces at work in solids, gases, and especially liquids, we can turn to the origin of the surface tension that keeps the tack on top of the water. Since the water in the glass is well below its boiling point, virtually all the water molecules exert relatively large forces of attraction on all their neighboring molecules—those to their sides, in front and behind, and above and below. Throughout the bulk of the liquid the total force of attraction exerted by any one water molecule on all its neighbors is dispersed spherically, in all directions.

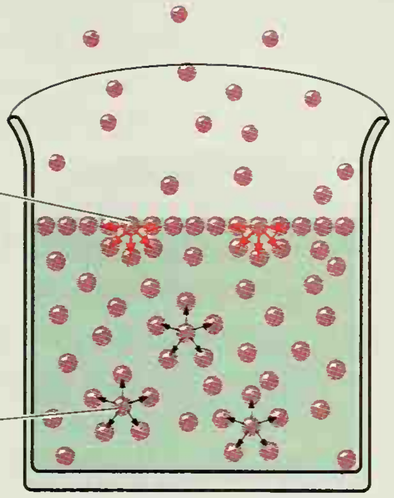


Figure 11.8
The origin of surface tension.

At the water's surface, though, things are different. Above the surface there exist only occasional molecules of the gases of the air and the very few water molecules that have escaped by evaporation. The only nearby water molecules are below and to the sides of those at the surface. At the surface, then, the forces of attraction become focused toward the sides and downward. This particularly strong attraction of the surface molecules for each other and for the molecules immediately below them results in the cohesion of the surface that we call surface tension and that keeps bugs and tacks and other dense but lightweight things from sinking (Fig. 11.8). It's the same phenomenon that allows you to fill a glass to its brim, and then add even more water until the surface of the water bulges up above the rim of the glass.

As your friend pokes the toothpick into the water the small bit of detergent on its tip lowers the surface tension sharply and the tack drops to the bottom. Now we'll examine the connection between the detergent's molecular structure and its effect on surface tension.

QUESTION

Would you expect the surface tension of cold water to be greater than the surface tension of hot water? Explain your answer. ____________________

11.6 Soaps, Detergents, and Surfactants

Detergent comes from the Latin *dētergēre*, meaning "to wipe off" or "to clean." A detergent is anything that cleans, especially if it removes oily or greasy dirt. To see how detergents work, we'll look first at one particular kind of detergent, a soap. Soaps are detergents in the sense that they help clean oily and greasy dirt from fabrics, metals, our skin and hair, and the like. But soaps make up a very narrow class of detergents. We restrict the term *soap* to the *sodium (or, less often, potassium) salts of long-chain carboxylic acids*. As we saw in Section 10.17, a carboxylic acid is marked by the presence of a carboxyl group, —CO_2H. With the anion of the carboxyl group balanced by a sodium cation and tied by a covalent bond to a long chain of —CH_2— groups that terminate in a CH_3— group, we have a soap molecule. Sodium palmitate, the sodium salt of palmitic acid, is a typical soap. (It's a salt in the same sense that NaCl, KI, $MgSO_4$, and $CaCO_3$ are salts; see Section 10.2.)

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$$

or

$$CH_3—(CH_2)_{14}—CO_2H$$

palmitic acid

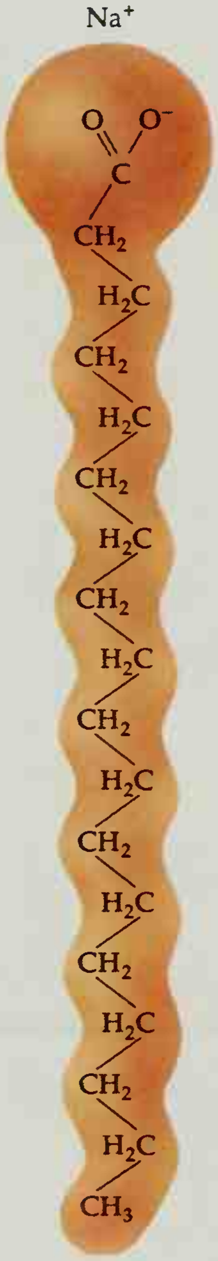
$$CH_3—(CH_2)_{14}—CO_2^- \ {}^+Na$$

sodium palmitate, a soap

Figure 11.9
A typical soap molecule.

Hydrophilic head shuns hydrocarbon-like substances but is attracted to water molecules

Anionic portion of molecule



Hydrophobic tail shuns water but is attracted to oily, greasy, hydrocarbon-like substances

With sodium palmitate serving as a specific illustration, we can generalize the molecular structure of a soap molecule as

$$CH_3—(CH_2)_n—CO_2—\ Na^+$$

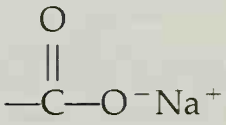
where the subscript $_n$ represents an even number, usually ranging from 8 to 16. (The entire carbon chain, including both the methyl carbon and the carboxylate carbon, runs from 10 to 18 carbons.) With this structure a soap molecule possesses two opposing chemical tendencies.

On the one hand, the long chain of methylene groups that ends in the methyl group

$$CH_3—(CH_2)_n—$$

resembles quite closely the long chains of the hydrocarbon molecules of Chapter 7. Like the molecules of gasoline and mineral oil, this part of the soap molecule tends to dissolve readily in materials that are or that resemble hydrocarbons, but not in water. All these long chains of —CH_2— groups of soaps and of hydrocarbons and hydrocarbon-like materials intermingle easily, but they don't mix readily with the H_2O molecules of water.

The other end of the molecule, though, is ionic.



$$—\overset{\overset{\displaystyle O}{\|}}{C}—O^-Na^+$$

Like sodium chloride and other ionic compounds, that ionic end tends to dissolve in water, but not in hydrocarbon solvents. As a result, we have here something resembling a chemical schizophrenia. One molecule has two opposite and contradictory tendencies. Part of it, a *hydrophilic* structure, is attracted toward water molecules but shuns hydrocarbons and other oily and greasy substances; the other part, a *hydrophobic* structure, shuns water but is attracted toward those very oily, greasy substances that repel the hydrophilic part (Fig. 11.9). With its long chain of —CH_2— groups, this hydrophobic portion of the soap molecule follows the old adage that oil and water don't mix.

All detergent molecules, like those of soaps, consist of a hydrophilic portion and a hydrophobic portion. When they enter water, detergent molecules head for the single location where both tendencies can be accommodated, the surface. There the hydrophilic end of the molecule becomes comfortably embedded among the water molecules that make up the surface while the hydrophobic tail sticks up, out of the water. As shown in Figure 11.10, the detergent molecules become interspersed among the molecules at the water's surface. In disrupting this tightly knit layer of molecules, the detergent lowers the strong attractive forces that the surface water molecules normally exert on each other and so lowers the surface tension. This is why the tack drops when the toothpick introduces the detergent into the water.

Soap, detergents, and any other substances that accumulate at surfaces and change their properties sharply, especially by lowering the surface tension, are *surface-active agents* or, more briefly, *surfactants*. Substances other than surfactants can also change surface tension, but not nearly as effectively as surfactants. Even a small amount of a surface active agent can produce dramatic effects. At a concentration of 0.1%, for example, soap lowers water's surface tension almost 70%. In contrast, sodium hydroxide, which is not a surfactant and which diffuses homogeneously throughout its water solutions rather than concentrating at the surface, actually raises water's surface tension very slightly. At a 5% concentration sodium hydroxide increases water's surface tension by about 6%.

Figure 11.11 illustrates the relationship among the three terms: *surfactant*, *detergent*, and *soap*. All surfactants act at surfaces. Some surfactants, the detergents, are also good cleaning agents. Some detergents, the soaps, are sodium or potassium salts of long-chain carboxylic acids. While other detergent molecules have different structures, all detergents have a typical molecular structure in common: a long, hydrophobic carbon chain that resembles a molecular "tail," which is connected to a hydrophilic "head." In Section 11.14 we'll examine some detergents that aren't soaps.

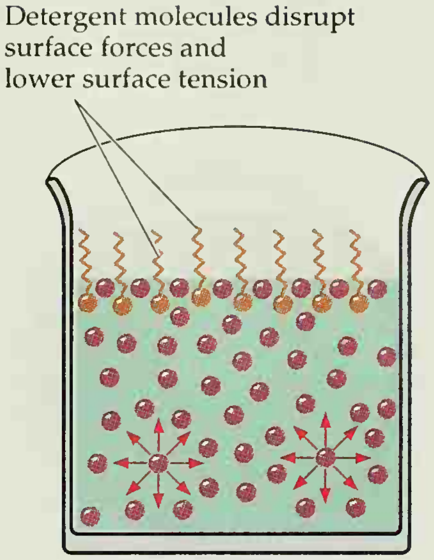


Figure 11.10
Surface effect of detergent molecules.

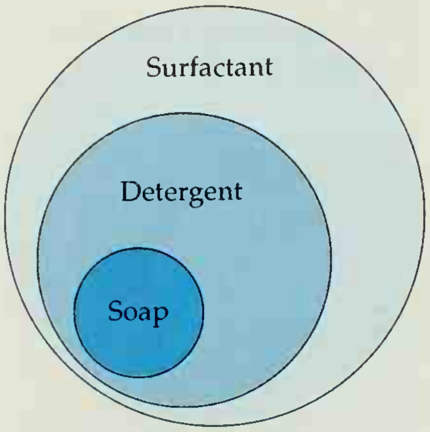


Figure 11.11
All soaps are detergents; all detergents are surfactants.

QUESTION

Describe the structures and properties of the two molecular fragments that are common to all detergents. ______

11.7 Micelles, Colloids, and John Tyndall

As the water's surface becomes filled with surfactant molecules and even more detergent is added, the additional detergent molecules soon become crowded out of the surface. They begin shielding their hydrophobic tails from water molecules in a different way. They begin clustering into **micelles** within the bulk of the water.

Micelles are submicroscopic globules or spheres of one substance distributed throughout another, usually a liquid. As detergent molecules accumulate into micelles in the interior bulk of the water, their hydrophilic heads form the spheres' surfaces and their hydrophobic tails point inward, shielded from the water molecules in an accommodating environment made up of other, similar, hydrophobic hydrocarbon chains (Fig. 11.12).

Although these detergent micelles are well dispersed in the water, they aren't actually dissolved. They're present as a **colloid**. A colloidal dispersion

Micelles are submicroscopic globules or spheres of one substance distributed throughout another, usually a liquid.

A **colloid** is made up of particles of one substance dispersed throughout another. The particles of the dispersed substance range in diameter from about 10^{-7} to 10^{-4} cm.

Figure 11.12

Cross-section of a spherical detergent micelle.

differs from a true solution largely in the size of the dispersed particles. In a colloid the particles run from about 10^{-7} to 10^{-4} cm in diameter. In contrast, the diameter of a chloride ion is 3.6×10^{-8} cm; for a sodium ion it's barely 2×10^{-8} cm. As we've seen in earlier chapters, sodium chloride dissolves in water to form a true solution of Na^+ cations and Cl^- anions.

There's no sharp, well-defined division between the size of a particle dispersed as a colloid and one that's dissolved in a true solution. As with acids and bases, we have to rely on observable phenomena to determine which we're dealing with. The easiest way to see the difference between a solution and a colloidal dispersion is to shine a light through each of them. Shining a flashlight beam through a solution of sodium chloride in water doesn't show much. The beam passes through the clear solution without producing any observable effect. But shine the beam through a mixture of soap and water, even one containing very little soap, and you see the beam's path clearly illuminated, especially if you view the mixture against a dark background. This *Tyndall effect*, caused as the colloidal particles scatter the light to all sides, was discovered by John Tyndall, a British physicist born in Ireland in 1820. It's one of the more easily observed properties of a colloidal dispersion, one that readily distinguishes it from a true solution (Fig. 11.13).

John Tyndall discovered the Tyndall effect, which allows us to detect colloidal dispersions in transparent materials, such as air and water.

The Tyndall effect isn't limited to detergents. A few drops of milk in a glass of water also show the path of the light. Milk is essentially an aqueous mixture of colloidal fats and proteins along with dissolved lactose (milk sugar) and minerals. You can even see the Tyndall effect outdoors on a foggy night as the fog, a colloidal dispersion of water in air, scatters the headlight beams of automobiles.

With one exception, colloids can form when each of the three states of matter—solids, liquids, and gases—disperse in each of the others. Since all gases are infinitely soluble in each other, no gas forms a colloidal dispersion in any other gas. Examples of the various kinds of dispersions appear in Table 11.3.

Figure 11.13

The Tyndall effect is produced as beams of sunlight pass through a cloud, revealing a dispersion of colloidal particles in the atmosphere below.

TABLE 11.3 Colloidal Dispersions

	Common Name	Example
Solid dispersed in		
Solid		Ruby glass—glass colored red by a colloidal dispersion of solid gold particles
Liquid		Clay, paint, putty, toothpaste
Gas	Aerosol	Smoke
Liquid dispersed in		
Solid	Gel	Gelatin, jelly
Liquid	Emulsion	Milk, salad dressing
Gas	Aerosol	Fog
Gas dispersed in		
Solid		Popcorn
Liquid	Foam	Whipped cream
Gas		(Does not exist)

QUESTION

Which of the following would you expect to show a Tyndall effect: (a) smoke from a backyard grill, (b) a mixture of helium and argon, (c) sugar water, (d) a well shaken vinegar-and-oil salad dressing, (e) the interior of a cloud? ____________

11.8 How Soap Cleans: Wet Water

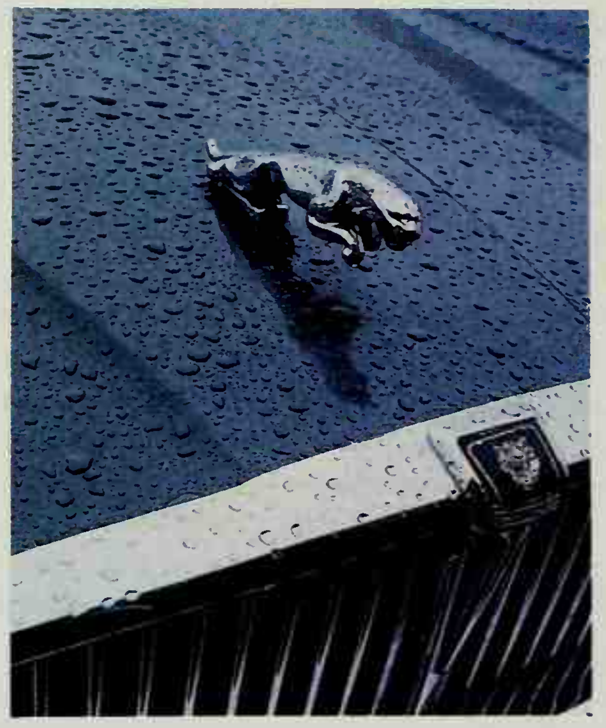
Now we can begin to understand why soap acts as a detergent. Soap cleans by

1. decreasing water's surface tension, making it a better wetting agent,
2. converting greasy and oily dirt into micelles that become dispersed in the soapy water, and
3. keeping the grease micelles in suspension, thereby preventing them from coalescing back to large globules of grease that could be redeposited on a clean surface.

Each of these functions has its basis in the structure of the soap molecule.

Our common sense tells us that water wets whatever it touches, but if we look closely we find that water isn't a particularly effective wetting agent after all. Examine the waxy surface of a well-polished auto just after a rain and you'll see the water forming small beads rather than spreading evenly over the surface. Water doesn't wet the waxed surface very well. Look at your clothing or at the top of an umbrella after you've been out in a light drizzle and you'll see the rain forming small beads on the fabric before it penetrates into the cloth. Generally, water simply doesn't do a very good job of wetting most ordinary substances.

In washing, though, water must penetrate well and deeply into the substance that we want to clean. We've already seen, with the dropping tack,



Water's surface tension holds it in small beads on the polished surface of a car. The water does not wet the surface evenly.

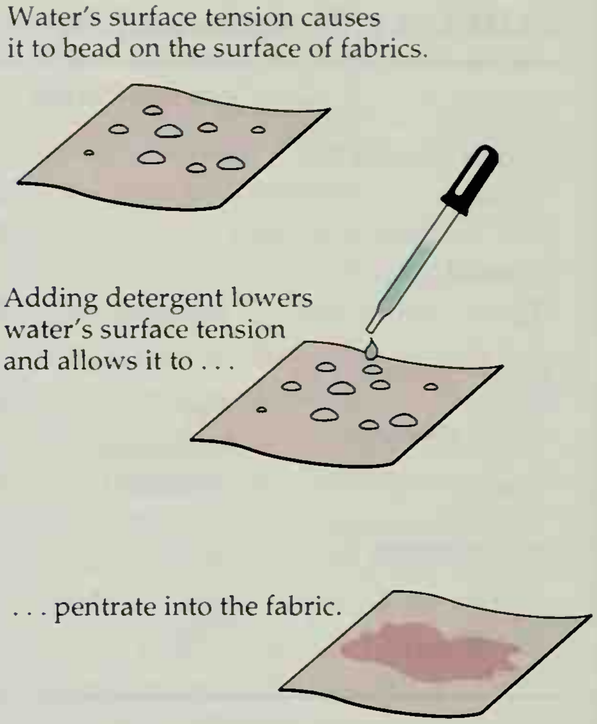


Figure 11.14
Detergents enable water to penetrate rapidly into fabrics.

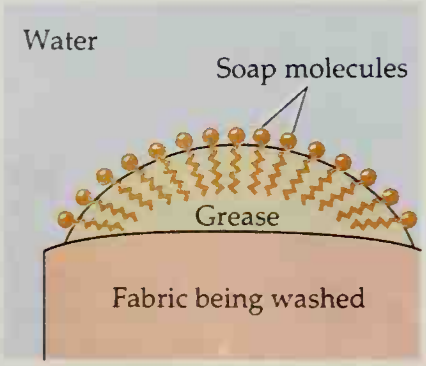
that a detergent lowers water's surface tension. In its action as a detergent, then, soap first lowers surface tension so that the water carrying the micelles can get to the dirt (Fig. 11.14). In the following section we'll see how the soap molecules perform the next two functions by converting the grease into micelles and dispersing them in the wash water.

QUESTION

How does a detergent perform its function of making water wetter than it is normally? ____________________

11.9 How Soap Cleans: Getting the Dirt Down the Drain

Figure 11.15
Water, grease, and soap.



When the soap micelles reach the embedded dirt, the soap molecules that form these micelles once again find themselves at a surface. This time it's the surface between the water and the grease that makes up (or carries with it) most of the dirt. Now, as the hydrophilic heads of the soap molecules remain surrounded by water molecules, the soap micelles break up and the hydrophobic hydrocarbon tails, which had remained in the interior of the spherical micelles, become embedded in the grease. With this greasy dirt providing as compatible a chemical environment for the hydrophobic tails as the water provides for the hydrophilic heads, the tails are just as much at home in the grease as the heads are in the water. With their heads embedded in the water and their tails in the grease, the soap molecules effectively nail the two phases together (Fig. 11.15).

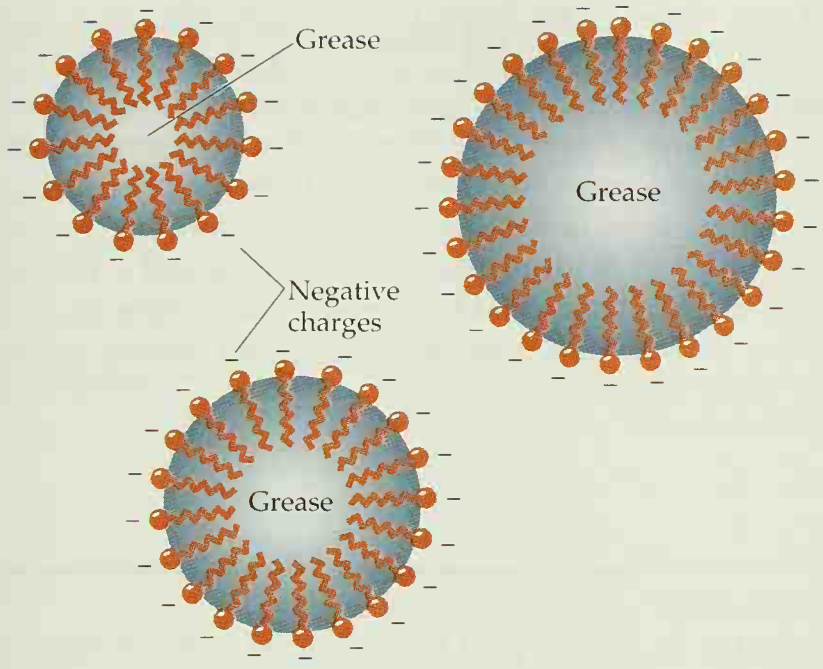


Figure 11.16
Grease micelles with embedded soap molecules.

Agitation now breaks the grease into micelles whose surfaces are covered by the negatively charged carboxylate groups, the hydrophilic —CO_2^- groups of the embedded soap molecules (Fig. 11.16). With a coating of negative electrical charges enveloping the entire surface of each micelle, the grease droplets repel each other and remain suspended in the wash water instead of coalescing and redepositing on the material being cleaned. In the end, they go down the drain with the wash water. (While all this is going on the sodium ions move about freely and independently in the wash water, just as they did in the electrolyte solution of the light bulb demonstration that began Chapter 1.)

Since the anionic carboxylate groups of the soap molecules place a cover of negative electrical charge on the micelles' surfaces, soap falls into the class of anionic detergents.

QUESTION

If we used distilled water to wash our clothes, would the wash water act as an electrolyte? Explain. ____________________

11.10 A Little Soap History

Each time you use a bar of soap you go back a long way, chemically, into an uncertain history. There's reason to believe the Babylonians knew how to make soap almost 5000 years ago. While the Phoenicians and ancient Egyptians may have manufactured it, too, most historians give the Romans the real credit for discovering soap, or at least for writing down the secrets of its preparation and passing them along. The Romans knew that heating goat fat with extracts of wood ashes, which contain strong bases, produces soap. They also used lye (sodium hydroxide, NaOH), a stronger base than the ash extracts and more effective in converting fat into soap. The word *lye* itself is connected to soap and soapmaking through an intricate linguistic path that includes a long list of words from Latin, Greek, Old English, Old Irish and other languages, with meanings such as "lather," "wash," "bathe," and even "ashes".

Knowledge of soapmaking dimmed for a while after Rome fell, then traveled from Italy to Germany, France, Spain, and then, in the 14th century, to England. The manufacture of soap came to America in 1608 with the arrival of Polish and German soapmakers in Jamestown, Virginia. Until the rise of commercial soapmaking in the 19th century, the process remained a household art, practiced much as the Romans must have made soap some 20 centuries earlier, or even as the Babylonians may have produced it long before the Romans.

11.11 Esters

However soap is made, whether by boiling goat fat and wood ashes in ancient kettles or through the modern methods of 20th-century factories, it's all the same chemically. Soap comes from the hydrolysis of naturally occurring fats and oils, which are themselves members of a class of organic compounds known as *esters*. **Hydrolysis** is the decomposition of a substance, or its conversion to other substances, through the action of water.

Hydrolysis is the decomposition of a substance, or its conversion to other substances, through the action of water.

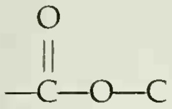
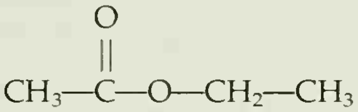
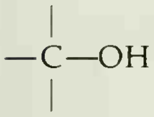
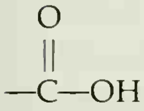
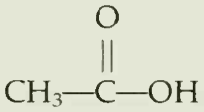
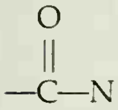
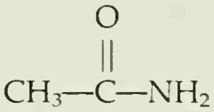
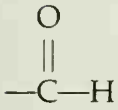
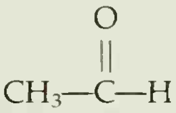
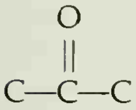
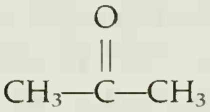
A **functional group** is a small set of atoms, held together by covalent bonds in a specific, characteristic arrangement that is responsible for the principal chemical and physical properties of a compound.

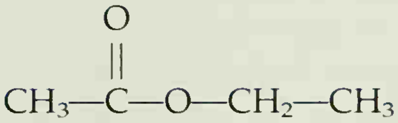
These esters, as well as the alcohols and the carboxylic acids and their salts that we've already examined, and the various other organic compounds we've yet to examine as we progress, all illustrate the classification of organic compounds through their **functional groups**. A functional group is a small set of atoms, held together by covalent bonds in a specific, characteristic arrangement that is responsible for the principal chemical and physical properties of a compound. They influence melting points, boiling points, densities, and the ways in which a molecule reacts with other molecules. It's through these functional groups that we can approach the study and practice of organic chemistry in a rational way.

It would be both foolhardy and futile to try to learn the chemistry of each of the millions upon millions of individual organic compounds now known to exist. Instead we focus our attention on the functional groups that form the reactive portions of their molecular structures. Since all compounds that bear the same functional group undergo the same sort of chemical reactions—some faster than others in the same class, some slower, some with interesting and unusual twists—learning the chemistry of these relatively few functional groups allows us to generalize our knowledge to include enormous numbers of individual organic compounds, each bearing the same group. What's more, knowing the chemistry of each functional group allows us to predict the chemistry of new compounds, as yet undiscovered or unknown to us. Several of the more common functional groups, including the *ester*, appear in Table 11.4. We have already examined alcohols in Chapter 7 and carboxylic acids in Chapter 10. We'll examine other functional groups individually as we discuss the compounds in which they occur.

All naturally occurring fats and oils are esters of fairly complex molecular structures. We'll start instead with a simpler ester, *ethyl acetate*, which is used as a food flavoring and as a common, commercial solvent found in many brands of nail polish and paint remover. (Ethyl acetate doesn't occur in fats, though.)

TABLE 11.4 Common Functional Groups

Structure	Functional Class	Representative Compound
 $-\overset{O}{\overset{\|}{C}}-O-C$	Ester	 $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$ Ethyl acetate
 $-\overset{\mid}{\underset{\mid}{C}}-OH$	Alcohol	CH_3-CH_2-OH Ethyl alcohol
 $-\overset{O}{\overset{\|}{C}}-OH$	Carboxylic acid	 $CH_3-\overset{O}{\overset{\|}{C}}-OH$ Acetic acid
 $-\overset{O}{\overset{\|}{C}}-N$	Amide	 $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ Acetamide
 $-\overset{O}{\overset{\|}{C}}-H$	Aldehyde	 $CH_3-\overset{O}{\overset{\|}{C}}-H$ Acetaldehyde
 $C-\overset{O}{\overset{\|}{C}}-C$	Ketone	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ Acetone


$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$$
ethyl acetate

Ethyl acetate results from the reaction of acetic acid and ethyl alcohol in the presence of a small, catalytic amount of a strong acid. As the acetic acid and the ethyl alcohol react, the oxygen atom of the alcohol becomes bonded to the carbonyl carbon of the acid (Section 10.17), while the H of the alcohol's —OH group and the entire —OH of the acid leave as a molecule of water, a by-product of this *esterification reaction* (Fig. 11.17). Although the carboxylic acid that takes part in this esterification is itself an acid, it's a relatively weak one (Section 10.11); the reaction requires the presence of a much stronger acid, such as HCl or H_2SO_4, as a catalyst. Catalysts, which affect the rate of a reaction but are not themselves reagents (Section 8.9) are usually written

Figure 11.17
An acid-catalyzed esterification.

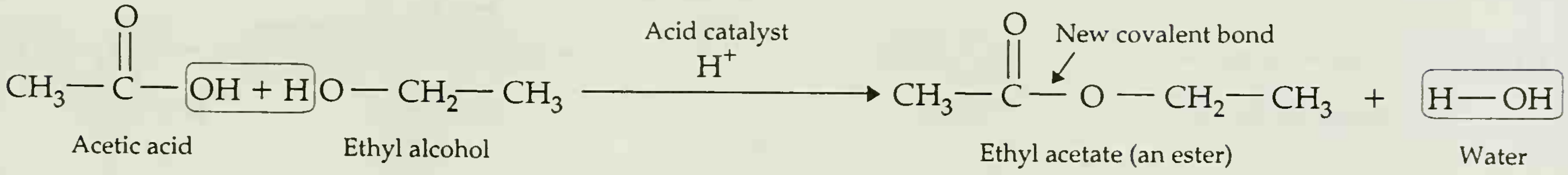
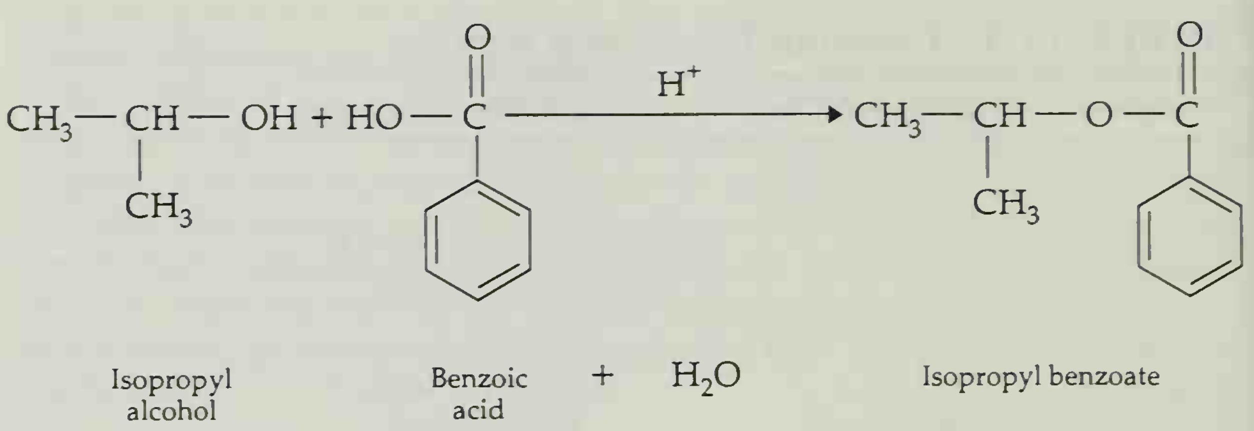
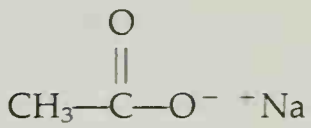

$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}O-CH_2-CH_3 \xrightarrow[]{\text{Acid catalyst } H^+} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + \boxed{H-OH}$$

Figure 11.18
Isopropyl benzoate.



above the reaction arrow along with required conditions, such as heat and pressure.

The name *ethyl acetate* reveals that the compound has structural connections to both *ethyl* alcohol and *acet*ic acid. The suffix *-ate* tells us we're dealing either with an ester or with a salt of a carboxylic acid, such as *sodium acetate.*



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \; {}^+Na$$

sodium acetate

In naming esters we give the name of the alcohol first, then the acid, with the suffix *-ate* replacing the acid's *-ic*. For example, the ester formed by the reaction of isopropyl alcohol with benzoic acid, in the presence of a strong acid, is *isopropyl benzoate* (Fig. 11.18).

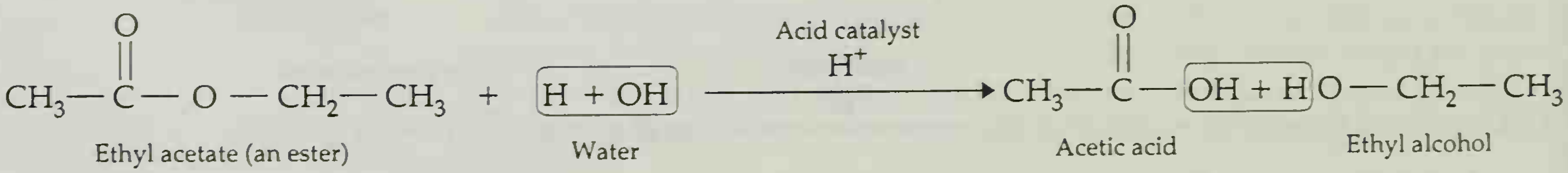
Heating an ester with water in the presence of either an acid or a base produces a hydrolysis, with water adding to the ester in a reversal of the esterification reaction. As shown in Figure 11.19, when the hydrolysis is carried out in the presence of an acid the reaction becomes precisely the reverse of the esterification. Here an ester reacts with water, forming an alcohol and a carboxylic acid. Carrying out the hydrolysis in the presence of a base, such as sodium hydroxide, produces the salt of the carboxylic acid rather than the acid itself. In this case the carboxylic acid and the base react with each other in a neutralization reaction (Section 10.2). In the presence of a base, and with the formation of the salt of the acid rather than the acid itself, the hydrolysis is called a **saponification** (Fig. 11.20), a term that brings us to the chemistry of soapmaking.

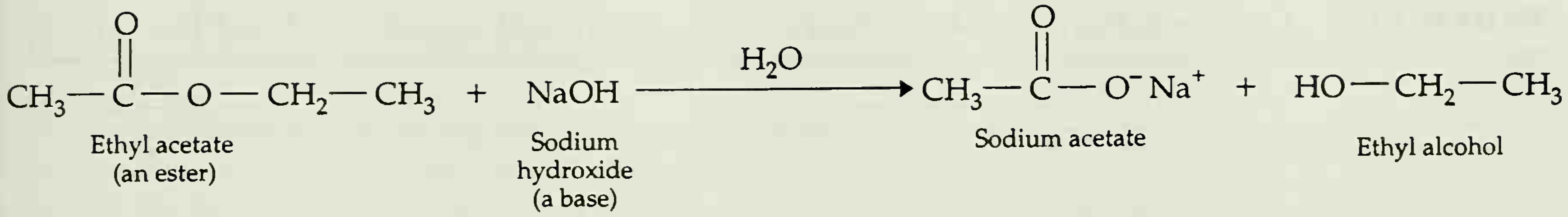
A **saponification** is a hydrolysis of an ester carried out in the presence of a base.

QUESTION

Write the structure of *methyl benzoate*. Write complete chemical reactions for the hydrolysis of methyl benzoate in the presence of (a) HCl; (b) KOH. Name each of the organic products produced in these reactions. ______________________

Figure 11.19
An acid-catalyzed hydrolysis. An ester reacts with water, producing an acid and an alcohol.



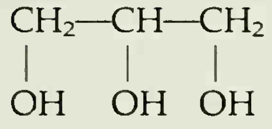


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3 + NaOH \xrightarrow{H_2O} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + HO-CH_2-CH_3$$

Figure 11.20
A basic hydrolysis; a saponification.

11.12 From Fats to Soap

Ethyl acetate, as we've seen, is a simple ester formed from an alcohol, ethyl alcohol, that bears a single —OH group. The fats and oils are more complex esters, formed from *glycerol*, a *triol* (or *tri*hydroxy alcoh*ol*) bearing three —OH groups. Glycerol is also known more commonly as *glycerin*, sometimes spelled with an added *e*, *glycerine*. Glycerol is used in many hand and body lotions to soften the skin.



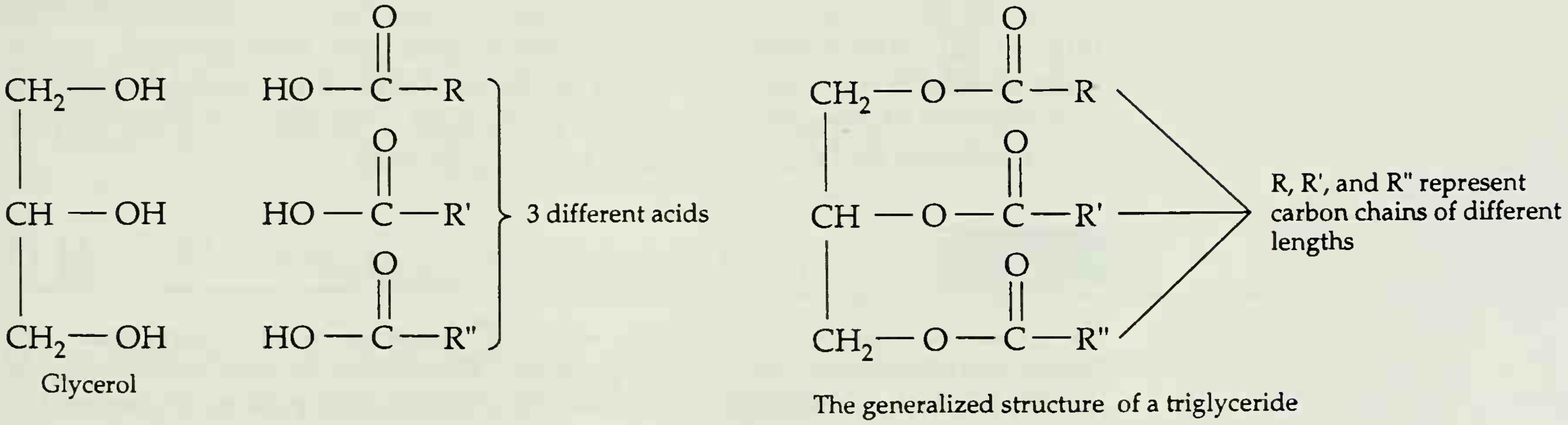
$$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

glycerol, also known as glycerin or glycerine

Each of glycerol's three —OH groups constitutes the hydroxyl functional group of an alcohol and so each one can enter into ester formation with a carboxylic acid. The result is a *triester* (Fig. 11.21) in which the three organic groups of the acids (R, R′ and R″ of Figure 11.21) can be identical or can differ from each other. The generalized triester of Figure 11.22 bears a variety of generic names. Most commonly, it's described as a *glyceride* or a **triglyceride**. While the structures of the three acids that combine with glycerin can vary, almost all of the acids formed by saponifying fats and oils show certain structural similarities. Virtually all of them consist of straight, unbranched chains containing even numbers of carbons. Sodium salts of the **fatty acids** containing from 10 to 18 carbons make the best soaps (Table 11.5). Triglycerides are

Triglycerides are the principal organic compounds of animal fats and vegetable oils. **Fatty acids** are the acids we get through their hydrolysis.

Figure 11.21
A triester of glycerol.



The generalized structure of a triglyceride

TABLE 11.5 Common Fatty Acids of Soap

Structure and Name	*n* of $CH_3—(CH_2)_n—CO_n—CO_2H$
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$ Caprylic acid	6
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$ Capric acid	8
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$ Lauric acid	10
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$ Myristic acid	12
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$ Palmitic acid	14
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2H$ Stearic acid	16
$CH_3—(CH_2)_7—CH{=}CH—(CH_2)_7—CO_2H$ Oleic acid	—
$CH_3—(CH_2)_4—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—CO_2H$ Linoleic acid	—

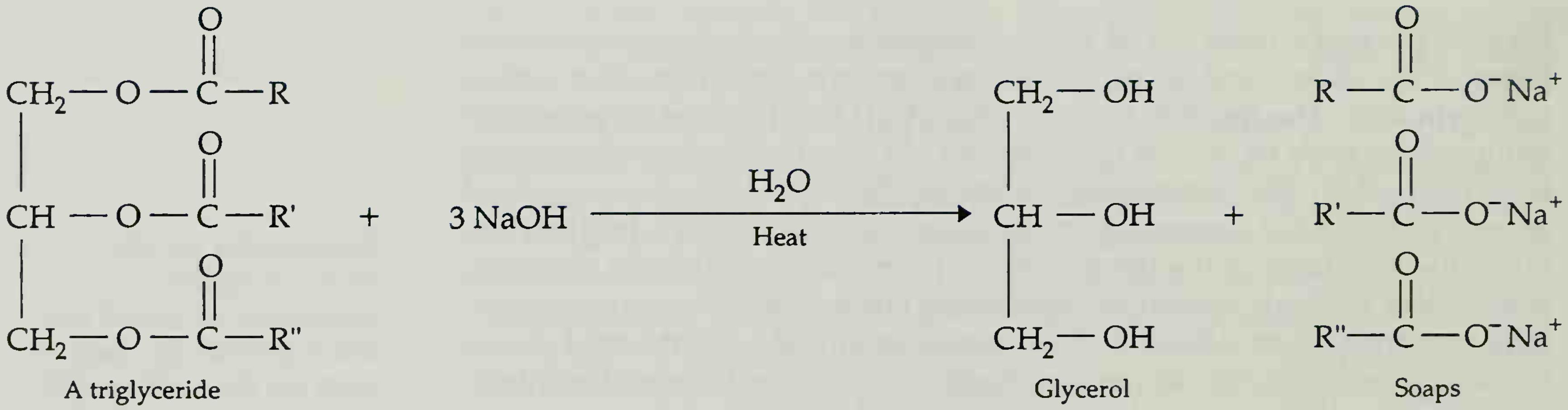


Figure 11.22

The saponification of a triglyceride.

the principal organic compounds of animal fats and vegetable oils, and fatty acids are the acids we get through their hydrolysis.

To sum up, then, we can produce a soap by heating a triglyceride—an animal fat or a vegetable oil—in an aqueous solution of sodium hydroxide (Fig. 11.22). Hydrolysis of the triglyceride generates both glycerol, which remains dissolved in the water, and the sodium salts of the various acids that make up the triglyceride. These salts of the fatty acids congeal at the surface as the mixture cools and we scoop them up as soap.

QUESTION

Using the information in Table 11.5, write the structures of (a) glyceryl triacetate, (b) glyceryl tripalmitate, and (c) ethyl palmitate. Which if any of these would undergo hydrolysis in the presence of NaOH? Which, if any, would produce a soap on hydrolysis with NaOH? ________________

11.13 The Problem: Hard Water

As we saw in Section 9.13, the drinking water of many regions contains various minerals, dissolved in slightly acidic rainwater as it filters through the soil. Water that's rich in the salts of calcium, magnesium, and/or iron is called *hard water*. (*Soft water*, on the other hand, is virtually free of these minerals.) The mineral cations of hard water combine with fatty acid anions and remove them from water as waxy, insoluble salts. In regions where the water is particularly hard, you can actually see these precipitates deposited as gray rings, known as *curd*, or *soap curd*, around bathtubs and sinks after washing with soap. This curd is made up of the calcium, magnesium, and/or iron salts of the fatty acids of soap.

$$2CH_3{-}(CH_2)_n{-}CO_2^-\ {}^+Na + Ca^{2+} \rightarrow CH_3{-}(CH_2)_n{-}CO_2^-\,Ca^{2+}\ {}^-O_2C{-}(CH_2)_n{-}CH_3 + 2Na^+$$

curd, or *calcium soap*
(the ring that forms around the bathtub
in regions with hard water)

Hard water wastes soap because much of the soap that would otherwise be used in cleaning is consumed in curd formation as it reacts with the mineral ions of hard water. In hard water, a certain amount of soap has to be used up initially in combining with the mineral cations and removing all of them from solution before additional soap can act effectively as a detergent. What's more, this curd deposits on the surface of laundered clothes, dulling the surface of the cloth and giving washed goods a slightly gray appearance.

You can see the effect of hard water on soap by first shaking up some soap in distilled water. A piece of bar soap or soap flakes such as Ivory Snow will do nicely for this demonstration, but laundry detergent won't work for reasons we'll come to soon. Distilled water, which you can get in a supermarket or convenience store, is free of the mineral ions of hard water and generates a good deal of suds with the soap. Now add some hard tapwater to the sudsy mixture or, if you live in an area of soft water, add about a tablespoon of milk, which contains considerable calcium. (Skim milk also works well, as does a solution of an antacid that contains calcium.)

As you stir the hard water or the milk into the soapy water, the suds vanish as the fatty acid anions are converted into their insoluble calcium salts. You'll probably be able to see the curd swirling in the water.

Soap forms rich suds in soft water. In hard water soap is less efficient. The mineral cations of hard water combine with the soap, forming curds and reducing the soap's effectiveness.

QUESTION

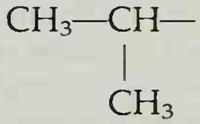
What would you expect to happen if you add a teaspoon of each of the following to the sudsy mixture produced by shaking soap in distilled water: (a) table salt; (b) $MgSO_4$ (epsom salts; see Section 10.2); (c) ground chalk ($CaCO_3$; see Section 10.2)? ______

11.14 The Solution: Synthetic Detergents

In the 1940s chemical science and technology solved the problem of using hard water for washing by devising economical, commercially useful *synthetic detergents*. In the most successful of these, the *alkylbenzenesulfonates*, a sulfonate functional group, —SO_3^-, rather than a carboxylate group, —CO_2^-, acts as the hydrophilic structure.

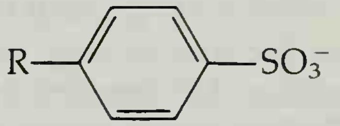
—CO_2^-	—SO_3^-
a carboxylate group	a sulfonate group

The great advantage of the sulfonate anion is the great water solubility of virtually every one of its mineral salts. Unlike soaps, alkylbenzenesulfonates remain dispersed and effective in hard water. [The term *alkyl* refers to the group produced by removal of a hydrogen atom from an alkane, (see Section 7.3). Alkyl groups we've already seen include the methyl group, CH_3—, the ethyl group, CH_3—CH_2—, the *n*-propyl group, CH_3—CH_2—CH_2—, and the isopropyl group.]



$$\begin{array}{l} CH_3\text{—}CH\text{—} \\ \quad\quad\;\; | \\ \quad\quad CH_3 \end{array}$$

Since there's no simple, economical way to place a sulfonate group directly onto a long hydrocarbon chain in large-scale production, commercially successful synthetic detergents don't mimic exactly the structure of a soap molecule. Some simple, commercially feasible reactions do exist, though, that allow chemists to place both a hydrocarbon chain and a sulfonate group onto the same benzene ring (Section 7.10). Combining these reactions in successive steps produces the synthetic alkylbenzenesulfonate detergents



an alkylbenzenesulfonate anion
(R represents an alkyl group in the form of a long hydrocarbon chain.)

One of the reactions used in the synthesis, *Friedel–Crafts alkylation*, places an alkyl group on an aromatic ring (Section 7.10) through the combination of an alkyl halide, a Lewis acid, and an aromatic compound. In the example of Figure 11.23 methyl chloride, an alkyl halide, reacts with benzene in the presence of aluminum chloride, $AlCl_3$ (which serves as a catalyst), to produce toluene, a valuable solvent and an intermediate in the preparation of more complex organic compounds. (On a commercial scale, most toluene comes from petroleum rather than from a synthesis like this. The reaction in Figure 11.25 serves only as a simple illustration of the Friedel–Crafts reaction.)

Figure 11.23
Friedel–Crafts alkylation of benzene to toluene.

This alkylation was discovered in 1877 by Charles Friedel, a French chemist and mineralogist who was at the time professor of mineralogy at the Sorbonne, in Paris, and James Mason Crafts, an American organic chemist studying with Charles Friedel. Fifteen years later James Mason Crafts was appointed professor of organic chemistry at the Massachusetts Institute of Technology. In 1898 he became president of MIT.

The benzene used in the manufacture of alkylbenzenesulfonate detergents comes from petroleum, and so do the hydrocarbons that form the long-chain alkyl halides used to place the hydrophobic tail onto the ring. With the tail secured in position, the hydrophilic sulfonate group is introduced through the action of sulfuric acid, H_2SO_4, or sulfur trioxide, SO_3. The sequence of these two reactions

- Friedel–Crafts alkylation, which places an alkyl group on the ring
- sulfonation, which places a sulfonic acid group, —SO_3H, on the ring

produces an alkylbenzenesulfonic acid. Conversion of the acid to its sodium salt yields the synthetic detergent itself (Fig. 11.24). Like soaps, sodium alkylbenzenesulfonates are waxy, solid, anionic detergents.

With a variety of synthetic reactions at hand, the chemist can tailor the structure of a detergent molecule to specific needs. Anionic detergents, which make up the great bulk of all synthetic detergents used, are particularly effective at cleaning fabrics that absorb water readily, such as those made of natural fibers of cotton, silk, and wool. *Nonionic* detergents, many of which have large numbers of covalently bonded oxygens in their hydrophilic structures, are especially useful in cleaning synthetic fabrics. Most nonionic detergents are liquids and produce little foam. They are used, along with anionic detergents, in formulating dishwashing liquids and liquid laundry detergents.

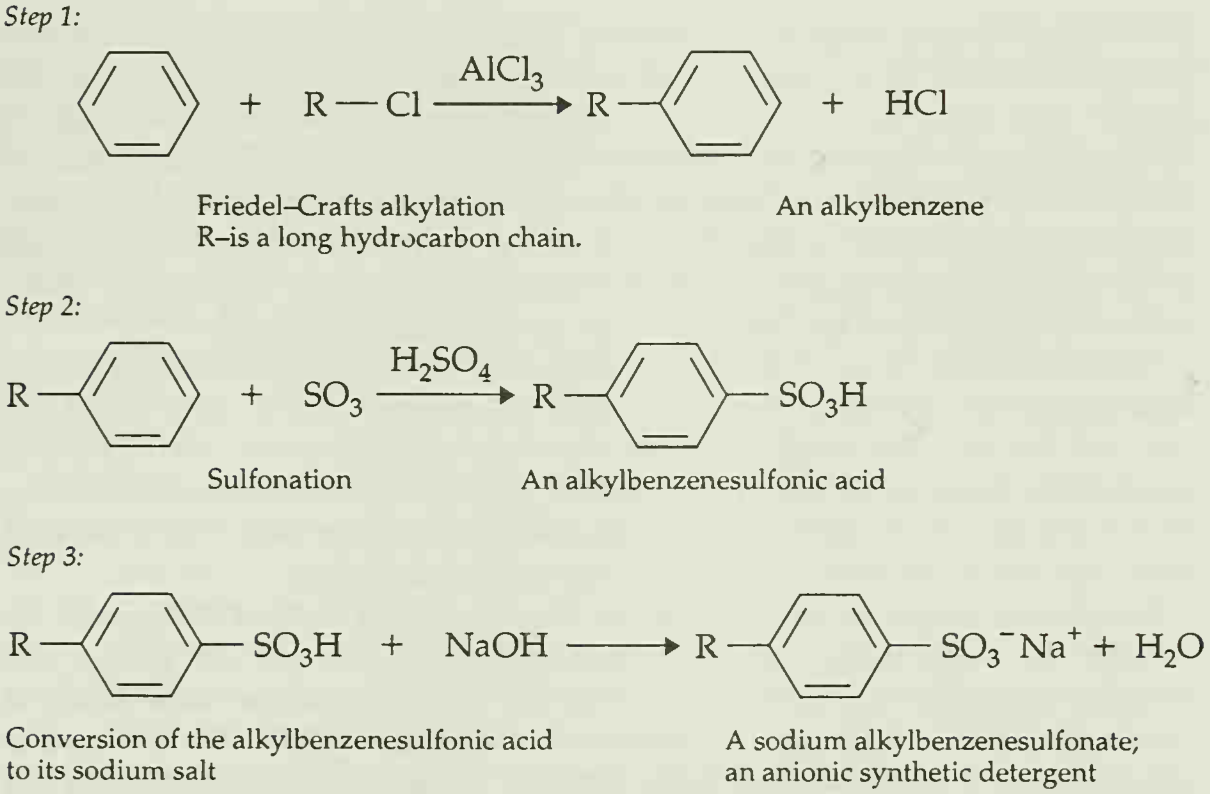
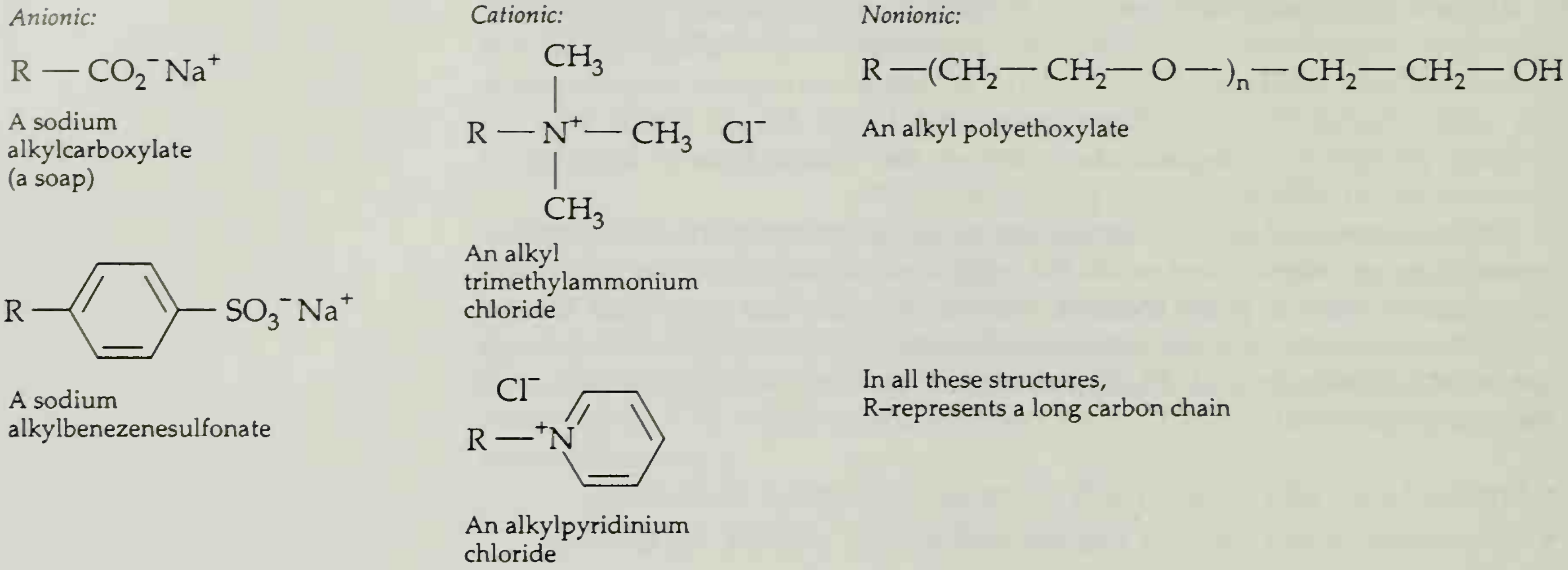


Figure 11.24
Synthesis of an alkylbenzenesulfonate detergent.



A sodium alkylcarboxylate (a soap)

A sodium alkylbenezenesulfonate

An alkyl trimethylammonium chloride

An alkylpyridinium chloride

An alkyl polyethoxylate

In all these structures,
R–represents a long carbon chain

Figure 11.25
Typical detergents.

Most *cationic* detergents are ammonium salts (Section 10.4) that also happen to be effective germicides. They're used in antiseptic soaps and mouthwashes, and also in fabric softeners since their positive charges adhere to many fabrics that normally carry negative electrical charges. Molecular structures of some typical nonionic and cationic detergents appear in Figure 11.25.

QUESTION

Write a complete reaction for the preparation of *ethylbenzene* from benzene, an alkyl chloride, and any other compounds, reagents, and catalysts you may need. Show all the reactants and products. ____________________

PERSPECTIVE: The Magic of a Box of Detergent

The next time you step into a grocery store, supermarket, or convenience store, think of it as a special kind of chemistry stockroom, one set up by people who want to work a little magic of their own. Some of the magic is on the packages themselves, written in the bold print on the fronts of dozens of boxes of detergents, toothpastes, shampoos, hand soaps, and other household and personal care items. The rest of it is in the chemicals listed in small print on the sides. That part carries the same sort of "magic" that let us "float" tacks and manipulate toothpicks in our opening demonstration.

What's on the front of the boxes promises you brighter, cleaner clothes, dazzling smiles, beautiful hair, and other good things of life, all if you'll just use this brand. The small print on the side offers you the nitty-gritty of alkylbenzenesulfonates and other anionic, cationic, and nonionic surfactants, and of sodium tripolyphosphate, sodium sulfate, and the like. That's the stuff that does the work in the tub and in the sink and shower.

Most manufacturers have access to the very same sets of chemicals, especially the surfactants that lower surface tension and get the grease into micelles and down the drain. They also use pretty much the same kinds of other chemicals to help the surfactants do their work. Generally, it's hard to tell one alkylbenzenesulfonate from another. To help us differentiate one box

TABLE 11.6 Components of a Typical Detergent Formulation

Component	Example	Function
Surfactant	A sodium alkylbenzenesulfonate	Detergency
Phosphates	Sodium tripolyphosphate: $Na_5P_3O_{10}$	Softens water and increases surfactant's efficiency
Sodium carbonate	Na_2CO_3	Softens water and increases surfactant's efficiency
Processing agent	Sodium sulfate: Na_2SO_4	Keeps detergent pouring freely
Washer protection agents	Sodium silicates: Na_2SiO_3, $Na_2Si_2O_5$, Na_4SiO_4, etc.	Coat washer parts to inhibit rust
Enzymes	—	Remove protein stains
Carboxymethylcellulose (CMC)	—	Helps keep dirt from redepositing on fabric
Fabric whitener	—	Makes white clothes appear brilliantly white
Perfume	—	Adds appealing odor

of chemicals from another, made by a different manufacturer but containing just about the same long alkyl chains, sulfonate groups, benzene rings, and the like, we get packages with bold printing, dazzling graphics, and glowing colors. The magic is designed to differentiate, in our minds, the chemicals of one box from the chemicals of another. Maybe it works. After all, if you think your handkerchiefs and socks are cleaner and brighter with one brand of detergent than with another, that's what counts. But still, the same sort of extraordinary chemistry is behind it all, from one brand to another.

The ingredients in a box of detergent.

This chapter has been about the extraordinary chemistry that gets things clean with the chemicals in all those packages. But even chemically there's more to a box of detergent than just detergent. The consumer products we pour out of a box or bottle into the wash water contain, in addition to the detergent, plenty of other substances added to increase cleaning efficiency and make our clothing, dishes, and the like not only cleaner but more appealing to the nose and the eye as well.

In addition to the surfactant, you'll also find most of the following on the ingredients label of a typical powdered laundry detergent, regardless of the brand: water softeners, enzymes to help remove protein stains, agents to protect the washing machine against rust and corrosion, a drying agent (sodium sulfate, Na_2SO_4) to keep the powder flowing freely, perfume for a pleasant smell, a fabric whitener, and an inert filler that adds bulk to the entire mixture. Some brands contain a bit more of one and a bit less of another than other brands. Some smell like a lilac, some like a pine tree.

Most liquid laundry and dishwashing detergents include both anionic and nonionic detergents, water and ethyl alcohol to dilute the detergent mixture so it pours freely, coloring agents to make the mixture attractive, and many of the components found in powdered detergents. Table 11.6 summarizes some of these additives and their functions. Still, no table can summarize everything that goes into a box of detergent, including the magic that comes along with the chemicals. All in all, though, its the extraordinary chemistry of all those hydrophilic heads and hydrophobic tails that keeps us clean.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

Both soaps and synthetic detergents consist of molecules made up of a ______ portion, which is usually a long, hydrocarbon chain, and a ______ portion. A ______ functional group forms the hydrophilic end of the ______ molecule, while the class of synthetic detergents known as ______ carry a ______ functional group at their hydrophilic end. The combined effects of the two classes of functional groups causes both soaps and synthetic detergents to accumulate at the surface of water and to lower the water's ______ . As a result, both of these classes of detergents belong to the larger category of ______ .

______ contains ______ cations. Because these ions form water-insoluble salts with long-chain ______ , soaps are inefficient detergents in hard water and form precipitates known as ______ . The sulfonate salts of these ions are generally soluble and these ______ are much more useful in regions where the water is hard.

alkylbenzenesulfonates
calcium, iron, and magnesium
carboxylate
carboxylic acids
curd
hard water
hydrophilic
hydrophobic
soap
sulfonate
surface tension
surfactants
synthetic detergents

2. Define, identify, or explain each of the following:

a. anionic detergent
b. boiling point
c. calcium soap
d. colloidal dispersion
e. density
f. ester
g. evaporation
h. fatty acid
i. glycerol
j. hydrolysis
k. melting point
l. micelle
m. saponification
n. soft water
o. triglyceride
p. Tyndall effect

3. Suppose you find each of the following on the surface of a lake: (a) an empty metal bucket, (b) a metal paper clip, (c) a bar of soap, (d) an aluminum rowboat, (e) a metal tack, (f) a cork stopper, (g) a model airplane made of balsa wood, (h) a piece of ice, (i) a wax candle. Which is floating and which is supported by surface tension?

4. Name and describe the three kinds of kinetic energy possessed by chemical particles.

5. Which of the following are likely to melt with sharp melting points and which are likely to soften over a range of temperatures: (a) sodium chloride, (b) butter, (c) gold, (d) citric acid, (e) asphalt?

6. Arrange the following in order of *decreasing* melting points, with the highest-melting substance first and the lowest-melting substance last: water, acetic acid, sodium chloride, benzene, gold, oxygen, ammonia.

7. Explain the difference between (a) weight and density, (b) boiling and evaporation, and (c) evaporation and sublimation.

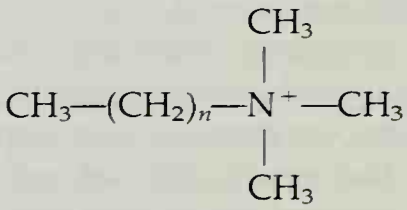
8. Describe the chemical basis of surface tension.

9. Is each of the following statements true or false?

a. All soaps are surfactants.
b. All surfactants are soaps.
c. All soaps are detergents.
d. All detergents are soaps.
e. All surfactants are detergents.
f. All detergents are surfactants.

10. Which of the following ions do *not* occur in *soft* water: (a) H^+, (b) Na^+, (c) Ca^{2+}, (d) Mg^{2+}, (e) Cl^-?

11. Explain what we mean when we say that a detergent molecule (a) makes water wetter; (b) acts as a molecular nail.

12. 

$$CH_3{-}(CH_2)_n{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}{-}CH_3$$

represents the cation of a class of *cationic detergents*. What part of this molecule makes up (a) its hydrophobic tail? (b) its hydrophilic head?

13. What two functional groups are generated when an ester reacts with water by hydrolysis, in the presence of a strong acid?

14. What two chemical elements are common to all esters?

15. What trihydroxy alcohol is produced by the hydrolysis of *any* triglyceride?

16. When the ancient Romans made soap, what did they use as the source of (a) triglycerides? (b) bases?

17. Name or give the molecular structure of all the products of each of the following reactions:

a. heating ethyl acetate with a solution of sodium hydroxide in water
b. heating methyl acetate with a solution of HCl in water
c. saponification of methyl palmitate
d. heating a mixture of $CH_3—CH_2—OH$, $CH_3—CH_2—CO_2H$, and a catalytic quantity of HCl
e. heating a mixture of 2-chloropropane, benzene, and $AlCl_3$

18. Either name or write equations for the *three* chemical reactions used in converting benzene, an alkyl halide, and either H_2SO_4 or SO_3 into a sodium alkylbenzenesulfonate.

19. What property of cationic detergents that are ammonium salts makes them useful in mouthwashes?

20. List five ingredients of a commercial laundry detergent, other than the surfactant, and describe the function of each.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

21. You have three sheets of plastic, each 1 cm thick. *A* is a square that's 2 cm on each side and weighs 2 g. *B* is a rectangle that's 1 cm on one side and 3 cm on the other, and weighs 4 g. *C* is a rectangle 2 cm x 2.5 cm and weighs 3 g. Which, if any, of the plastic sheets will float?

22. You immerse a small piece of jewelry made of gold into a measuring cup containing water and find that the jewelry has a volume of 5 mL. What does it weigh?

23. What's the volume of a 1-oz coin made of pure gold (1 oz = 28.3 g)?

24. How large does a piece of aluminum have to be to weigh the same as 10 cm^3 of lead?

25. We've seen in Section 11.7 that colloidal particles range from about 10^{-7} to 10^{-4} cm in diameter. A simple calculation shows that spheres with this range of diameters run from about 5×10^{-22} to 5×10^{-11} cm^3 in volume. We also know that there are 6.02×10^{23} water molecules in 18 g of water and that 1 g of water occupies very nearly 1 cm^3. Given these values, calculate the diameter a water molecule would have if it were a perfect sphere. Using this approximate volume of a water molecule predict whether a mixture of 1 mL of water in 100 mL of ethyl alcohol would show a Tyndall effect. Describe your reasoning.

THINK, SPECULATE, REFLECT AND PONDER

26. In the opening demonstration we made a tack drop to the bottom of a glass of water by adding a small amount of detergent to the water. Would an aluminum rowboat sink in a pond if enough detergent were added to the pond? Explain.

27. Would you expect a hydrogen ion (a proton) to exhibit kinetic energy through (a) vibrational motion? (b) rotational motion? (c) translational motion? Describe your reasoning.

28. When a piece of dry ice is heated in the open air, it is transformed directly into a gas. When a piece of paper is heated (to a high enough temperature) in the open air, it too is transformed (almost entirely) into a gas. Describe the difference between these two events.

29. In the winter, fallen snow sometimes disappears slowly from the ground even though the temperature remains below freezing for long periods. What is the process by which the snow vanishes?

30. A felt eraser removes chalk marks made on a chalkboard. Is the eraser acting as a detergent? Is it acting as a surfactant? Describe your reasoning.

31. What is the source of the mineral ions present in hard water?

32. Would you expect a soap to act as an effective detergent in sea water? Would you expect a synthetic detergent (an alkylbenzenesulfonate) to act as an effective detergent in sea water? Explain.

33. Why doesn't the identity or chemical behavior of *anions* present in water affect the water's hardness?

34. You have two samples of water. One sample is hard water and the other is soft water, but you don't know which is which. Explain how you could use a mixture of soap and distilled water to determine which sample is the hard water and which is the soft water.

35. Could you use a solution of alkylbenzenesulfonate detergent in distilled water instead of soap in distilled water to distinguish between the sample of hard water and the sample of soft water? Explain.

36. Again you have two samples of water, but this time both are hard water. One is very hard, with a high concentration of calcium ions, the other is not as hard, with a lower concentration of calcium ions. Show how you could use a solution of soap in distilled water and a dropper or other measuring device to determine which is the harder water.

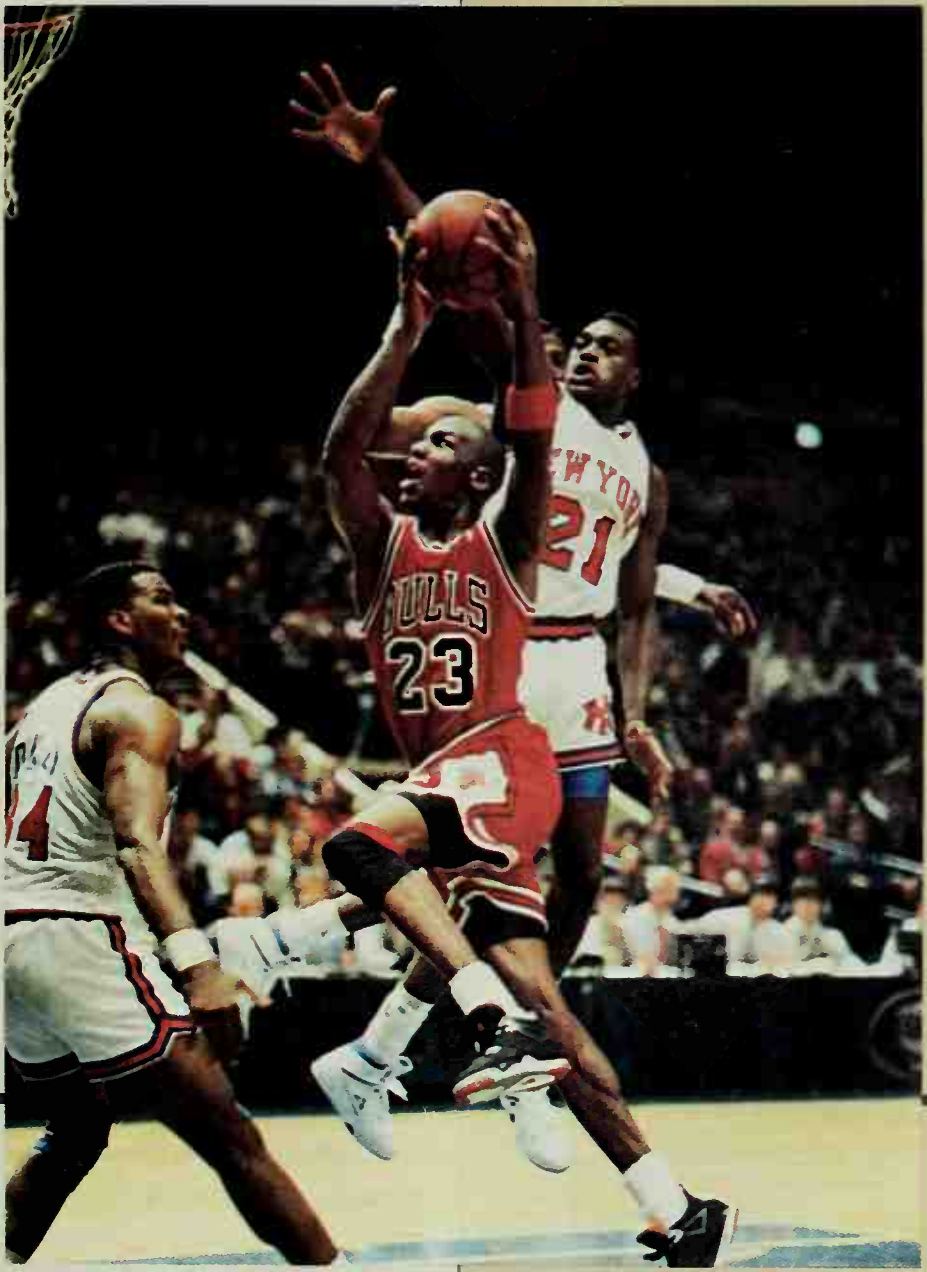
37. Describe how you might demonstrate the Tyndall effect to someone.

38. No colloidal dispersion of one gas in another is known to exist. Yet when gaseous HCl and gaseous NH_3 are mixed, a fog results that clearly produces a Tyndall effect. Explain why.

Food

12

FUEL FOR THE HUMAN ENGINE



Energy for living.

Warming Up with Work

You can duplicate the results of several of the greatest, most important experiments ever carried out in the history of science by just rubbing your hands together (Fig. 12.1). Rub them together lightly, without putting much effort into it. Not much happens. Now bear down. Press them together hard and rub vigorously. Put some energy into it and they get hot, instantly. The more effort you put into it, the hotter they get. *Be careful!* With enough work you could produce a blister.

What's heating them up? It's not warm blood rushing to the surface. You can demonstrate that by folding up two newspapers, placing one on a sturdy surface, and rubbing the other firmly against it. The harder you rub one against the other, the warmer they get. You can start a fire by rubbing two sticks together next to dry leaves. The more energy you put into it, the sooner the fire starts.

All these have one thing in common: Work generates heat. The more work you do rubbing your hands together, the hotter they get. The same holds true for newspapers, sticks, or anything else. That's what this chapter is about. Here we begin a series of discussions of where the energy of our own bodies comes from, how we connect the work that we do and the weight that we gain or lose with the energy that food provides, and how we relate both to measurements of heat. In earlier chapters we examined the energy of the nucleus, the energy we get from batteries, and the energy we get from the hydrocarbons of gasoline. Here and in the next few chapters we look at food, our most important source of energy. Whatever we do requires energy, and all of our bodily energy comes from just one source: the chemicals we call food.

Figure 12.1
Doing work generates heat. As you rub your hands together, they become warm.

12.1 Food, Chemicals, and Energy

Food, whatever else we may call it, is nothing but chemicals: chemicals that give us the material substances of our bodies and the physical energy to make them function. Of all the ordinary things we use in our everyday lives, these peculiar chemicals we call "food" are perhaps the most extraordinary. Before we turn to an examination of these unusual chemicals, we'll learn in this chapter a bit about the chemical and physical nature of the energy they bring to us, which we use for both the necessities and the pleasures of our lives.

Energy itself is simply the capacity to do work. When we work, we use energy; when we use energy, we do work. Earlier, in Chapter 6, we saw that we can *obtain* one kind of energy, electrical energy, *from* chemical reactions and, conversely, that we can *use* electrical energy to *produce* chemical work. Construct a Daniell cell from zinc, copper, and solutions of zinc sulfate and copper sulfate, and the resulting redox reaction

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu} + \text{energy}$$

produces a significant electrical voltage. The electrolysis of a sodium chloride solution, on the other hand, consumes electrical energy as it generates chlorine gas, hydrogen gas, and sodium hydroxide (Section 6.17).

Heat represents another form of energy produced by chemical reactions. In Chapter 8, for example, we saw how the internal combustion engine converts heat released by the combustion of hydrocarbons into the kinetic energy that moves vehicles. While energy comes in many forms—electrical, thermal, kinetic, and more — it's usually described most simply and most conveniently in terms of heat. We'll look now at the origins of our modern view of heat and we'll see how heat is related to work and to chemical energy.

QUESTION

Which of the following release energy and which consume energy: (a) burning charcoal, (b) a steak being cooked, (c) burning gasoline, (d) boiling water, (e) the evaporation of water from the ocean, (f) rain striking the ground? ____________

12.2 How Francis Bacon Died Attempting to Discover the Benefits of Refrigeration

In the history of science, ideas sometimes get lost for a while. Even an especially shrewd and perceptive idea, one that sits firmly on the right track and that could lead to great advances in our understanding of the world around us, can vanish for a period of time. It's ignored and it goes underground while other, less useful and sometimes more bizarre theories blossom, attract the best minds, and then wither away as the earlier, more productive idea comes forth once again to revitalize the exploration of science. That's exactly what happened to Francis Bacon's theory of heat.

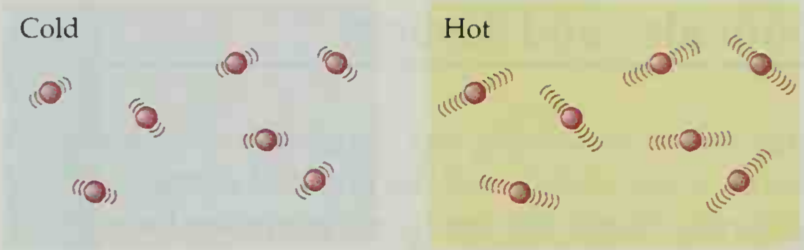


Figure 12.2
Heat results from the "brisk agitation" of the particles of matter.


Francis Bacon, who wrote that heat results from motion.

Francis Bacon, born in 1561 to a family of considerable influence and power in the court of Queen Elizabeth I of England, was a statesman, an essayist, and the father of inductive logic and of modern experimental science. Back in 1620, with considerable insight, he wrote about his idea that heat results quite simply from *motion*. "[The] very essence of heat," he proposed, "is motion, and nothing else." Heat, Francis Bacon concluded, is neither more nor less than a "brisk agitation" of the very particles that compose matter (Fig. 12.2).

He died in the practice of those very same investigative experimental methods that he championed so vigorously. On a snowy March day in 1626, while riding in his coach somewhat north of London, he was seized by the idea that cold—simple cold—might prevent the decay of meat. He stopped his carriage and rushed out into the snow to buy a freshly butchered piece of poultry. To test his theory, Bacon gathered up the snow with his bare hands and stuffed it into the animal. He never knew the results. Instead of discovering the modern technique of preserving food by refrigeration, Francis Bacon caught a chill during the experiment and soon died of bronchitis.

12.3 What Happened When Count Rumford Bored Cannons


Benjamin Thompson, Count Rumford, demonstrated that mechanical work produces heat.

Bacon's theory, that the basis of what we call *heat* lies in the motion of particles of matter, was overwhelmed for over 150 years by the *caloric* theory of heat. (*Calorie* and *caloric* come from the Latin *calor*, meaning "heat.") Until nearly the very last year of the 18th century most scholars believed that heat was a mysterious sort of fluid, which they called the "caloric," that flowed spontaneously from a hot body to a cooler one. This "caloric," which was proposed as the basis of heat, was a very strange substance. It had no weight (substances neither gain weight as they grow warm nor lose weight as they cool) but nonetheless occupied space (things tend to expand as they heat up and shrink as they cool) and permeated all things.

The scientific reign of this mysterious caloric fluid was ended by Benjamin Thompson, Count Rumford, with the help of several cannons. The story is a classic example of how a simple but elegant experiment can affect the course of science. Benjamin Thompson, born in 1753 in Woburn, Massachusetts, moved to England during the American Revolution. Later he traveled to continental Europe and, after several years of service to the Duke of Bavaria, he was named Count Rumford of the Holy Roman Empire.

While supervising the manufacture of cannons in the Bavarian city of Munich, the Count became intrigued by the amount of heat generated in the process of hollowing out their solid cores. It was well known at the time that boring out the cannons produced both a tremendous amount of heat and lots of very fine metal shavings. According to the prevailing caloric theory of heat,

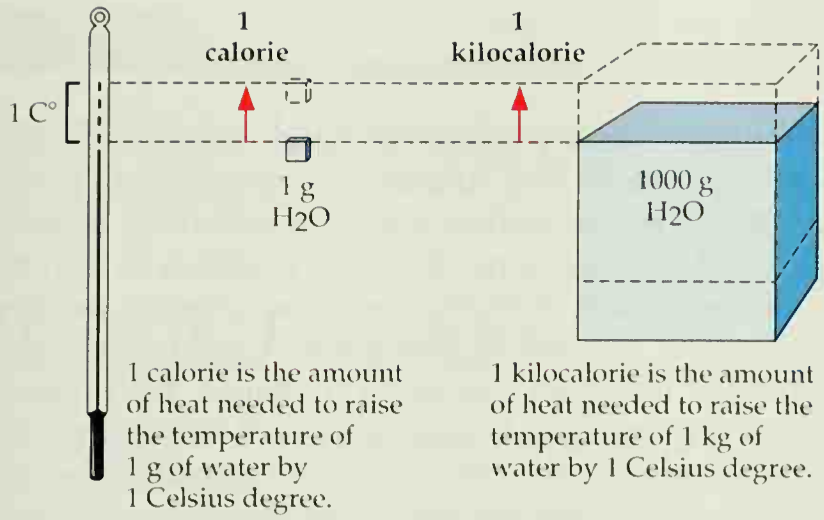


Figure 12.3
The calorie and the kilocalorie.

the solid metal of the (unbored) cannons supposedly had a greater capacity for holding the mysterious caloric fluid than did the finely ground shavings. As the metal of the cannons' cores was ground out into the very small particles of the shavings, it lost its capacity to hold the caloric. This lost caloric was perceived by the workers as heat, or so the explanations of the times would have it.

Count Rumford chose to test this theory with an ingenious experiment. With a well-dulled cannon borer (to produce a considerable amount of friction), he attacked a solid cannon blank immersed in 12 kg of cold water (26.5 pounds of water according to his report; the metric system was not in use at the time). Two and a half hours of steady grinding brought the water to a boil and generated 269 g of finely powdered metal (or 4145 grains as he measured it in the units of his day). Count Rumford then demonstrated that exactly the same amount of heat was required to raise the temperature, by 1°C, of both the 269 g of finely powdered metal and an equivalent 269 g of solid, unbored cannon metal. With this demonstration he showed that the metal had lost none of its capacity for holding heat as it was ground down. The great quantity of heat that raised the mass of water to boiling, then, did not come from a mysterious caloric fluid drained out of the cannon blank. It came, instead, from the two and a half hours of hard work done in grinding out the core of the cannon.

In 1798 Count Rumford described to the British Royal Society the results of this investigation into the nature of heat as "An Enquiry concerning the Source of Heat which is excited by Friction." Heat, the Count showed, isn't a substance at all. Heat comes from the vigorous movements of the grinding. Heat is the physical equivalent of work. Shades of Francis Bacon!

The caloric theory of heat has long since passed into the history of quaint scientific ideas, but it left us with the **calorie** as a unit of energy. A *calorie* is the amount of heat (or energy) needed to raise the temperature of one gram of water by one degree Celsius. One thousand calories, the amount of heat needed to raise the temperature of one *kilogram* of water by one degree Celsius, make up one *kilocalorie* (*kcal*) (Fig. 12.3).

A **calorie** is the amount of heat (or energy) needed to raise the temperature of one gram of water by one degree Celsius. A **kilocalorie** is 1000 calories.

QUESTION

How many kilocalories of work did the Count do simply in heating the 12 kg of water from 0 to 100°C in his two and a half hours of boring work? ____________

12.4 A Legacy of Joules

James Prescott Joule proved that all work produces heat and determined the relationship between the amount of work done and the quantity of heat produced.

A **joule** is the work done by one watt of electricity in one second. A joule is equivalent to 0.24 calorie.

Despite the elegance of Rumford's work with the cannons, wrong ideas die hard. It took more than Bacon's theory and Rumford's experiment to bring us to where we are today. Along the way other scientists reaffirmed repeatedly, by various experimental demonstrations, that heat is simply one form of work. At about the same time that Count Rumford was grinding out his cannons, for example, the English scientist Sir Humphrey Davy rubbed two chunks of ice against each other inside an evacuated container. Both pieces melted despite the fact that everything nearby was kept well below zero. In melting, the ice must have absorbed heat, but the heat that melted the ice could have come from nothing other than the very work of rubbing the two pieces of ice together. Once again, work is heat and heat is work.

It was left to the English physicist James Prescott Joule, who lived from 1818 to 1889, to establish that work of *any* kind has its exact equivalent in heat. Joule's legacy is twofold, a legacy of demonstration and a legacy of measurement. He *demonstrated* that mechanical work, electrical work, and chemical work all produce heat, and that the amount of heat produced is directly proportional to the amount of work done and is absolutely independent of any other factors. In Joule's own words, "The amount of heat produced by friction is proportional to the work done and independent of the nature of the rubbing surfaces." He also *measured*, quite accurately, the numerical ratio of the amount of work done to the amount of heat produced.

In his honor we have, in addition to the calorie, the **joule** as a unit of work or energy. One *joule* is now defined as the work done by one watt of electricity in one second. A joule is equivalent to just under 0.24 calorie. For our purposes

$$1 \text{ joule} = 0.24 \text{ calories}$$

$$1 \text{ calorie} = 4.2 \text{ joules}$$

While both the joule and the calorie provide us with convenient units for measuring work and energy, the joule is now favored for scientific measurements and calculations. Nonetheless, we'll stick to the calorie in our discussions of energy since it's still widely used in nutritional comparisons. We can always convert from one to the other by using the relationship described above.

Before leaving the giants of science and the work they did to provide us with our modern view of energy, let's look at the work you did in our opening demonstration. By rubbing your palms together you produced Bacon's "brisk agitation," the very friction that Rumford recognized as the source of heat generated in grinding out cannons. And you generated heat equally well by rubbing together the surfaces of your palms or the surfaces of two newspapers. Joule would have applauded. Moreover, the amount of heat you generated was directly proportional to how hard you rubbed, to the amount of work you did. Joule would have applauded even harder, doing more work himself and generating some heat. Once again, what we know of the universe comes directly from the questions we ask, the experiments we do, and our interpretation of the results. It's the scientific method in action.

QUESTION

How many joules of work are needed to raise the temperature of 12 kg of water from 0 to 100°C? For how many hours would this much energy keep a 40-watt light bulb glowing at full brightness? ____________________

12.5 The Calorimeter

The technique of measuring the amount of heat that is equivalent to a specific amount of energy or work is called *calorimetry* and the device used in carrying out the measurement is a *calorimeter*. You can carry out a very simple bit of calorimetry with a kilogram of water, a liter laboratory flask, a thermometer, and a lighter or a candle. Measure the temperature of the kilogram of water in the liter flask, then heat the water for a short time and measure its temperature again. The increase in temperature, in Celsius degrees, gives you the number of kilocalories absorbed by the kilogram of water in the flask (Fig. 12.4). Very roughly, heating for 1 minute adds about 1 kilocalorie of energy to the water in the flask. The exact value depends, of course, on the specific conditions and techniques you use.

Figure 12.4

A calorimeter is an instrument for measuring quantities of heat absorbed or released.

QUESTION

Assume that the calorimeter just described is set up in such a way that heating the water in the flask for 1 minute adds exactly 1 kilocalorie to it. If the flask contained 500 g of water rather than 1 kg, what would the increase in temperature be after 1 minute of heating? ____________________

12.6 The Storehouse of Chemical Energy

The burning hydrocarbons of the lighter or the candle release energy in the form of heat just as the burning hydrocarbons of gasoline release energy, again as heat, in the cylinder of the internal combustion engine. Following are balanced chemical equations for the combustion of the butane of the lighter and of the pentane of gasoline:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O + \text{energy}$$

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O + \text{energy}$$

The actual amounts of energy released by the combustion of various alkanes appear in Table 12.1. Naturally, the values shown in this table are determined by a much more accurate form of calorimetry than the one described in Section 12.5.

Even at first glance we can see a direct connection between the molecular weight of the alkane molecule and the amount of heat it releases on combustion. Clearly, the larger the alkane molecule—the greater its carbon content—the more energy it releases as it burns. But the basis for this relationship isn't obvious. The combustion of one mole (or one molecule) of *n*-pentane

TABLE 12.1 Heats of Combustion of Alkanes (as Gases)

Alkane	Molecular Formula	Approximate Number of Kilocalories Released per Mole of Hydrocarbon Undergoing Combustion
Methane	CH_4	213
Ethane	C_2H_6	373
Propane	C_3H_8	531
n-Butane	C_4H_{10}	687
n-Pentane	C_5H_{12}	845

releases very nearly four times as much energy as the combustion of one mole (or one molecule) of methane. Yet the pentane molecule contains 5 times as many carbons, 3 times as many hydrogens, and 3.4 times as many atoms (of carbon and hydrogen combined) as the methane molecule. Superficially, there doesn't seem to be anything about the pentane and methane molecules that accounts for the ratio of 4:1 in their release of energy on combustion. Similarly, there's no obvious, quantitative correlation between the way any of the other alkane molecules are put together and the amount of energy they release.

Yet a very real, quantitative correlation with molecular structure does exist. You can find it by working through the following:

1. How many covalent bonds are there in a molecule of methane? When methane burns, how many kilocalories are released per mole of covalent bonds in methane?
2. How many covalent bonds (C—H and C—C bonds, combined) are there in a molecule of ethane? How many kilocalories are released per mole of covalent bonds in ethane?
3. What values are produced by similar calculations for propane, *n*-butane and *n*-pentane?

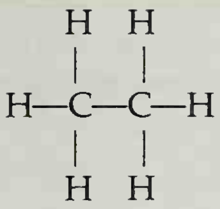
One mole of methane releases 213 kcal. Since each molecule of methane contains 4 covalent bonds, each mole of methane must contain 4 mol of covalent bonds, all of them C—H bonds. For methane, then, we answer the question by dividing 213 kcal per mole of CH_4 by 4 mol of covalent bonds per mole of CH_4, as in the following illustration:

$$\frac{213 \text{ kcal}}{\text{mol of } CH_4} \times \frac{1 \text{ mol of } CH_4}{4 \text{ mol of covalent bonds}} = 53.2 \frac{\text{kcal}}{\text{mol of covalent bonds}}$$

EXAMPLE HOW MUCH ENERGY?

How much energy does the combustion of ethane release per mole of covalent bonds?

From Table 12.1 we learn that the combustion of ethane releases 373 kcal/mol. Each molecule of ethane contains 7 covalent bonds: 6 C—H bonds and 1 C—C bond.



$$\mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}H}$$

ethane

Since each molecule of ethane contains 7 covalent bonds, each mole of ethane must contain 7 mol of covalent bonds. For ethane,

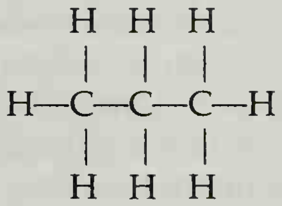
$$\frac{373\ \text{kcal}}{\text{mol of CH}_3\text{—CH}_3} \times \frac{1\ \text{mol of CH}_3\text{—CH}_3}{7\ \text{mol of covalent bonds}}$$

$$= 53.3\ \frac{\text{kcal}}{\text{mol of covalent bonds}}$$

EXAMPLE AND NOW HOW MUCH?

How much energy does the combustion of propane release per mole of covalent bonds?

Table 12.1 reveals that the combustion of propane releases 531 kcal/mol of propane. Molecular propane contains a total of 10 covalent bonds: 8 C—H bonds and 2 C—C bonds.



$$\mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}H}$$

propane

For propane,

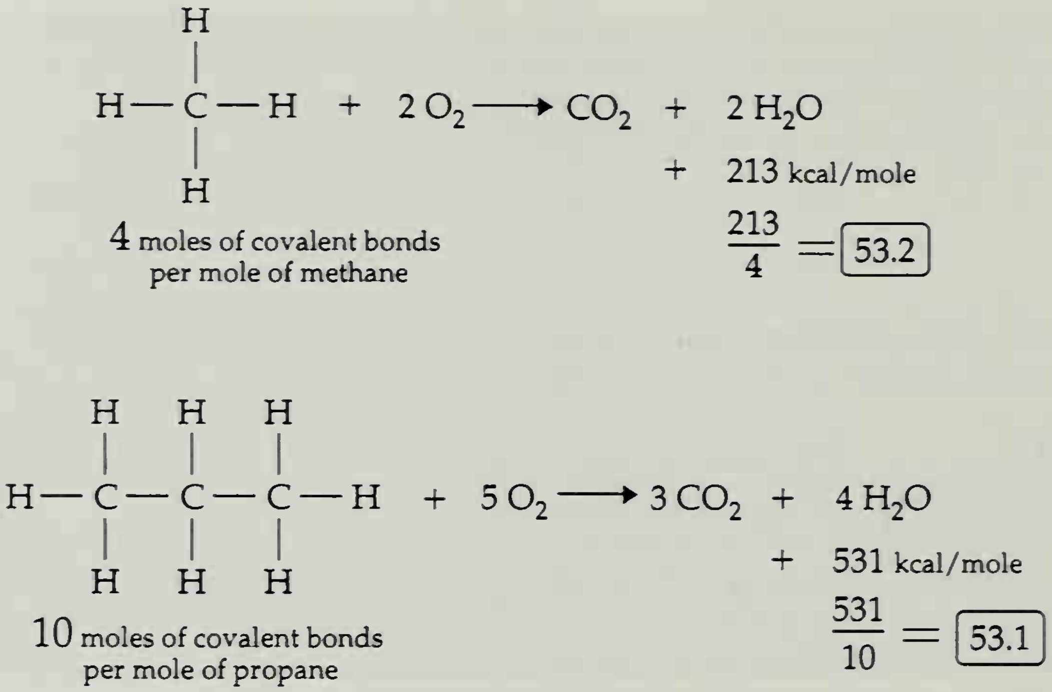
$$\frac{531\ \text{kcal}}{\text{mol of CH}_3\text{—CH}_2\text{—CH}_3} \times \frac{1\ \text{mol of CH}_3\text{—CH}_2\text{—CH}_3}{10\ \text{mol of covalent bonds}}$$

$$= 53.1\ \frac{\text{kcal}}{\text{mol of covalent bonds}}$$

Similar examination of *n*-butane and *n*-pentane gives a value of 52.8 for each of these two alkanes.

In each case we find that the combustion of an alkane of Table 12.1 releases very nearly 53 kcal per mol of covalent bonds (Fig. 12.5). The consistency of this value for methane, ethane, propane, and other alkanes suggests that we've found an important generalization: *Almost all of the chemical energy contained in any substance is stored in its chemical bonds.*

Figure 12.5
Chemical bonds as the storehouse of chemical energy.



The generalization is true and useful, but the way we reached it was something of a lucky accident. Actually, while all chemical bonds are storehouses of energy, some retain more energy than others. If, in any specific chemical reaction, the total amount of energy contained in all the bonds of all the products is *less* than the total amount of energy in all the bonds of all the reactants, the difference in energy between the product bonds and the reactant bonds is liberated as heat. Heat is released by the reaction because some of the energy stored in the bonds of the reactant molecules is liberated to the surroundings (as heat) when the reaction occurs.

When an alkane burns, for example, the total energy of all the O=C=O bonds and all the H—O—H bonds among the products is less than the total energy of all the C—H and C—C bonds of the alkane and all the O=O bonds of the oxygen, and so the reaction releases the difference in energy as heat. A reaction of this sort, one that releases energy as it proceeds, is called **exothermic**.

An **exothermic** reaction is a reaction that releases heat as it proceeds.

Conversely, if the total energy of all the bonds of all the products is *greater* than that of all the reactants, the reaction must absorb energy from its surroundings as it progresses. In this case the chemicals absorb energy from their surroundings and store it as the energies of their bonds. This kind of reaction is **endothermic**. Almost all the chemical reactions that occur spontaneously in our everyday world are *exo*thermic reactions. Examples include the burning of gasoline, charcoal, and candle wax and the discharge of batteries.

An **endothermic** reaction is a reaction that absorbs heat as it proceeds.

Spontaneous *endo*thermic chemical reactions are hard to find in our common experience. One endothermic process familiar to all of us is the melting of ice. Ice absorbs energy—heat—as it melts. Pack some ice around cans of soda and as the ice melts it absorbs energy from the cans, cools them, and keeps them cold as long as there's any ice left. It's a spontaneous endothermic process, although we might consider it to be an example of a physical change rather than a chemical change since it doesn't involve making or breaking chemical bonds.

Notice that since it's the difference in bond energies between the reactants and the products of a reaction that determines whether a reaction will be endo- or exothermic, the reverse of any exothermic reaction must be an endothermic reaction. The reactants of one direction become the products of the other. The reverse of alkane combustion, for example, must be endothermic.

exothermic: $CH_4 + 2O_2 \rightarrow CO_2 + H_2O$

endothermic: $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

Each different kind of chemical bond possesses a different bond strength and so any calculation of the amount of energy liberated or absorbed in a chemical reaction must take each of the individual bond strengths into account. It happens, though, that the various bond strengths of alkanes, oxygen, carbon dioxide, and water interplay in such a way that we can simplify matters and use the value of 53 kcal/mol of covalent bonds of the alkane for a good estimate of the heat liberated in alkane combustion.

QUESTION

Using the value of 53 kcal/mol of covalent bonds, calculate the quantity of heat liberated by the complete combustion of 1 mol of *n*-hexane. The measured value is 995 kcal/mol. What is the percentage difference between your calculated value and the measured value? ____________________

12.7 Energy for the Human Engine

We can think of the human body as an incredibly complex engine that operates in the physical world like any other engine, using energy to perform work and functioning always under the constant supervision of every known law of the physical universe. Just as hydrocarbons provide the fuel for lighters, candles, stoves, furnaces, electric generators, and auto engines, the chemicals of food furnish the fuel for our bodies. In one important sense, then, our bodies are like the internal combustion engines of cars. Each uses fuel to produce energy and to do work. Gasoline fuels our cars; food fuels our bodies.

Understanding this, we can penetrate the body's complexity by taking a fairly simple and straightforward approach. We'll examine the human body as if it were an ordinary engine, one that acquires, stores, and uses energy, always in complete accordance with the universal laws of the physical sciences. In brief, we'll look at this biological machine as if it were no more than an engine that uses food as fuel, expends energy in doing work in various forms, and stores its excess energy as fat. And with all this we'll think of energy in terms of heat.

Food: Fuel for the human engine.

QUESTION

To continue the analogy between the human engine and a car's engine, what's the bodily equivalent to filling a car's tank with gasoline? ____________________

12.8 The Energy Equation


Eating: Energy In.

One of the physical laws that controls the operation of all machines is the Law of Conservation of Energy, which states that energy can neither be created nor destroyed but can only be converted from one form of energy into another (Section 4.12). (At the subatomic level, matter can certainly be converted into energy and energy can be transformed into matter, as we saw in the chapters on atomic energy. For this discussion, though, we'll stick to the larger region of the physical world in which we feel more at home and in which the Law of Conservation of Energy holds well.) With energy being conserved, *all* the energy that comes into our bodies as food must be accounted for. It must be either used or stored. We can state this requirement in mathematical terms as an *Energy Equation* that relates energy consumption (from food), energy expenditure (in several ways we'll soon examine), and energy storage (as body fat):

$$\text{Energy In} = \text{Energy Out} + \text{Energy Stored}$$

To put the whole, sometimes complex relation between body energy and human nutrition into simple terms, either we burn up the energy of the food we eat or we store it as fat. The Energy Equation tells us that if we want to lose weight we have to make sure that "Energy Out" is larger than "Energy In." In more common terms this means exercising more and/or eating less. (Of course to *gain* weight we eat more and/or exercise less so that "Energy In" becomes larger than "Energy Out.")

One more matter needs to be dealt with. As we saw in Section 12.3, physical scientists define the *calorie* as the energy (or amount of heat) needed to raise one gram of water by one degree Celsius. For many years, and largely in fields outside the physical sciences, this calorie has been known occasionally as the "small calorie." In a parallel fashion the kilocalorie, 1000 cal, is sometimes called the "large calorie." This same kilocalorie or "large calorie" is also a common unit in the field of nutrition, where it's always written as a capitalized *Calorie* and abbreviated as a capitalized *Cal*. Each of these Calories of nutritional energy, then, represents the same amount of energy as 1 kcal, or 1000 of the "small" calories.

In actual practice, there's seldom any confusion between the Calorie (1000 cal) and the calorie. To avoid mistaking one for the other, we'll take care never to begin a sentence with the word "calories" unless the meaning is quite clear. When the word is capitalized in these discussions we'll know that we're referring to the nutritionist's Calorie.

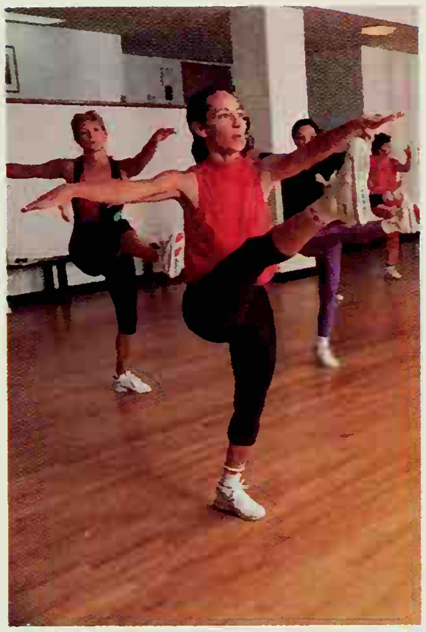
QUESTION

(a) How many calories are there in 0.1 Calorie? (b) How many Calories are there in 0.1 calorie? ________________

12.9 Energy Out: Exercise, Specific Dynamic Action, and Basal Metabolism

The human body consumes energy in three different ways, through

- exercise,
- specific dynamic action, and
- basal metabolism.



Exercise, one form of energy expenditure.

Exercise, the path we know best, includes more than the standard pushups, jogging, swimming, tennis, and the like. Exercise, in the sense we're using here, is the composite of all the physical work we do with our bodies. The rate of energy expenditure through exercise ranges from the most vigorous physical activities, such as a strenuous game of tennis or competitive swimming, to just sitting, letting time pass. (Even while sitting we're exercising in this particular sense. We're burning up a minute amount of energy as we use muscles to keep our balance and to keep our head up and eyes open.) We use our muscles, more or less strenuously, in an enormous range of physical activities, and we do an equally great range of work in all these activities. Table 12.2 presents some estimates of the rates at which we use energy in various activities. Table 12.3 presents the numbers of Calories of typical foods and their equivalents in exercise.

Specific dynamic action, often abbreviated *SDA*, accounts for the energy consumed in digesting and metabolizing food and converting its energy into our own, for use through exercise and basal metabolism. It's the price we pay, in energy, for extracting energy from food. In this sense it's analogous to the energy cost of refining petroleum into gasoline, heating oil, diesel fuel, and other products through distillation, isomerization, and similar refinery processes (Chapter 8). It takes energy to refine crude petroleum into the

TABLE 12.2 Approximate Rates of Energy Expenditure for a 70-kg (154-lb) Person

Level	Examples	Calories Expended	
		Per Minute	Per Hour
Very light	Sitting, reading, watching television, writing, driving	1.0–2.5	60–150
Light	Slow walking, washing, shopping, light sports such as golf	2.5–5.0	150–300
Moderate	Fast walking, heavy gardening, moderate sports such as bicyling, tennis, dancing	5.0–7.5	300–450
Heavy	Vigorous work, sports such as swimming, running, basketball, and football	7.5–12.0	450–720

TABLE 12.3 Calorie Content of Typical Foods and Their Exercise Equivalents for a 70-kg (154-pound) Person

		Time (Minutes) Spent				
Food (Portion)	Calories	Lying Down, Resting	Walking	Bicycle Riding	Swimming	Running
Apple (large)	101	78	19	12	9	5
Bacon (2 strips)	96	74	18	12	9	5
Carrot, raw	42	32	8	5	4	2
Chicken, fried ($\frac{1}{2}$ breast)	232	178	45	28	21	12
Egg, boiled	77	59	15	9	7	4
Egg, fried	110	85	21	13	10	6
Halibut steak ($\frac{1}{4}$ pound)	205	158	39	25	18	11
Hamburger sandwich	350	269	67	43	31	18
Malted milk shake	502	386	97	61	45	26
Orange juice (1 glass)	120	92	23	15	11	6
Pizza, cheese ($\frac{1}{8}$)	180	138	35	22	16	9
Potato chips (1 serving)	108	83	21	13	10	6
Soda (1 glass)	106	82	20	13	9	5
Tuna fish salad sandwich	278	214	53	34	25	14
Shrimp, French fried (1 piece)	180	138	35	22	16	9

products we can use to generate energy. Similarly, it takes energy (SDA) to refine food into the chemical materials our bodies use in generating our own energy.

We can sometimes sense SDA in operation as we grow a little warmer and find our heart beating a bit faster after a meal. The warmth and the higher pulse are both signs that our body is hard at work digesting food and using up energy through SDA. (Drowsiness after a large meal comes from the diversion of blood from the brain to the digestive system. The body is working hard to process all the fuel that's just been brought in and—first things first—digestion takes momentary precedence over mental alertness.)

The actual amount of energy lost through SDA depends on what we're eating. For fat it's about 4% of the energy content of the food; for carbohydrates, roughly 6%; for protein, around 30%. But measuring SDA is not a simple matter. A complex interaction among our foods causes the digestion of one foodstuff to affect the SDA demanded by another. As a result, the total SDA resulting from any particular meal isn't necessarily the sum of the individual SDAs we might assign to each of the macronutrients of the meal. As a very rough estimate, about 10% of the energy we get from food is spent in SDA. That is, something like 10% of food energy goes toward the very act of extracting and using the remaining 90%.

Basal metabolism, the third of the three routes, accounts for all the work that goes on inside our bodies just to keep us alive. It's the energy we spend as our heart pumps, as our lungs expand and contract, and as the liver, the kidneys, and other major organs work to maintain life.

The standard technique for measuring basal metabolism determines our total energy output in the absence of both exercise and specific dynamic action. In this measurement a person lies at rest and awake, after 12 hours of fasting. In a healthy adult the energy spent in this condition—through basal metabolism—amounts to roughly one Calorie per hour per kilogram of body weight. Basal metabolism increases with any bodily stress, desirable (such as pregnancy or lactation) or not (illness, for example).

Lying at rest eliminates from this measurement virtually all energy expenditure by exercise. The added 12-hour fast precludes energy expenditure through specific dynamic action.

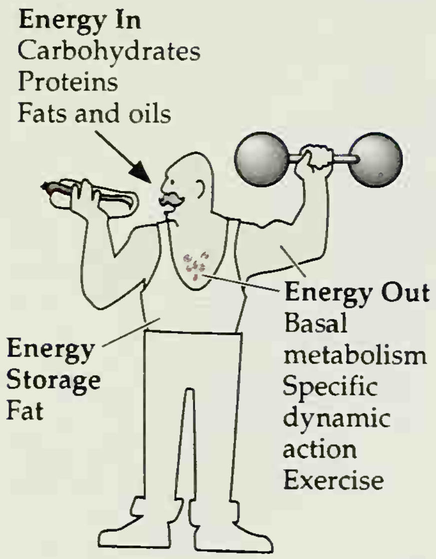
Another useful measure of energy expenditure is *resting metabolism*, which represents the combination of basal metabolism and SDA. In effect, resting metabolism measures our entire energy output excluding the various forms of exercise we do throughout the day.

QUESTION

(a) A person in normal health and weighing 165 pounds (75 kg) fasts for 36 hours while lying still in bed. What is the total number of Calories lost during the last 24 hours of the fast? (b) Now suppose that this same person is leading a perfectly normal life, working and exercising in various ways, and also consuming a total of 3000 Cal in all meals and snacks during the day and evening. Can you calculate the total amount of energy lost through resting metabolism in the 24-hour period? If your answer is "yes," what is the calculated resting metabolic output of energy? If it's "no," explain why not. ____________________

12.10 Energy In: The Macronutrients

Figure 12.6
Energy and the human machine.



And where does all this energy come from? From the *macronutrients* of our food. These substances we call macronutrients are the three classes of chemicals making up the great bulk of our food supply, the chemicals that serve as the only source of energy for the human machine. Specifically, they are the food chemicals we classify as

- fats and oils,
- carbohydrates, and
- proteins.

Through the elegant, intertwined complex of chemical reactions that constitute human metabolism, the chemical energy of these chemical compounds becomes transformed into the human energy of our lives (Fig. 12.6).

The actual quantity of energy provided by each of these classes of macronutrients is well known. Fats and oils furnish 9 Cal per gram, carbohydrates 4 Cal per gram, and proteins 4 Cal per gram. The amount of energy each of these chemicals delivers to our bodies is independent of the kind of food in

Nutrition labels reveal the quantities of each of the macronutrients in processed foods and the number of Calories in an average serving.

which it occurs and is also independent of the presence or absence of other macronutrients. One gram of fat or oil provides 9 Cal whether it comes from, say, butterfat, peanuts, beef, or corn. A meal containing 10 g of fat, 15 g of carbohydrate, and 20 g of protein, for example, would deliver to our bodies

$$\left(10 \text{ g fat} \times \frac{9 \text{ Cal}}{\text{g fat}}\right) + \left(15 \text{ g carbohydrate} \times \frac{4 \text{ Cal}}{\text{g carbohydrate}}\right)$$
$$+ \left(20 \text{ g protein} \times \frac{4 \text{ Cal}}{\text{g protein}}\right) = 90 \text{ Cal (from fat)}$$
$$+ 60 \text{ Cal (from carbohydrate)} + 80 \text{ Cal (from protein)} = 230 \text{ Cal}$$

EXAMPLE MORE FAT

Suppose we change our illustration by increasing the amount of fat in the meal by 5 g and keeping the weights of the carbohydrate and protein the same. That is, we go from 10 to 15 g fat. What's the new energy content?

At 9 Cal/g of fat, we've added

$$5 \text{ g fat} \times \frac{9 \text{ Cal}}{\text{g fat}} = 45 \text{ Cal}$$

The meal now delivers $230 + 45 = 275$ Cal.

EXAMPLE COMPARING CALORIES

Now suppose that instead of adding 5 g of fat to the meal, we add 5 g of carbohydrate. What's the new energy content?

At 4 Cal/g of carbohydrate, we've added

$$5 \text{ g carbohydrate} \times \frac{4 \text{ Cal}}{\text{g carbohydrate}} = 20 \text{ Cal}$$

The meal now delivers $230 + 20 = 250$ Cal.

Adding fat to our diet increases the number of calories we consume far more quickly than adding carbohydrate or protein.

In later chapters we'll examine more closely the chemistry of the fats and oils, carbohydrates, proteins, and still other food chemicals. We'll also take a closer look at how we store energy as body fat. As we close this chapter, though, we emphasize that at the level of 9 Cal per gram, fats and oils provide the most concentrated form of energy available, 2.25 times as much as carbohydrates or proteins (each of which, you'll recall, yields 4 Cal/g). Alcohol, or more correctly *ethyl alcohol* (Section 5.5), another substance that many of us consume along with food, also provides dietary energy. At 7 Cal per gram it's a bit closer to fats and oils than to carbohydrates and proteins in the number of Calories per gram it can add to our total intake.

QUESTION

The nutrition information panel on a can of a typical commercial chicken noodle soup reveals that one serving contains 13 g of protein, 15 g of carbohydrates, and 5 g of fat. (a) How many Calories does one serving of this soup provide? (b) How many hours of basal metabolic activity would this provide to the normal, healthy, 165-pound person mentioned in the question at the end of Section 12.9? ______________

PERSPECTIVE: Counting Calories, Math or Myth?

"I can eat as much as I want and I don't gain a pound, and I never exercise."

"There's a special enzyme in grapefruit that burns up fat calories."

"One calorie from candy puts more weight on you than one calorie from carrots."

"You burn up calories of the food you eat for breakfast, but calories you eat before you go to bed turn into fat."

"Calories don't count."

How many times have you heard each of these? Are calories a myth or do they add up relentlessly, like numbers on a computer? As usual, there are few simple, clear-cut answers and plenty of complexities, coupled with perceptions that may fool us. The person who eats everything and never gains a pound, without exercising, may be running up and down steps far more than it appears, or may not think of hours spent bending down and straightening up while gardening as "exercise," or may simply have an unusually high basal metabolism.

No, there's no special enzyme in grapefruit or anything else that magically burns up calories. Calories are a measure of energy and the only way to expend energy is to do work. The physical laws of the universe take care of that. You can burn calories quickly by running fast up a steep hill or slowly by just lying down and breathing slowly. Either way you have to use energy to burn calories, at one rate or another.

Do you burn up breakfast calories more quickly than dinner calories? Sure you do, if you go to work after breakfast and work hard all day long, but then go to sleep shortly after dinner. A day's work uses up more energy, and more calories, than a night's sleep.

Do calories count? Is every calorie just like every other? "Yes" to both questions, but with a twist. In the sense that each and every calorie represents exactly the amount of energy it takes to heat 1 g of water by 1°C, every calorie is exactly like every other. Every beaker of water in the universe is equally ready to be warmed up by the same amount, 1°C per gram of water for every calorie added. But in the sense that our bodies are more complex than containers of water, each of us responds a shade differently to the universe we live in. Each of us can respond just a bit differently to a food calorie. Differences in individual basal metabolism take care of that. So do subtleties of specific dynamic action. We've already seen that the macronutrients can interact as they are digested, with one affecting the specific dynamic action of another. Still, the Energy Equation in Section 12.8 does hold fast for everyone. Energy In does equal Energy Out plus Energy Stored. There's no way around that.

What's an eater to do? First, remember that a calorie is a precisely defined unit of energy. Calories add up neatly in beakers of water and maybe a bit less neatly in our own bodies. Nonetheless, they do accumulate.

Next, remember that your body is neither a beaker of water nor a computer. It's an individual, complex structure of blood, tissue, hormones, and bones that follows all the rules of the physical universe, but sometimes in its own characteristic way. Eat sensibly and moderately and respect your own complexity. Calories do count, but the arithmetic can be fuzzy.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

______ is a form of ______ , which is simply the capacity to do ______ . The ______ , which is the amount of energy needed to raise the temperature of ______ by ______ , is a common unit of nutritional energy. Another unit, the ______ , is more widely used in the physical sciences. It is the amount of work done by 1 watt of ______ in 1 second. Chemical energy is stored as the energy of ______ . If the total amount of energy stored among all the ______ of a chemical reaction is less than the total amount of energy stored among the ______, energy is released as the reaction occurs. The actual measurement of energy and work is accomplished through the technique of ______ .

Carbohydrates, proteins, and ______ are the macronutrients that provide us with all of our bodily energy. We use the energy that they and our other macronutrients provide to do physical work, for the ______ necessary to the digestion and metabolism of our food and for the ______ that keeps our organs running and our bodies alive.

1000 g of water
1° Celsius
basal metabolism
Calorie
calorimetry
chemical bonds
electricity
energy
fats and oils
heat
joule
products
reactants
specific dynamic action
work

2. Identify each of the following and describe briefly his contribution to our understanding of the physical nature of heat: (a) Francis Bacon; (b) Benjamin Thompson, Count Rumford; (c) Sir Humphrey Davy; (d) James Prescott Joule.

3. Write the Energy Equation and describe each of its terms.

4. Using the terms of the Energy Equation, describe the conditions under which a person's weight (a) increases; (b) decreases; (c) remains constant.

5. Is it possible for a person to *gain* weight even while eating less and consuming fewer calories? Explain.

6. What are the three processes by which we consume or burn the energy provided by food?

7. What factors or conditions can affect a person's basal metabolism?

8. What is *resting metabolism*?

9. Why do people sometimes feel warm after a heavy meal?

10. What are the three macronutrients of our foods?

11. Which macronutrient contributes the greatest amount of energy per gram to the body?

12. How do our bodies store unused energy?

13. What chemical name is applied to the class of compounds we use to store energy?

14. What consumer product is made from the kinds of compounds we use to store energy within our bodies?

15. Write a balanced equation for (a) an exothermic chemical reaction and (b) an endothermic chemical reaction.

16. Label each of the following as exothermic or endothermic:

a. burning hydrocarbons of a candle
b. nuclear fission
c. steam condensing to water
d. ice melting to water
e. electricity passing through the filament of a light bulb
f. water boiling to steam
g. nuclear fusion
h. chlorine gas reacting with sodium metal
i. electrolysis of water to hydrogen and oxygen

17. Describe how a calorimeter works.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

18. How many calories does it take to heat 25 g of water from 40 to 50°C?

19. How many calories are released as 25 g of water cools from 60 to 50°C?

20. What is the final temperature of the 50 g of water formed as 25 g of water at 60°C is mixed with 25 g of water at 40°C? Assume that all of the heat released by the warmer water is absorbed by the cooler water.

21. What is the final temperature of the 50 g of water formed as 10 g of water at 60°C is mixed with 40 g of water at 40°C?

22. How many Calories are furnished by 1 g of each of the following: (a) protein, (b) carbohydrate, (c) fat or oil?

23. Many food labels now proclaim that they are fat-free to a specified percentage. If a label claims that a processed lunch meat is "80% fat-free," what percentage of the calories of that lunch meat comes from fat? (Assume that if the meat is 80% fat-free, it contains 20% fat and the rest of it is a combination of carbohydrate and protein.)

24. The following are the amounts of each of the macronutrients provided by one standard serving of several commonly available packaged foods. How many Calories does one serving of each of these foods provide?

a. Bumble Bee chunk light tuna in water

carbohydrate	0 g
protein	12 g
fat	2 g

b. V8 vegetable juice

carbohydrate	9 g
protein	1 g
fat	0 g

c. Campbell's chicken broth

carbohydrate	2 g
protein	3 g
fat	2 g

d. Farm Best low-fat milk

carbohydrate	11 g
protein	8 g
fat	5 g

e. Breyers mint chocolate chip ice cream

carbohydrate	17 g
protein	3 g
fat	9 g

f. Planter's Sweet-N-Crunchy peanuts

carbohydrate	15 g
protein	4 g
fat	8 g

g. Charles Chips potato chips

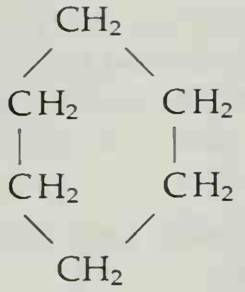
carbohydrate	15 g
protein	1 g
fat	10 g

25. How long would it take a 70-kg person to burn up the energy provided by one standard serving of each of the foods (a–g) in Exercise 24 through the operation of basal metabolism alone?

26. How long would it take this same 70-kg person to burn up the energy provided by one standard serving of each of the foods (a–g), in Exercise 24 through the energy expenditure of 5 Cal per minute during a moderate exercise such as brisk walking?

27. A 100 watt electric light bulb was placed in a calorimeter and turned on. After a period the temperature of 1000 g of water in the calorimeter rose by exactly 10°C. Using the information in Section 12.4, calculate the length of time the light bulb was on.

28. Using the data in Section 12.6, calculate the quantity of heat liberated on combustion of 1 mol of *cyclohexane*:



Experimentally, combustion of cyclohexane is found to liberate 937 kcal/mol. What is the percentage difference between this observed value and the value you calculated?

29. Suppose you weigh 154 pounds and have just eaten a lunch of consisting of a glass of orange juice, a hamburger, a malted milk shake, and a serving of potato chips. How long would you have to run to use up the calories you absorbed from the lunch? (Refer to Table 12.3.)

30. Repeat Exercise 29, but this time for a lunch consisting of a glass of orange juice, a tuna fish sandwich, a raw carrot, and a glass of soda.

31. Suppose gasoline costs $1.00 per gallon and you have a car that gives you 10 miles per gallon on very short trips. You shop at a store that's 0.5 mile away (for a round trip of 1.0 mile). Assuming that the cost of a trip by car is due entirely to the gasoline you use, what does it cost you to drive the round trip to the store?

32. Repeat Exercise 31 with the following changes. Suppose you walk to the store instead of driving, and you can walk the mile in half an hour. Assuming that a fast-food hamburger costs you $1.00, and that you use the calories you get from the hamburger for your walking, what does it cost you—in terms of what you paid for the hamburger calories—to walk the round trip to the store?

33. How does the cost of gasoline's energy for transportation compare with the cost of food energy for transportation? (Refer to your answers to Exercises 31 and 32.)

THINK, SPECULATE, REFLECT, AND PONDER:

34. Do you think the comparison of Exercises 31 through 33 is fair and reliable? Explain.

35. A person who is ill with a fever is releasing energy more rapidly than normal. This energy raises the body temperature, which we detect as the fever. Which one of the three energy expending processes increases as a result of the illness?

36. You have an electric hot plate that transfers heat directly to whatever is on it, with negligible losses. How could you determine the wattage rating of the hot plate experimentally?

37. It takes energy to accelerate a car from zero to 50 miles an hour. Through the Law of Conservation of Energy we know that the kinetic energy of the car traveling at 50 miles an hour has to come from the transformation of some other form of energy into the car's kinetic energy. Where does the car's energy come from? It also takes energy to bring a car traveling at 50 miles an hour to a complete stop. The kinetic energy of the car has to be transformed into some other form of energy. Into what kind of energy is the car's kinetic energy transformed as it slows to a stop?

38. Table 12.3 shows that a fried egg provides 110 Cal, while a boiled egg gives us 77 Cal. Since eggs are often fried in butter, margarine, or vegetable oil, what do you suppose is the source of the additional calories in the fried egg. What do you think would be the calorie content of an egg fried without the use of butter, margarine, or oil (in a nonstick frying pan)?

39. Describe a device or a process by which the following transformations occur:

a. chemical energy is transformed into electrical energy
b. chemical energy is transformed into heat
c. chemical energy is transformed into kinetic energy
d. electrical energy is transformed into chemical energy
e. electrical energy is transformed into heat
f. electrical energy is transformed into kinetic energy
g. kinetic energy is transformed into electrical energy
h. kinetic energy is transformed into heat

40. Francis Bacon, Sir Humphrey Davy, and Count Rumford used the scientific method in the investigations described in this chapter. State the question each asked and describe the experiment each devised to answer the question, the results each obtained (or would have obtained, had Bacon lived), and the conclusions drawn.

41. Using commonly available materials, how would you demonstrate that (a) work produces heat and (b) heat can be used to do work?

42. Do you consider water to be a food? Explain.

Fats and Oils

13

THE ENERGY WE RUN WITH

Body fat.

Iodine and Cooking Oils

It's easy to spot the difference between a fat (butter, for example, or the solid pieces of grease on assorted cuts of meat) and an oil (such as corn oil or olive oil): Fats are solids and oils are liquids. But two different oils—each from a different source, yet each a liquid—can differ also, often in subtle ways that aren't clear at first. Their more obscure differences can be as important to our health as the obvious difference between either one of them and a fat. Here's how to see one of these subtle differences between two different oils.

Put a little safflower oil in one small glass or flask and put the same amount of peanut oil in another. (Olive oil also works well, but peanut oil is often closer to the color of the safflower oil. Changes in color are important in this demonstration.) Now add a few drops of a drugstore iodine solution to each. (Use the same kind of tincture of iodine you used in the opening demonstration in Chapter 6.) It's important to add about the same amount of iodine to each of the oils. A small dropper can be convenient for this. You can use 10 to 20 mL (a little less than a fluid ounce) of each of the oils, along with a few drops of the iodine solution. The iodine solution won't dissolve in the oils, so swirl each carefully and gently to disperse the iodine in small droplets.

Now let each mixture of oil and iodine stand for a while. How long depends on the temperature. If a change does not occur within about 10 minutes at room temperature, heat the oils *very gently*, so they don't splatter. Heating them simultaneously ensures that they are both heated to the same temperature for the same amount of time. Within a few minutes you'll see the safflower oil turn clear. The peanut oil retains the red-violet tint of the iodine (Fig. 13.1). (If the peanut oil turns clear as well, you may have to add a little more iodine to each to see the safflower oil decolorize the iodine solution while the peanut or olive oil retains the iodine's tint.)

This isn't a parlor stunt like the cabbage breath test in Chapter 10 or the dropping tack in Chapter 11, nor is it an example of a phenomenon so profound that it influenced the course of science. But it does reveal something about the chemistry of foods that could affect your health and even your life span. We'll examine the chemistry behind this demonstration, and how and why it's important to us, as we proceed in our study of fats and oils.

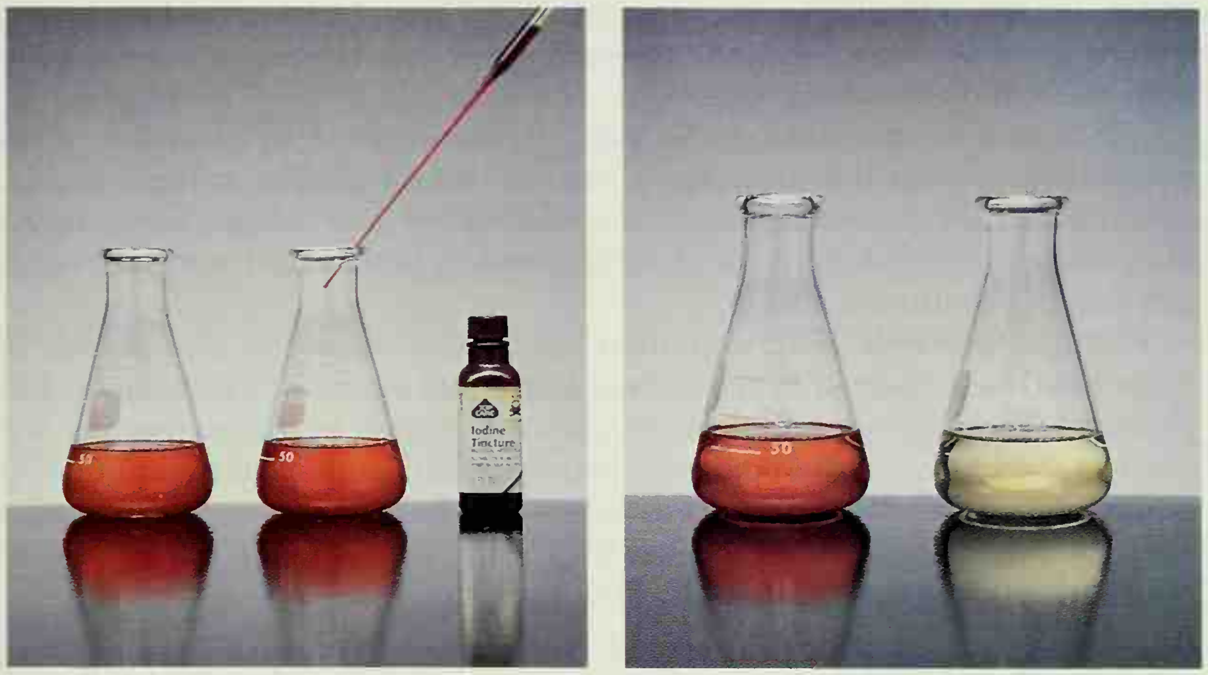
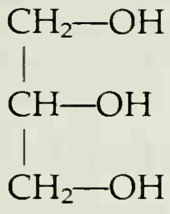


Figure 13.1

The effect of polyunsaturation. Adding a few drops of iodine to peanut oil and sunflower oil produces a red color in each. The color in the sunflower oil disappears more quickly than the color in the peanut oil because the sunflower oil is more highly polyunsaturated.

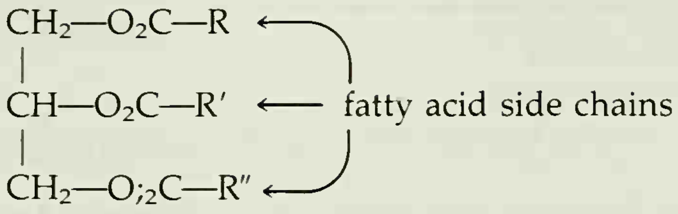
13.1 Fats and Oils

We've already encountered fats and oils in our study of soaps (Chapter 11) and our review of the macronutrients (Chapter 12). We now know them as triglycerides, esters of the triol glycerol with three fatty acids. (You may wish to review the chemistry of esters, triglycerides, and fatty acids in Sections 11.12 and 11.13.)



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array}$$

glycerol



$$\begin{array}{l} CH_2\text{—}O_2C\text{—}R \\ | \\ CH\text{—}O_2C\text{—}R' \\ | \\ CH_2\text{—}O;_2C\text{—}R'' \end{array}$$

general structure of a triglyceride (R, R′, and R″ represent the long, fatty acid side chains.)

As we've seen, the difference between **fats** and **oils** is a very practical one and can be expressed in very simple terms. At ordinary temperatures fats are solids and oils are liquids. Since all triglycerides (both fats and oils) are triesters of glycerol, the only differences among their molecules must lie in the structures of their fatty acid side chains. Generally, short side chains result in low molecular weights and low melting points. The shorter the side chain, the more likely that the triglyceride is an oil. What's more important, though, is the degree of unsaturation of the side chain. The more highly *unsaturated* the side chain, the lower the melting point (for reasons we'll soon see) and,

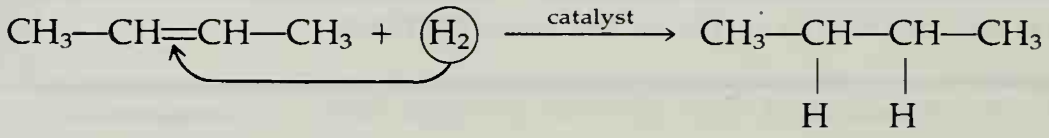
Fats are solid triglycerides. **Oils** are liquid triglycerides.

again, the more likely that the triglyceride is an oil. In terms of human nutrition, the presence of unsaturation in the side chains weighs more heavily with us than do the chain lengths.

As we saw much earlier, in Section 7.9, unsaturation in an organic compound comes from the presence of carbon–carbon double or triple bonds. Alkanes are fully saturated since all four valences of their carbons are occupied in bonding to other atoms through single covalent bonds. No chemical reagent can add to a saturated alkane.

With the presence of unsaturation, though, each carbon of a double or triple bond is connected to fewer than four other atoms. It's possible to add chemical reagents, for example molecular hydrogen or a halogen (Section 3.7) such as the iodine of the opening demonstration, until a maximum of four atoms become bonded to each carbon (see Fig. 7.17). As a simple illustration we have the hydrogenation of 2-butene with a catalyst in a reaction known, appropriately enough, as **catalytic hydrogenation**:

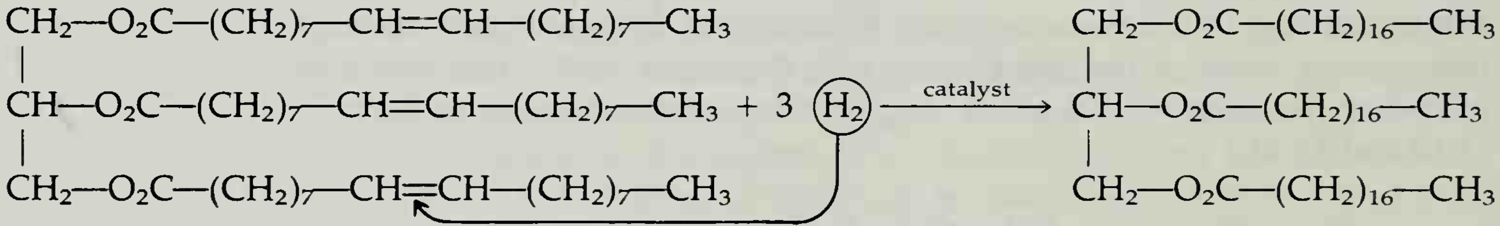
Catalytic hydrogenation is the addition of hydrogen atoms to the double bonds of a molecule through the use of a catalyst. Hydrogen also adds to triple bonds if they are present.



$$CH_3—CH{=}CH—CH_3 + H_2 \xrightarrow{\text{catalyst}} CH_3—\underset{H}{\underset{|}{CH}}—\underset{H}{\underset{|}{CH}}—CH_3$$

addition of a molecule of hydrogen to an unsaturated carbon chain through catalytic hydrogenation

More to the point is the hydrogenation of double bonds in a more complex triglyceride. The notation $—(CH_2)_n—$ in the following structures represents a string of n $—CH_2—$ groups.



$$\begin{array}{l} CH_2—O_2C—(CH_2)_7—CH{=}CH—(CH_2)_7—CH_3 \\ | \\ CH—O_2C—(CH_2)_7—CH{=}CH—(CH_2)_7—CH_3 \\ | \\ CH_2—O_2C—(CH_2)_7—CH{=}CH—(CH_2)_7—CH_3 \end{array} + 3\,H_2 \xrightarrow{\text{catalyst}} \begin{array}{l} CH_2—O_2C—(CH_2)_{16}—CH_3 \\ | \\ CH—O_2C—(CH_2)_{16}—CH_3 \\ | \\ CH_2—O_2C—(CH_2)_{16}—CH_3 \end{array}$$

catalytic hydrogenation of an unsaturated triglyceride

A **monounsaturated** fatty acid is one with a single carbon–carbon double bond in its carbon chain. A **polyunsaturated** fatty acid contains two or more carbon–carbon double bonds.

Each fatty acid side chain in the unsaturated triglyceride shown above has a single carbon–carbon double bond located within its string of carbons. It is therefore **monounsaturated**. (Only unsaturation represented by the carbon–carbon double bond is important to the chemistry of human nutrition; carbon–carbon triple bonds are of little or no significance.) Molecules containing several double bonds are more highly unsaturated than those containing only a single double bond; carbon chains with two or more double bonds are **polyunsaturated**. The polyunsaturated oils of foods such as margarines that claim to be "high in polyunsaturates" are simply triglycerides with two or more carbon-carbon double bonds in their fatty acid side chains. *Why* the manufacturers of margarines and other foods want us to know that they are "high in polyunsaturates" (as well as why some other statements appear

TABLE 13.1 Representative Fatty Acids of Dietary Fats and Oils

Name	Melting Point (°C)	Class	Structure
Myristic acid	58	Saturated C-14	$CH_3—(CH_2)_{12}—CO_2H$
Palmitic acid	63	Saturated C-16	$CH_3—(CH_2)_{14}—CO_2H$
Stearic acid	71	Saturated C-18	$CH_3—(CH_2)_{16}—CO_2H$
Oleic acid	16	Monounsaturated C-18	$CH_3—(CH_2)_7—CH{=}CH—(CH_2)_7—CO_2H$
Linoleic acid	−5	Polyunsaturated C-18	$CH_3—(CH_2)_4—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—CO_2H$
Linolenic acid	−11	Polyunsaturated C-18	$CH_3—CH_2—CH{=}CH—CH_2—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—CO_2H$

much more quietly in the small print of ingredient labels) are topics we'll take up after we understand a bit of the chemistry behind the claims.

Table 13.1 presents the names, structures, and melting points of some of the saturated and unsaturated fatty acids that contribute side chains to the fats and oils of common foods. (The notations C−14, C−16, and C−18 in this table and in other tables and figures refer to the number of carbon atoms in the chain of each of the acids. These notations don't indicate isotopes of carbon as in Chapters 4 and 5.) Notice that, like the melting points of triglyceride esters, the melting points of the fatty acids that go into them also depend on the degree of unsaturation. The greater the number of double bonds in the chain, the lower the melting point and the more likely the acid is to be a liquid rather than a solid.

Fats (solid triglycerides) and an oil (a liquid triglyceride).

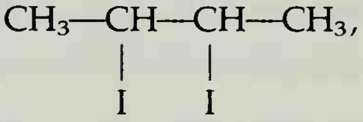
QUESTION

Based on the degree of unsaturation in their side chains, which one of the following would you expect to have the *lowest* melting point? The *highest* melting point? (a) glyceryl trioleate (the triester of glycerol and oleic acid); (b) glyceryl trilinolenate; (c) glyceryl tristearate; (d) glyceryl trilinoleate? ____________________

13.2 Additions to Carbon–Carbon Double Bonds: Iodine Numbers and Hydrogenation

Except for hydrolysis, which we examined in Sections 11.11 and 11.12, most of the important chemistry of fats and oils centers on the degree of unsaturation of their side chains. As we saw in Section 13.1, unsaturation in the form of carbon–carbon double bonds allows the addition of hydrogen, halogens, and other chemical species to the carbon chain. The addition of molecular iodine, I_2, which can be monitored closely and measured accurately in the laboratory through changes in the color of iodine solutions, allows us to compare the relative degrees of unsaturation in various fats and oils. While I_2

itself is responsible for the red-violet color of a tincture of iodine solution (the kind used as an antiseptic), iodine loses its color as it adds to a carbon–carbon double bond. The product of this addition is colorless. For example, the product of the addition of iodine to 2-butene,



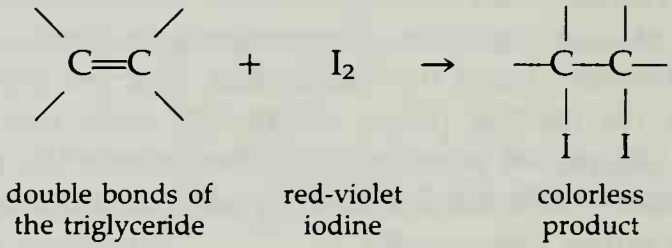
$$CH_3-\underset{\displaystyle I}{\underset{|}{CH}}-\underset{\displaystyle I}{\underset{|}{CH}}-CH_3,$$

is colorless.

We saw chemistry of this sort in action in the opening demonstration. The triglycerides of safflower oil are more highly unsaturated—their carbon chains contain more double bonds—than those of peanut oil. As a result, the safflower oil reacts with more iodine molecules than does an equal amount of peanut oil. The safflower oil removes the iodine's color in the process. If we use the right proportions of everything the color persists in the peanut oil simply because of the residue of iodine that remains in the peanut oil.

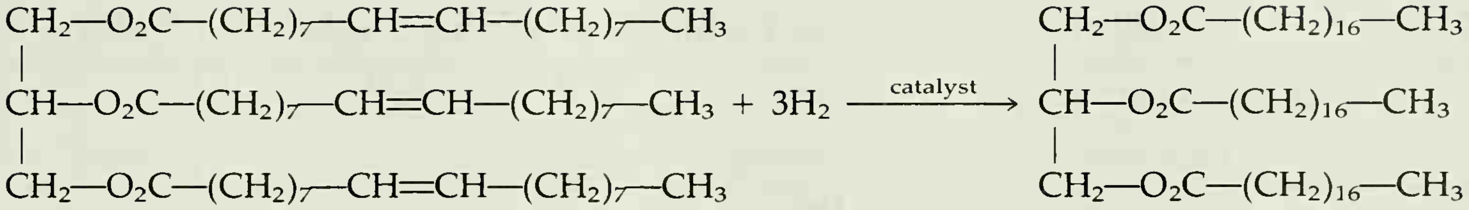
A triglyceride's **iodine number** represents the number of grams of iodine that add to 100 g of the triglyceride.

The degree of unsaturation in a triglyceride is reflected nicely by a value known as the **iodine number**, which represents the number of grams of iodine that add to 100 g of the triglyceride.



The larger the value of the iodine number, the greater the extent of unsaturation. As we might expect from the connection among iodine numbers, carbon–carbon double bonds, and melting points, vegetable oils generally show larger iodine numbers than animal fats. As we might also expect, safflower oil has a higher iodine number than peanut oil. (We'll see both of these confirmed later, in Table 13.3 and its associated figure.) These iodine numbers, incidentally, are important only as indicators of the amount of unsaturation in the side chains. They have nothing whatever to do with the actual presence of iodine in our diets.

While the addition of iodine to triglycerides is used only as an analytical tool for the determination of the degree of unsaturation in the side chains, the catalytic addition of hydrogenation is an important chemical reaction in the preparation and manufacture of food products. Catalytic hydrogenation leads to a reduction of the number of double bonds, a decrease in the degree of unsaturation (an increase in saturation), and therefore an increase in the melting point of the triglyceride. With few or no double bonds in the side chain, the triglyceride is likely to be a solid. Catalytic hydrogenation thus can turn a liquid triglyceride (an oil) into a solid triglyceride (a fat). Because of its ability to raise the melting points of triglycerides, catalytic hydrogenation is also known as *hardening* of vegetable oils. Through this hardening process the liquid triglyceride *glyceryl trioleate* can be converted to the brittle solid, *glyceryl tristearate*.



$$\begin{array}{l} CH_2{-}O_2C{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3 \\ | \\ CH{-}O_2C{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3 \\ | \\ CH_2{-}O_2C{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3 \end{array} + 3H_2 \xrightarrow{\text{catalyst}} \begin{array}{l} CH_2{-}O_2C{-}(CH_2)_{16}{-}CH_3 \\ | \\ CH{-}O_2C{-}(CH_2)_{16}{-}CH_3 \\ | \\ CH_2{-}O_2C{-}(CH_2)_{16}{-}CH_3 \end{array}$$

glyceryl trioleate,
a liquid

glyceryl tristearate,
a brittle solid not
useful in processed foods

QUESTION

What effect, if any, does catalytic hydrogenation have on iodine numbers? ______

13.3 Misleading Food Labels, Cholesterol, . . .

Catalytic hydrogenation is important to the production of such processed foods as margarines, chocolate candy bars, and solid, vegetable-based shortenings. With complete hydrogenation of all the carbon–carbon double bonds of a typical vegetable oil the resulting fully saturated side chains produce a hard and brittle triglyceride with a consistency much like that of candle wax. Because of this harsh physical characteristic, fully saturated triglycerides have little or no value in the manufacture of processed foods. More useful are the partially hydrogenated vegetable oils that retain just enough unsaturation to produce our soft or semisolid margarines, candies, and similar consumer products.

The label on a can of a typical solid shortening used for frying foods states that it is "made from the finest vegetable oils (soybean, palm, and sunflower) which are partially hydrogenated for freshness and consistency." (We'll have more to say about the matter of the freshness of oils later in this chapter.) On the carton of a popular margarine we read that it is "made from 100% pure corn oil" and that it contains, among other ingredients, "liquid corn oil and partially hydrogenated corn oil." It's the partial hydrogenation of the side chains that gives these products their desirable, semisolid consistency.

While it is true that these and similar products are, indeed, *made from* highly unsaturated vegetable oils, some of them no longer actually *contain* these same vegetable oils in significant amounts. The partial hydrogenation of the "100% pure corn oil" used in manufacturing the margarine converts the triglycerides of the liquid oil into a mixture of more highly saturated triglycerides with properties more like fats and, as a result, more suitable for the manufacture of the solid margarine. Margarine and similar solid and semisolid foodstuffs are hardly identical to the raw materials from which they are manufactured.

The use of these partially hydrogenated oils in foods brings with it a mixed story that centers on *cholesterol* (Fig. 13.2). Cholesterol is a waxy substance that falls into the class of *steroidal alcohols*, or *sterols* (from a contraction of *ster*oidal alcoh*ols*). Cholesterol is present in virtually all animal cells. The similarity of its —OH group to the —OH groups of methyl alcohol (CH_3—OH), ethyl alcohol (CH_3—CH_2—OH), and the other alcohols we've studied identifies it clearly as an alcohol. It's also classified as a steroid because of its

Chocolate candies are made with partially hydrogenated vegetable oils that are solid but soften at body temperature.

Plant products, including vegetables and vegetable oils, are all free of cholesterol.

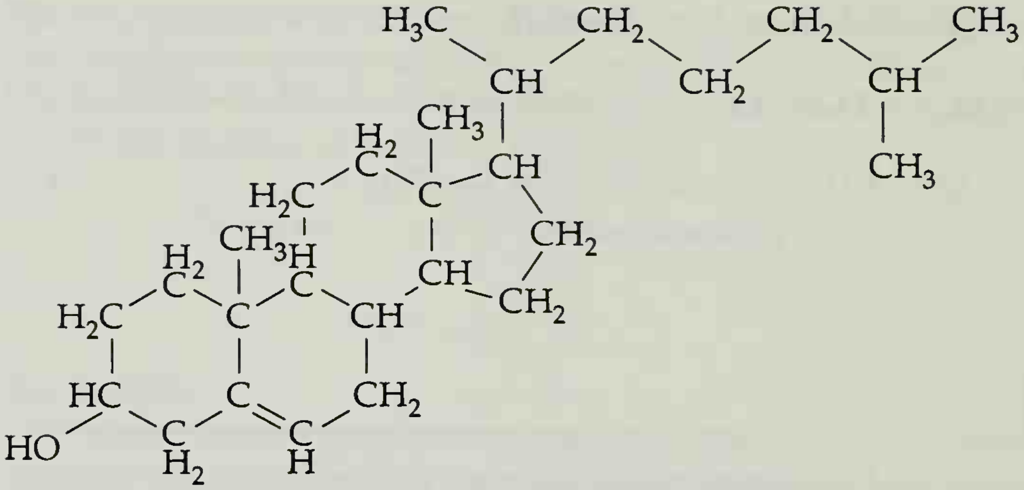


Figure 13.2
Cholesterol.

peculiar molecular structure, which consists of three rings of six carbons each connected to each other in an arc, with a fourth ring of five carbons attached as shown in Figure 13.2. All steroids share this same carbon skeleton arranged into the three six-membered rings and one five-membered ring of the figure.

High levels of *serum cholesterol,* which is cholesterol present in the blood, are closely associated with atherosclerosis, a stiffening and thickening of the walls of the arteries sometimes known simply as hardening of the arteries. It's a condition that leads to high blood pressure and heart disease. High levels of cholesterol in the blood are thus implicated as one cause of heart disease. Serum cholesterol appears to have two origins, that which is present in our diet, and that which is manufactured by our bodies from other substances.

Controlling the first of these, our intake of dietary cholesterol, is largely a matter of avoiding foods rich in this sterol. Highest on the list are egg yolks. Red meat, animal organs, cream, butter, and many cheeses also contain high levels. On the other hand, egg whites, yogurt, and fat-free milk are among the animal products lowest in cholesterol. Since cholesterol occurs only in animal tissue, we can be certain that all fruits, vegetables, and vegetable oils are cholesterol-free. Table 13.2 lists the fat and cholesterol content of typical foods.

A set of complex, interacting factors appears to govern the second source, cholesterol produced in our own bodies. These include genetics (over which we have no control), exercise, emotional stress, and still other influences, possibly including the amount and kinds of fiber in our diets. At any rate, the cholesterol generated within our own bodies comes from our liver, which manufactures cholesterol for us from saturated fats. Reducing the amount of animal fats in our diets, especially those from red meats, is one recommended way of controlling serum cholesterol. Actually, animal fats pose a double threat. Not only do they provide the liver with the raw materials for its own production of cholesterol, but animal fats carry high levels of cholesterol with them as they enter our digestive systems. Cholesterol, a waxy substance with many of the properties of alkanes, doesn't dissolve in water to any appreciable extent. Like the hydrophobic tails of soap molecules (Section 11.6), cholesterol seeks out and dissolves in fatty, greasy substances, including animal fat. Thus animal fat serves to concentrate cholesterol within itself.

Diets rich in animal fats, then, are believed to promote high serum cholesterol levels both by carrying their own with them and by providing our

TABLE 13.2 Cholesterol and Fat in Typical Foods (100-g Servings)

Food	Cholesterol (mg)	Fat and Oil Content (g) Saturated	Monounsaturated	Polyunsaturated
Beef	91	2.7	2.7	0.5
Butter	219	50.5	23.4	3.0
Cheese, cheddar	105	21.1	9.4	0.9
Cheese, cottage dry	7	0.3	0.1	0.02
Cheese, Swiss	92	17.8	7.3	1.0
Chicken (light meat, no skin)	85	1.3	1.5	1.0
Corn oil	0	12.7	24.2	58.7
Eggs, whole	548	3.4	4.5	1.4
Eggs, yolk	1602	9.9	13.2	4.3
Frankfurter (all beef)	51	12.7	14.8	1.2
Margarine, stick (from corn oil)	0	13.2	45.8	18.0
Milk, skim	2	0.1	0.05	0.007
Milk, whole	14	2.3	1.1	0.1
Olive oil	0	13.5	73.7	8.4
Peanut butter	0	9.7	23.3	15.2
Peanut oil	0	16.9	46.2	32.0
Safflower oil	0	9.1	12.1	74.5
Salmon (pink, canned)	35	1.0	1.8	2.7
Tuna (canned in water)	63	0.2	0.1	0.2
Turkey (light meat, no skin)	69	1.0	0.6	0.9
Yogurt (plain, lowfat)	6	1.0	0.4	0.04

liver with saturated fats. It makes sense, then, to welcome manufacturers' boldly written claims that their products are CHOLESTEROL-FREE, until we read the small print on the labels that spell out, more quietly, the content of hydrogenated vegetable oils. The more highly hydrogenated these vegetable oils are, the more they become like animal fats, the liver's raw materials for putting its own cholesterol into our bloodstream.

QUESTION

Compare the health aspects of using butter, margarine, and vegetable cooking oils for use in frying an egg. (a) What health advantage does margarine have over butter? (b) What health advantage does cooking oil have over margarine? ______________

13.4 . . . and Simplistic Nutritional Advice

For reasons we've discussed it seems prudent to replace the animal fats of our diets with vegetable oils and, perhaps, with fish oils as well. Superficially this appears to be reasonable nutritional advice, especially since we associate cholesterol and saturated triglycerides with heart disease. Yet on closer inspection the recommendation is a bit confusing and certainly simplistic. Some animal fats actually contain more *unsaturated* than saturated side chains. Indeed, while the *proportion* of unsaturated side chains is, in fact, usually higher in the oils than the fats, using the term *saturated fat* to describe all our dietary triglycerides of animal origin either ignores or oversimplifies some very important chemistry.

Nature isn't so neat and simple as to form animal fats exclusively from highly saturated fatty acids and to generate plant oils exclusively from unsaturated acids with plenty of double bonds. Instead, the fats and oils of our diets are complex mixtures of triglycerides containing a considerable variety of side chains: some long, some short, some fully saturated, some monounsaturated, some polyunsaturated. While fats are, as we've noted, generally richer in the saturated side chains, no fat consists entirely of fully saturated side chains and no oil is free of them.

Table 13.3 and Figure 13.3 illustrate this complexity with data showing the relative proportions of the various fatty acids in representative fats and oils. (To be more accurate, the triglycerides don't actually *contain* these acids. Instead they consist of triglycerides that give the saturated and unsaturated acids on hydrolysis.) The entries in the table show percentages of the fatty acids in typical fats and oils obtained from both animal and vegetable products.

For emphasis and clarity, data for six of these fats and oils also appear in the pie charts of Figure 13.3. All the shaded areas of the pie charts represent fully saturated acids while the clear segments symbolize their unsaturated counterparts. The numbers within the larger segments and those following the names of the lesser acids show the percentage of the whole pie that each segment represents.

The percentages in Table 13.3 and Figure 13.3 are typical and representative values, rather than exact averages. The actual values depend on the specific source of the fat or oil as well as its age and history. For example, the oleic acid of butterfat, shown as 27%, probably ranges from about 20% to nearly 35%. Despite these variations, the numbers do reveal the approximate compositions of our dietary triglycerides. In addition, the triglycerides' iodine numbers are also shown, usually as ranges of values.

We can see in all these data clear illustrations of general trends. As a whole, vegetable oils and fish oils furnish a higher level of unsaturated side chains than do the fats. But there are exceptions. Lard, for example, carries a higher proportion of unsaturated side chains than either palm kernel oil or coconut oil. (Coconut oil is a major ingredient of many nondairy creamers and other prepared foods.) The iodine numbers associated with these three substances reflect the relative extent of unsaturation in each. While a dietary switch from animal fats to vegetable oils will certainly guarantee a reduction of our cholesterol intake, it will not necessarily ensure a nutritional turn to the unsaturated side chains. If we want to replace the saturated triglycerides of our

TABLE 13.3 Fatty Acid Content of Fats and Oils, by Percentage[a]

Fat or Oil	Iodine Number	Myristic Acid (Saturated) C-14	Palmitic Acid (Saturated) C-16	Stearic Acid (Saturated) C-18	Palmitoleic Acid (Mono-unsaturated) (C-16)	Oleic Acid (Mono-unsaturated) C-18	Poly-unsaturated Acids C-18	Poly-unsaturated Acids Larger than C-18
Animal Fats								
Beef fat	35–42	6	27	14	—	50	3	—
Butterfat[b]	26–38	11	29	9	5	27	4	1
Human fat	68	3	24	8	5	47	10	3
Lard	47–67	1	28	12	3	48	6	2
Vegetable Fat								
Cocoa butter	33–42	—	24	35	—	38	2	—
Animal (Fish) Oils								
Cod liver oil	135–165	6	8	1	20	(combined, 29)		35
Herring oil	140	7	13	—	5	—	21	53
Menhaden oil	170	6	16	1	16	—	30	31
Sardine oil[c]	185	5	15	3	12	(combined, 18)		32
Vegetable Oils								
Coconut oil[d]	6–10	18	11	2	—	8	—	—
Corn oil	110–130	1	10	3	2	50	34	—
Cottonseed oil	103–111	1	23	1	2	23	48	1
Linseed oil	180–195	—	6	3	—	19	72	—
Olive oil	80–88	—	7	2	—	85	5	—
Palm oil	50–60	1	40	6	—	43	10	—
Palm kernel oil[e]	37	14	9	1	—	18	1	—
Peanut oil	90–100	—	8	3	—	56	26	7
Safflower oil	145	—	4	3	—	17	76	—
Sesame oil	103–117	—	9	4	—	45	40	1
Soybean oil	120–135	—	10	2	—	29	57	1
Sunflower seed oil	125–135	—	6	2	—	25	66	1
Tung oil	168	(all saturated combined, 5)			—	4	91	—
Wheat germ oil	125	—	13	4	—	19	62	1

[a] Some entries total 99% because of the effects of rounding.

[b] Butterfat also contains about 11% saturated acids smaller than C-14, and 2.5% other saturated acids not shown on this table.

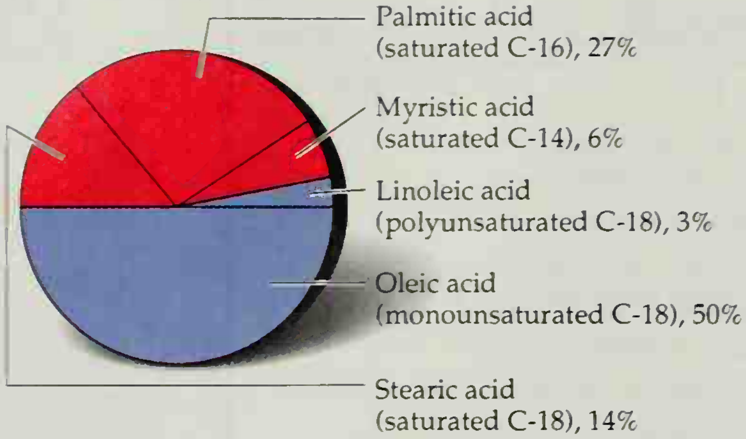
[c] Sardine oil also contains about 15% unsaturated C-14 acids.

[d] Coconut oil also contains about 60% saturated acids smaller than C-14.

[e] Palm kernel oil also contains about 57% saturated acids smaller than C-14.

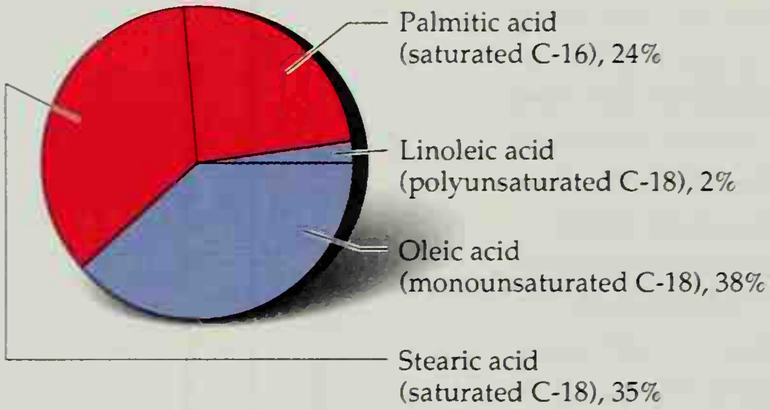
Animal fat

Beef fat
(iodine number, 35-42)



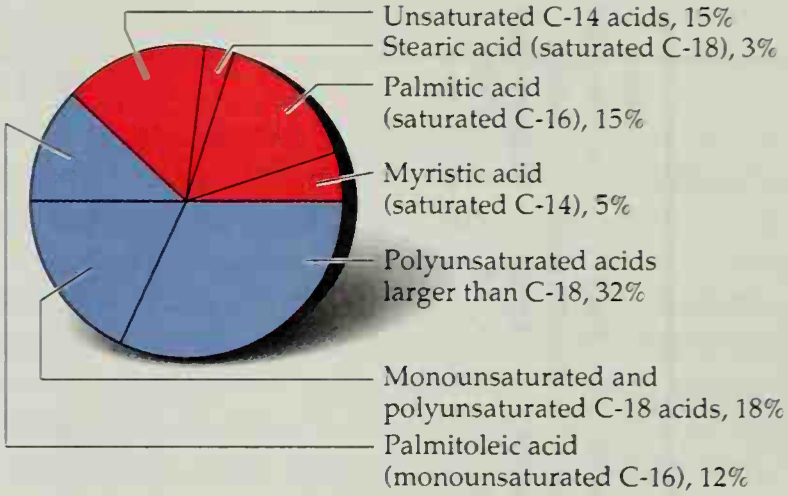
Vegetable fat

Cocoa butter
(iodine number, 33-42)



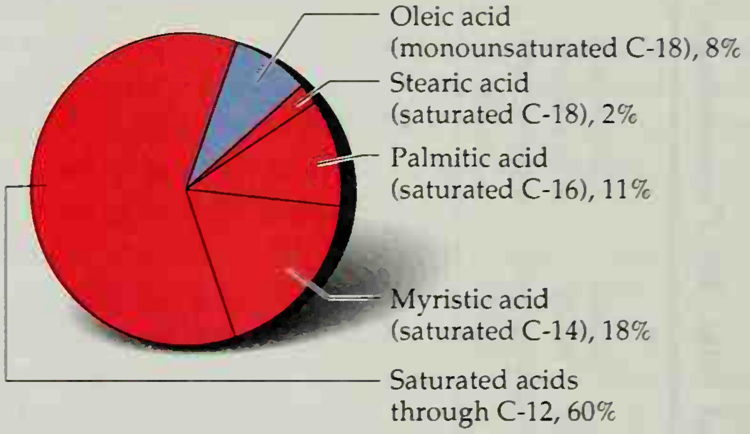
Animal oil

Sardine oil
(iodine number, 185)

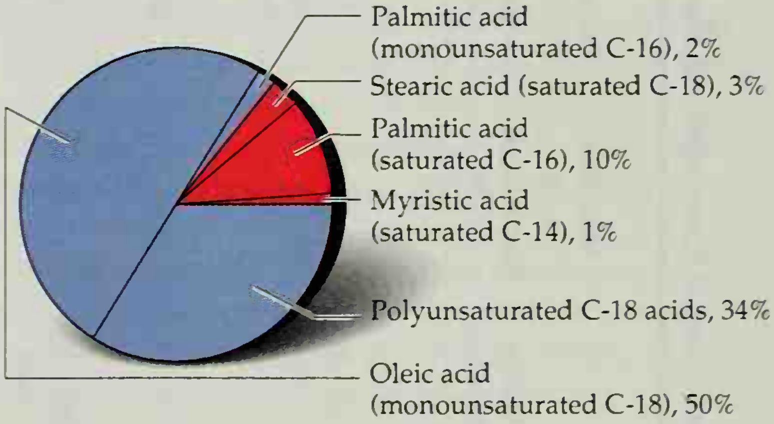


Vegetable oil

Coconut oil
(iodine number, 6-10)



Corn oil
(iodine number, 110-130)



Olive oil
(iodine number, 80-88)

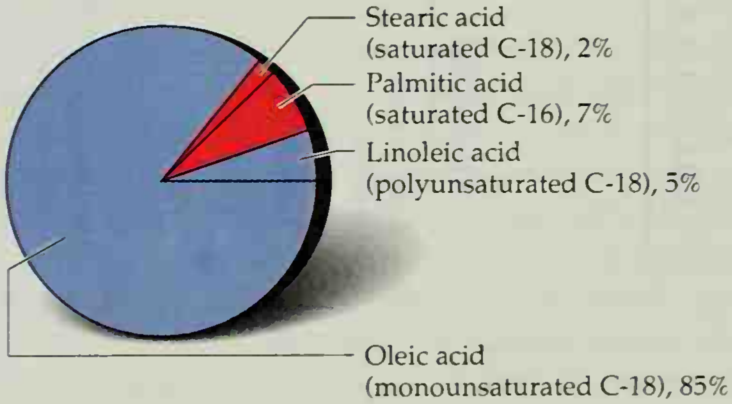


Figure 13.3

Fatty acid content of fats and oils (typical percentages).

diets with their polyunsaturated counterparts, it's not enough simply to substitute vegetable oils for our dietary fats. We've got to be sure that the oils we choose are, indeed, polyunsaturated. Otherwise we could end up with a diet of oils even richer in saturated triglycerides than the animal fats we abandon.

QUESTION

What are the iodine numbers of (a) peanut oil and (b) safflower oil? Are these consistent with the results of the opening demonstration? Explain. ____________

13.5 Oils That Spoil, Oils That Dry

Other chemical species, in addition to hydrogen and iodine, can also react with the double bonds of carbon chains. Atmospheric oxygen, for example, reacts with unsaturated chains of the triglycerides, fracturing them and converting them into a variety of smaller, foul-smelling molecules. The formation of these unpleasant oxidation products results in the rancidity of cooking oils that stand exposed to air for a considerable time. Chemicals that react preferentially with oxygen, thereby sparing the polyunsaturated oils from oxidation, are sometimes added to cooking oils and other foods to increase their shelf lives. Among these *antioxidant* food additives are the synthetic compounds BHA and BHT and the natural antioxidant, vitamin E. We'll examine these and other food additives more extensively in Chapter 17.

In addition to raising the melting and softening points of triglycerides, the partial hydrogenation used in the manufacture of shortening, margarines, and similar products also increases the shelf lives of the resulting triglycerides by decreasing the number of double bonds in their side chains and inhibiting their tendency to turn rancid. In this way the partial hydrogenation of triglycerides does help keep foods fresh.

The ability of polyunsaturated side chains to react with oxygen is put to good use in the *drying oils*. These highly unsaturated vegetable oils are added to lacquers, varnishes, oil-based paints, and some latex paints to produce tough, protective films as they dry. The drying of an oil-based paint isn't simply a matter of the evaporation of its solvent, usually mineral spirits or turpentine. In addition, the drying oil that remains on the painted surface reacts with atmospheric oxygen to form a tough web of triglyceride molecules linked to each other through oxygen atoms. Linseed oil and tung oil are especially useful as drying oils.

QUESTION

(a) Which would you expect to be the better drying oil, an oil with a very high iodine number or one with a very low iodine number? Why? ____________________

Oil-based paints are made with polyunsaturated drying oils such as linseed oil and tung oil. As they dry, they react with the oxygen of air to form a tough film of triglyceride molecules linked to each other through oxygen atoms.

13.6 Chemical Geometry

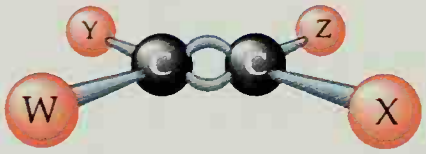


Figure 13.4
Planarity and the carbon–carbon double bond. The two carbons and atoms W, X, Y, and Z all lie in the same plane.

Repeatedly we've seen in this chapter the close connection between a triglyceride's physical state—liquid or solid—and the degree of unsaturation in its side chains. With a few easily explained exceptions, such as coconut oil and palm kernel oil (based on their short but highly saturated side chains), carbon–carbon double bonds occur more often in the molecular structure of a liquid oil than in a solid fat. This connection between carbon–carbon unsaturation and melting point or softening temperature hinges on a simple geometric requirement of the double bond: it must be planar, with the two carbons of the double bond and the four atoms attached to them, two to each carbon, all lying in the same plane (Fig. 13.4). This particular bit of chemical geometry is a necessary result of the way in which the carbon–carbon double bond forms.

The importance of this geometric peculiarity lies in a new kind of isomerism that it introduces. Isomerism, as we saw in Section 7.6, occurs when two different compounds share the same molecular formula. Here we encounter a new kind of isomerism, *geometric isomerism*. **Geometric isomers** are different compounds that have the same four groups bonded to the carbons of their double bonds, but with different geometries.

Geometric isomers are different compounds that have the same four groups bonded to the carbons of their double bonds, but with different geometries.

To illustrate geometric isomerism we'll look at 2-butene (Section 7.9). All four carbons of this compound, as well as the two hydrogens of the carbon–carbon double bond, lie in the same plane. Moreover, each carbon of the double bond carries two different substituents: a hydrogen and a methyl group. One geometric isomer of 2-butene, *cis*-2-butene, results when both methyl groups (and therefore both hydrogens as well) lie on the same side of the double bond. In the other geometric isomer, *trans*-2-butene, the two methyl groups lie on opposite sides of the double bond, as do the two hydrogens.

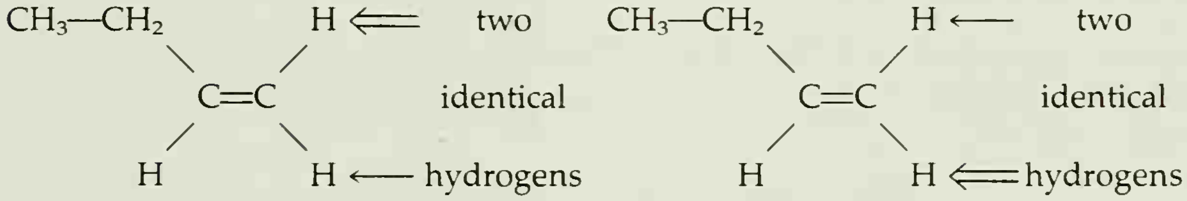
cis-2-butene

trans-2-butene

geometric isomers of 2-butene

As isomers, *cis*-2-butene and *trans*-2-butene are two different covalent compounds with different chemical and physical properties. *cis*-2-Butene, melts at -138.9°C, *trans*-2-butene at -105.5°C; the *cis* geometric isomer boils at 3.7°C, the *trans* at 0.9°C. *cis*-2-Butene and *trans*-2-butene are geometric isomers.

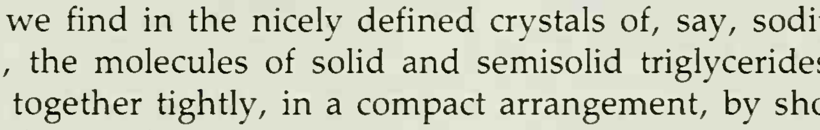
Notice a peculiarity here. Geometric isomerism can occur *only* when both carbons of the double bond bear two different groups. Geometric isomerism is impossible if either one of them holds two groups that are identical. In 1-butene, for example, the end carbon bears two identical groups, two hydrogens. Switching the geometry of the double bond doesn't change a thing. The two hydrogens of the end carbon are identical, so there are no geometric isomers of 1-butene.



This molecule of 1-butene is identical to *this* molecule of 1-butene, even though the two hydrogens have been switched.

All the double bonds of our dietary polyunsaturated triglycerides exist in the *cis* geometry, with an interesting consequence for their melting points or softening temperatures. As we saw in Section 11.4, crystalline solids melt as their chemical particles leave the orderly arrangement of a crystalline lattice and begin to move about more freely in the liquid phase. Although the molecules of our dietary fats don't form the regular, highly symmetrical crystalline lattices that we find in the nicely defined crystals of, say, sodium chloride and sucrose, the molecules of solid and semisolid triglycerides are nevertheless held together tightly, in a compact arrangement, by short-range intermolecular forces of attraction. These are the same sort of forces that bind together, for example, the large alkane molecules of candle wax, and they depend on the ability of the hydrocarbon chains to pack snugly against each other.

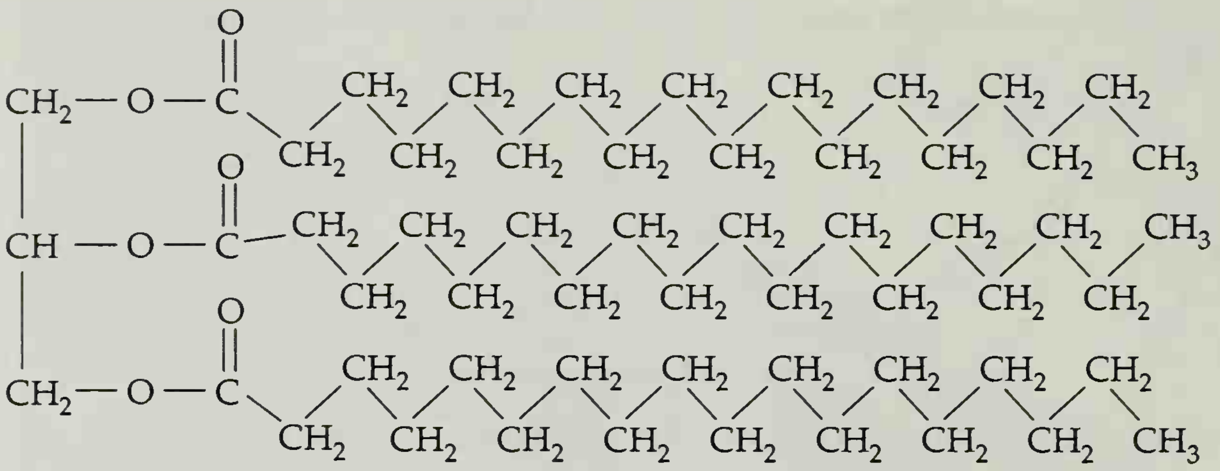
Long, fully saturated hydrocarbon chains, both those of alkanes and those of triglycerides, normally fold nicely into fairly regular zig-zag patterns, somewhat like the following:



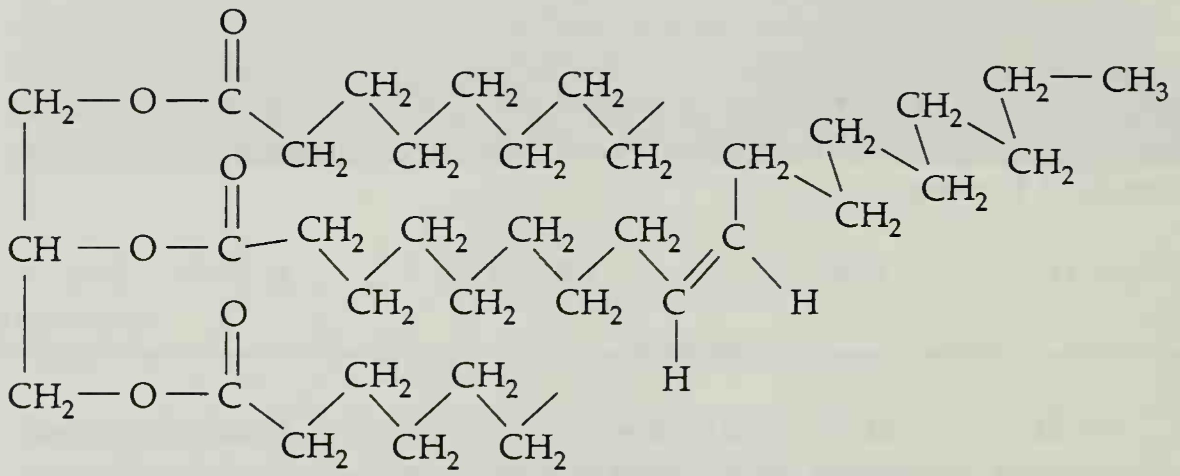
a portion of the regular pattern of a fat's side chain

Figure 13.5

Molecular packing in glyceryl tristearate and glyceryl trioleate. Polyunsaturation increases the space occupied by fatty acid side chains, causing polyunsaturated triglyceride molecules to lie farther from each other than molecules with more fully saturated side chains. This increased distance of separation decreases the attractive forces the polyunsaturated molecules exert on each other and lowers the melting points of polyunsaturated triglycerides.



Glyceryl tristearate; chains are packed closely



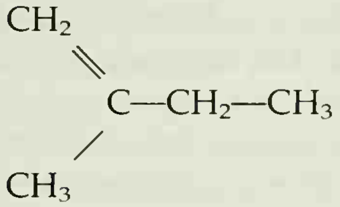
Glyceryl trioleate; double bonds prevent close packing
(For clarity, only the center chain is shown fully)

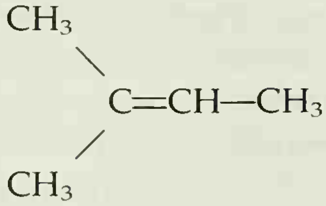
These regular, zig-zag arrangements allow the saturated side-chains, as well as the triglyceride molecules themselves, to fit compactly next to each other, thereby exerting effective attractive forces on each other and remaining solid even at temperatures as high (relatively speaking) as normal room temperature. Things are different, though, in the polyunsaturated oils. The plentiful *cis* units of unsaturation in a polyunsaturated vegetable triglyceride introduce repeated kinks into the carbon chains that, in effect, increase the bulk of the chains and prevent the close, orderly association of molecules that we find in the more highly saturated solid and semisolid animal fats. Polyunsaturation, as it occurs in most plant triglycerides, tends to move the triglyceride molecules farther apart, lower their intermolecular attractive forces, lower their melting points, and lead to liquid triglycerides, the oils (Fig. 13.5). That's why vegetable oils, most of which have a relatively high proportion of *cis* double bonds in their side chains, are liquids at room temperature. Substances like butter, beef fat, and lard, with relatively few *cis* double bonds, are solids.

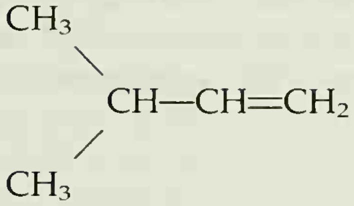
QUESTION

Which of the following, if any, can exist as geometric isomers?

a. $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$ b. $CH_3{-}CH{=}CH{-}CH_2{-}CH_3$

c.


d.


e.


13.7 Energy Storage: Fat

In the preceding chapter we saw that we retain and store the unused energy of our dietary nutrients. We expressed this in terms of the Energy Equation:

$$\text{Energy In} = \text{Energy Out} + \text{Energy Stored (fat)}$$

If we didn't store the unused chemical energy of our food, if the only metabolic energy available to us and to our ancestors were the energy immediately available to us from the macronutrients of a recent meal, none of us would be alive today. The human race would have vanished eons ago as a result of mass starvation. Without some means for storing energy in the body, a temporary and minor shortage of the animals hunted by our cave-dwelling ancestors or a brief scarcity of the grains, fruits, or vegetables they ate would have been catastrophic. It would have wiped out the human race. Even now, with food in plentiful supply and continuously available to those of us who live in the more highly developed regions of the world, energy storage within our bodies is literally a matter of life and death. Our hearts, lungs, and other vital organs would run out of energy between meals, even as we sleep, if it were not for our body's ability to store the excess fuel of each meal and then use that stored fuel to provide a continuous supply of energy between meals. The principal mode of energy storage available to our ancestors and to us operates through the formation, storage, and metabolism of body fat.

Body fat is stored energy. The body converts the unused carbohydrates, proteins, and triglycerides that make up our macronutrients into small globules of fat that it deposits in the specialized cells of **adipose tissue**, the fatty

Adipose tissue is the fatty tissue of the body. It stores chemical energy at about 3500 Cal per pound.

tissue of the body. One pound of adipose tissue stores (and provides when needed) roughly 3500 Cal of energy.

Converting an excess of a macronutrient into body fat and then converting this fat into energy later, when we need it, is a particularly effective means of long-term energy storage. With a gram of carbohydrate or protein providing only about 1/2.25 of the amount of energy of a gram of fat, storing excess energy in the form of either carbohydrates or proteins would raise our bulk and weight considerably and make us far less mobile. The high *energy density* of fat, its ability to store energy compactly in relatively little space and with relatively little weight compared with carbohydrates and proteins, allows us to carry our stores of energy with us. It gives us and other animals the mobility and freedom necessary for survival in a world that was, and can still be, unforgiving to those poorly equipped for survival. (Short-term energy storage, from one meal to another, occurs through a starchlike substance called *glycogen*, which we'll examine in Chapter 14.)

QUESTION

Adipose tissue consists of fat globules and cellular protoplasm, which is mostly water. Virtually all of the energy stored in adipose tissue, about 3500 Cal/pound, comes from the chemical energy of its fat globules. Given the relationships

1 pound = 454 g
1 g of fat = 9 Cal

you can calculate the percentage of fat in adipose tissue. For this calculation

- recognize that all of the energy stored in adipose tissue is stored in the triglycerides of its fat globules,
- calculate the energy content per gram of adipose tissue, and
- compare this value with the energy content of fat.

a. How many Calories are stored in 1 g of adipose tissue?
b. How many Calories are stored in 1 g of fat triglycerides?
c. What is the percentage of fat in adipose tissue? ____________________

PERSPECTIVE: Fats and Oils, the Perfect Examples

To sum up, in this chapter we have demonstrated that the fats and oils of our foods are indeed chemicals and that they follow all the laws of chemistry. They are triglyceride esters that contain scattered within their molecules the same carbon–carbon double bonds that occur in the unsaturated hydrocarbons we know as alkenes (Section 7.9). Water hydrolyzes them, and hydrogen and the halogens add to them. They are the raw materials of the soap industry.

They are chemicals we eat, chemicals we manufacture within our own bodies, and chemicals that provide the raw materials of major industries.

Fats and oils are also substances that work both for and against life and good health. We've already seen, for example, that body fat stores energy for us so that if we fast, miss a meal, or even sleep through a long night, we still have the energy to breathe and to keep our hearts beating. It also forms cushioning shields around our major organs. Thin layers of fat around each of our major organs protect them against damage from physical shock when we miss a curb or don't see the last step of a staircase. Fats also give flavor to our foods and vitamins to our bodies. Many of the flavors that add enjoyment to eating come from chemicals that are far more soluble in fats than in the more watery substances of food. It's the fat in meat that carries its flavor. Fatless meats would be tasteless. More importantly, we'll see in Chapter 16 that many of our vitamins are much more soluble in fats than in water. It's fat that carries vitamins A, D, E, and K from our foods to our tissues. Moreover, our own bodies use fatty acids in forming not only the triglycerides that are stored in our adipose tissue, but other compounds as well, including a vital class of compounds know as *prostaglandins*, which we'll discuss more fully in Chapter 22. In these syntheses we are able to manufacture in our own bodies all the fatty acids we need but one. We must get this single, essential fatty acid, linoleic acid (Table 13.1), from dietary sources.

Fats and oils clearly contribute to our life, health, and well being. On the other hand, in excess they can be dangerous. Obesity is linked with high blood pressure and diabetes. Dietary fat is implicated as a cause of heart disease and cancer. We've already discussed the connection among dietary fat, cholesterol, and atherosclerosis (Section 13.3). A high dietary consumption of fat (and perhaps protein as well) also seems to be at least one factor leading to breast, colon, and prostate cancer. While health and scientific organizations recommend that a maximum of 30% of our dietary calories come from fat, the average diet in the United States carries about 38% of its calories in these triglycerides.

Can this be harmful? A study of women in northwestern Italy revealed that those who received about half their calories from fat, especially the fat of whole milk, fatty cheese, and butter, ran about three times the normal risk of breast cancer. For women whose fatty calories came to less than 30% of their total diet (and who ate less protein too), the incidence of breast cancer ran about half the normal level. While correlations are not proof of cause and effect, cutting fatty calories to well below 30% seems desirable. This means eating plenty of fruits and vegetables, consuming not more than small portions of very lean meat, and largely abandoning the use of fats and oils for cooking and frying.

Fats and oils provide us with almost perfect examples of the chemical basis of our everyday world; of the risks, hazards, and benefits in chemicals; of the contrast between the benefits that can be derived from moderate amounts of a particular chemical and the damage that can be done by an excess; and of our need for a knowledge and understanding of chemistry so that we can make intelligent and productive choices from among the many options we face each day. Fats and oils are virtually the ideal chemicals for an examination of the extraordinary chemistry of ordinary things.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

The fats and oils of the human diet are ______ , or triesters of ______ and various ______ . Those that are solids under ordinary conditions are called ______ , while those that are liquids are the ______ of our diets. At the molecular level, the melting point of a triglyceride is determined by two factors: the ______ of the fatty acids' ______ and the degree of ______ . Triglycerides undergo several important chemical reactions, including ______ , which leads to soaps when it's carried out in the presence of a base, and the addition of ______ and of the halogens. ______ leads to an increase in the level of saturation of the side chains and an increase in the melting point of the triglyceride. The quantitative addition of iodine yields the ______ of a triglyceride, which is a measure of the extent of unsaturation in its molecules. It's undesirable to include large amounts of animal fats in a diet because these fats are rich in ______ and in the sterol ______ , which can produce atherosclerosis, or hardening of the arteries.

carbon chain
catalytic hydrogenation
cholesterol
fats
fatty acids
glycerol
hydrogen
hydrolysis
iodine number
length
oils
saturated side chains
triglycerides
unsaturation

2. Identify or define each of the following.

a. adipose tissue
b. antioxidant
c. drying oil
d. geometric isomerism
e. hydrogenation
f. polyunsaturation

3. How does an increase in the number of —CH_2— groups in a saturated fatty acid affect its melting point?

4. How does an increase in the number of carbon–carbon double bonds in a fatty acid, with no change in its carbon content, affect its melting point?

5. Given a sample of a triglyceride, how would you determine whether it is a fat or an oil?

6. Given the molecular structure of a triglyceride, what factors would lead you to predict whether the substance it represents is a fat or an oil? Explain your answer.

7. How would you use the iodine number of a triglyceride to decide whether the triglyceride is a fat or an oil?

8. Why did the color of the iodine disappear from the safflower oil more rapidly than from the peanut oil in the opening demonstration?

9. Name the major saturated fatty acid obtained by the complete hydrogenation and then the hydrolysis of each of the following oils: (a) corn, (b) cottonseed, (c) linseed, (d) olive, (e) peanut, (f) safflower, (g) sesame, (h) soybean, (i) sunflower seed, (j) tung, (k) wheat germ.

10. Of beef fat, cocoa butter, and coconut oil, which has the highest total percentage of fully saturated fatty acids? Which has the lowest?

11. What nutritional hazard to human health is present in beef but not in cocoa butter or coconut oil?

12. While vegetable oils provide the same number of calories as animal fats, replacing animal fats with vegetable oils usually decreases the dietary levels of two undesirable substances. What are they?

13. Which two vegetable oils produce a decrease of only one of the substances mentioned in Exercise 12? Which one is decreased?

14. Food labels occasionally claim that the product is made with partially hydrogenated vegetable oils "to preserve freshness." How does partial hydrogenation of a an oil help preserve freshness?

15. Why would a food product made of fully saturated triglycerides have little commercial value?

16. Name a sterol and explain why the compound is classified as a sterol.

17. Name a fatty acid that the body uses but cannot synthesize from other substances.

18. Which of the following foods is likely to contain the highest percentage of the essential fatty acid in Exercise 17: (a) beef fat, (b) cocoa butter, (c) olive oil, (d) palm kernel oil?

19. 2-Butene, $CH_3—CH{=}CH—CH_3$, exists as two geometric isomers, *cis*-2-butene and *trans*-2-butene. But there is only one structure for 1-butene,

$CH_2{=}CH{-}CH_2{-}CH_3$, which does *not* show geometric isomerism. Explain why 1-butene does not exist as geometric isomers.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

20. Which food in each of the following sets contains the highest percentage of saturated fats: (a) butter, Swiss cheese, whole milk; (b) olive oil, peanut oil, peanut butter; (c) beef frankfurter, white meat of chicken, white meat of turkey; (d) corn oil, egg yolk, whole milk?

21. Which food in each of the following sets contains the highest percentage of cholesterol: (a) butter, Swiss cheese, whole milk; (b) skim milk, whole milk, yogurt; (c) beef frankfurter, white meat of chicken, white meat of turkey; (d) beef, cheddar cheese, margarine?

22. Corn oil contains about 58.7% polyunsaturated triglycerides, but margarine, which is made from corn oil, contains only about 18% polyunsaturated triglycerides. Explain the difference.

23. Is the following statement true or false? "Animal fats contain a higher proportion of saturated fatty acid side chains than vegetable oils do (except coconut oil and palm oil)." Use the data in Table 13.3 to justify your answer.

THINK, SPECULATE, REFLECT AND PONDER

24. Based on your observations in the opening demonstration, why do you think iodine is particularly useful for establishing the degree of unsaturation in a triglyceride?

25. Suppose you want to modify the opening demonstration so that the safflower oil remains tinted with the iodine color while some other oil loses its color. Choose an oil that would turn almost colorless while the safflower oil remains tinted. What is the basis for your choice?

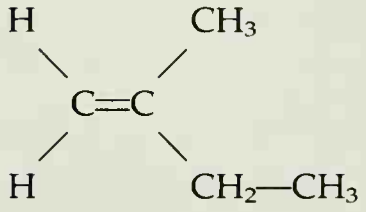
26. The oils obtained from fish found in very cold waters are generally more highly unsaturated than the oils of fish whose natural habitats are in warmer waters. In what way would an increase in unsaturation benefit fish living in very cold waters?

27. Even though cocoa butter comes from a plant, it is a fat. After comparing cocoa butter's content of the various fatty acids with those of other vegetable triglycerides (see Table 13.3), suggest a reason for its unusually high melting point.

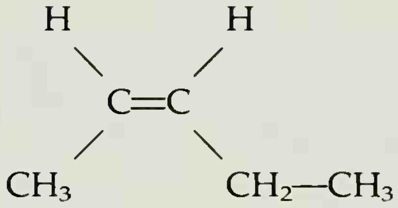
28. Give the names or structures of the organic product(s) produced by the reaction of glyceryl trioleate with an excess of each of the following: (a) NaOH and H_2O, (b) I_2, (c) H_2 and a catalyst.

29. Label each of the following as *cis* or *trans* or incapable of geometric isomerism:

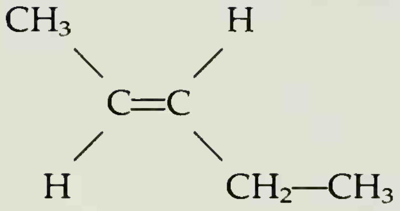
a.



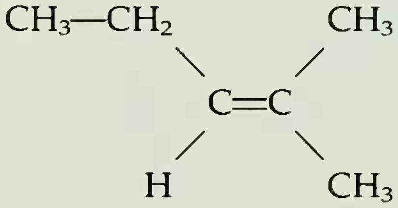
b.



c.



d.



30. Decane and the two geometric isomers of 5-decene, $CH_3{-}(CH_2)_3{-}CH{=}CH{-}(CH_2)_3{-}CH_3$ have the following melting points:

	Melting Point
decane	−30°C
trans-5-decene	−73°C
cis-5-decene	−112°C

Draw the structures of the two geometric isomers of 5-decene, label them as *cis* and *trans*, and suggest a reason for this sequence of melting points.

$CH_2{=}CH{-}CH{=}CH_2$, which does not show geometric isomerism. Explain why [illegible] does not exist as geometric isomers.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

20. Which food in each of the following sets contains the highest percentage of saturated fats: (a) butter, Swiss cheese, whole milk, (b) coconut oil, peanut butter, (c) beef frankfurter, white meat of chicken, white meat of turkey, (d) corn oil, egg yolk, whole milk?

21. Which food in each of the following sets contains the highest percentage of cholesterol: (a) butter, Swiss cheese, whole milk, (b) skim milk, whole milk, yogurt, (c) beef frankfurter, white meat of chicken, white meat of turkey, (d) beef, cheddar cheese, margarine?

22. Corn oil contains about 56% polyunsaturated triglycerides, but margarine (which is made from corn oil) contains only about 15% polyunsaturated triglycerides. Explain the difference.

23. Is the following statement true or false? "Animal fats contain a higher proportion of saturated fatty acid side chains than vegetable oils do (except coconut oil and palm oil)." Use the data in Table 13.3 to justify your answer.

THINK, SPECULATE, REFLECT AND PONDER

24. Based on your observations in the opening demonstration, why do you think iodine is particularly useful for establishing the degree of unsaturation in a triglyceride?

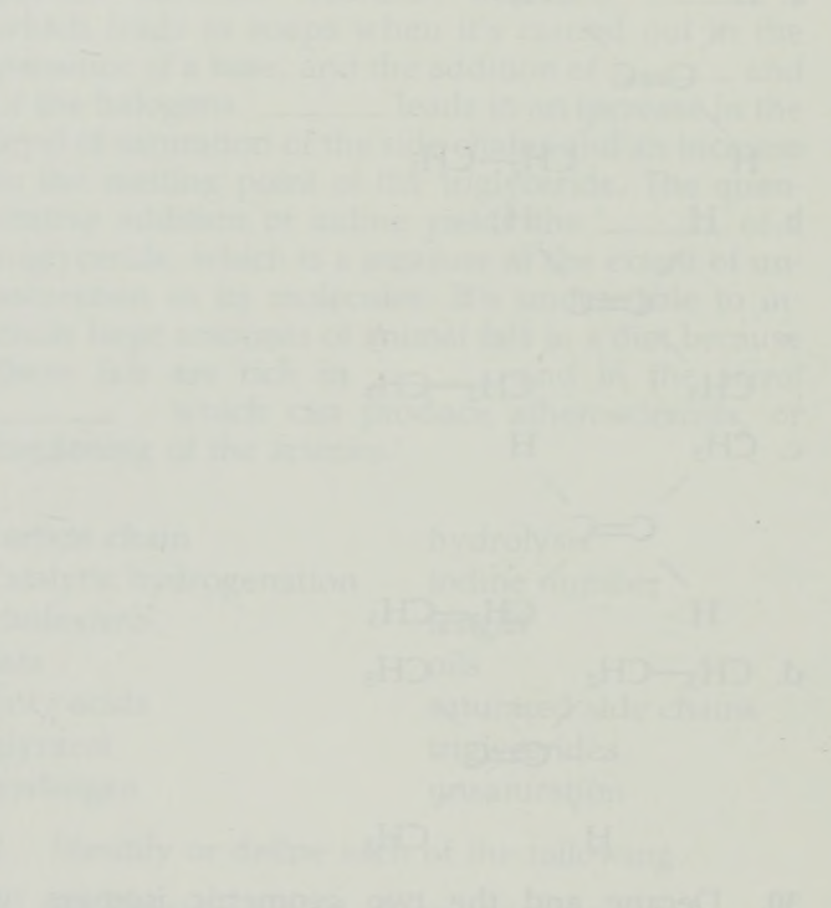
25. Suppose you want to modify the opening demonstration so that the safflower oil remains colored with the iodine color while some other oil loses its color. Just what oil would you use for the other oil, while the safflower oil remains colored? What is the basis for your choice?

26. In the oils obtained from fish that live in cold waters are generally more highly unsaturated than the oils of fish whose natural habitats are in warm waters. In what way would an increase of unsaturation benefit fish living in very cold waters?

27. Even though cocoa butter comes from a plant, it is a fat. After comparing cocoa butter's content of the various fatty acids with those of other vegetable triglycerides (see Table 13.3), suggest a reason for its unusually high melting point.

28. Give the names or structures of the organic products produced by the reaction of glyceryl trioleate with an excess of (a) NaOH and H_2O, (b) I_2, (c) H_2 and a catalyst.

29. Label each of the following as cis or trans or incapable of geometric isomerism:



30. Decene and the two geometric isomers of 5-decene, $CH_3{-}(CH_2)_3{-}CH{=}CH{-}(CH_2)_3{-}CH_3$, have the following melting points:

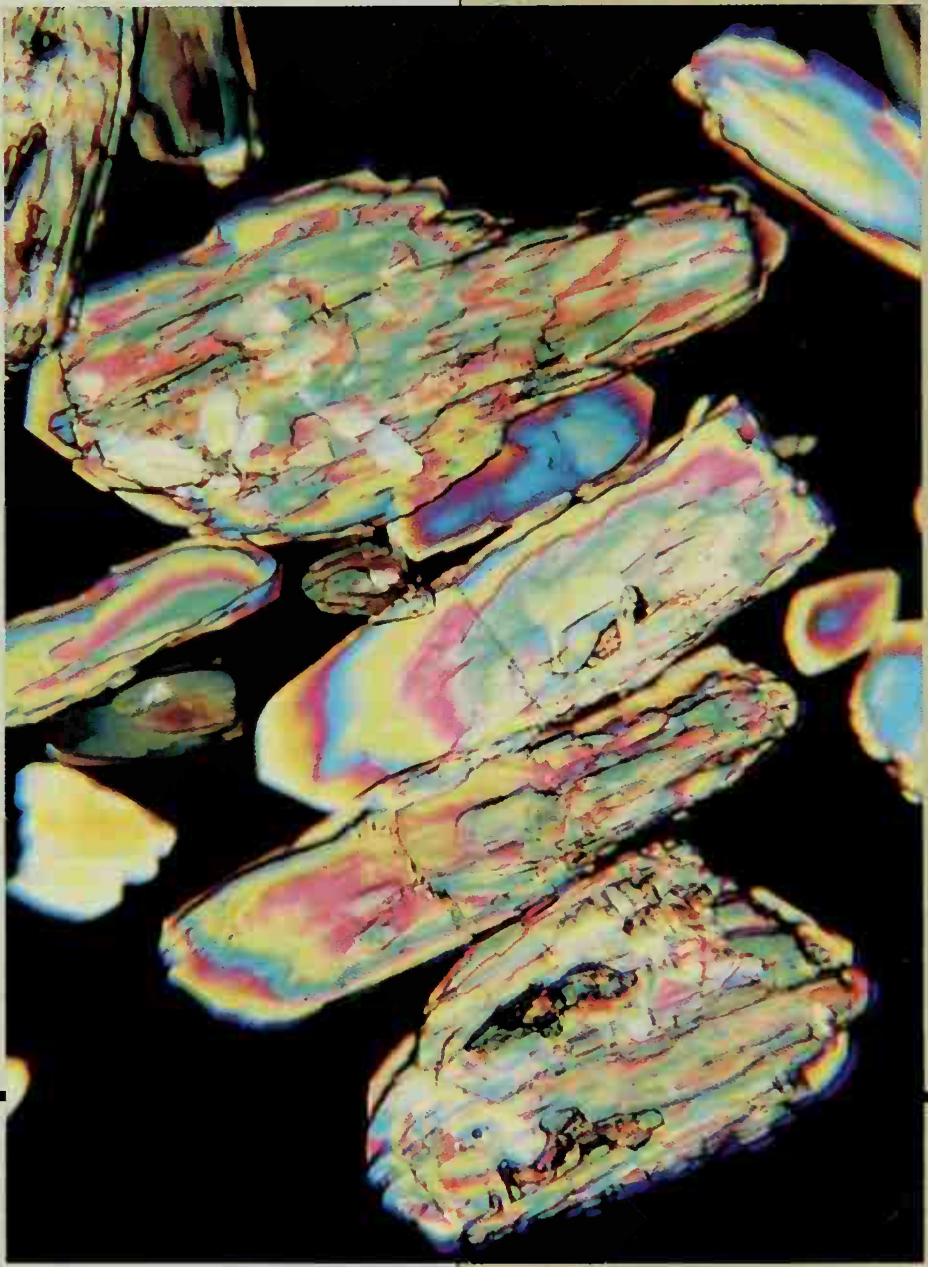
	Melting Point
decene	[illegible]
trans-5-decene	[illegible]
cis-5-decene	[illegible]

Draw the structures of the two geometric isomers of 5-decene. Label them as cis and trans, and account for the differences in melting points.

Carbohydrates

14

FOOD FOR THOUGHT



Crystals of sucrose illuminated with polarized light.

Figure 14.1
The color produced by an iodine solution distinguishes the starch of a potato from the cellulose of an apple. The iodine turns blue-black with starch, but remains reddish brown with cellulose.

How to Tell a Potato from an Apple, the Hard Way

You could tell one from the other by smelling or tasting them. Of course, you could just look at them. But there's a harder way to do it. It's more fun, too.

The interior pulp of an apple looks very much like the interior pulp of a potato. They're both pale and appear to have the same consistency. If you slice out a piece of the interior of a raw potato and of an apple it's hard to see any difference between them. But announce that you can do just that. You can tell which is a section of apple and which is a section of potato without smelling, tasting, or touching either one. Leave the room while a friend cuts out a piece of a raw potato and a similar piece of an apple (a ripe Delicious apple works well) and places them on a small dish, side by side, without any skin or other identifying characteristics on either one.

Now come back into the room with a small bottle of tincture of iodine, the kind used for demonstrations in earlier chapters. Put a few drops of iodine on each piece. When the iodine contacts the potato it turns a very dark purple, nearly black as you can see in Figure 14.1. While the apple might give a few small, dark spots too, for the most part the iodine on the apple retains the same reddish-brown color it has on skin when it's used on a cut. The piece that turns almost black is the potato; the one that's mostly reddish brown is the apple. Why? We'll see later in this chapter.

14.1 The Brain's Own Fuel

While you were reading the details of that demonstration, you were burning up energy. You still are, even as you read these words. Aside from the fundamental workings of basal metabolism and aside from the possibility of specific dynamic action, your brain and its associated network of nerves are hard at work interpreting these short, straight, and rounded lines you see before you, converting them to recognizable letters and to words and thoughts, and absorbing and digesting them. All this nibbles away at your stores of energy.

You do very little actual work in this sort of mental activity, but you do consume a small and measurable amount of energy. The fuel that supplies this energy to your brain is the carbohydrate *glucose*, also known to us as *dextrose* or *blood sugar*. Glucose is the specific and exclusive fuel of the brain and the nervous system. It is quite literally our food for thought. Glucose also supplies the energy that keeps our bodies at a constant temperature, moves our muscles, and keeps our digestive and respiratory systems running.

To provide a continuous supply of this fuel to the brain, nerves, muscles, and other bodily systems, the body maintains a concentration of about 0.06 to 0.11 weight percent glucose in the blood. Somewhere below this range the brain begins to lose its ability to function effectively. Above concentrations of about 0.16%, glucose begins to seep through the kidneys into the urine, producing one of the symptoms of diabetes. In this chapter we're going to examine the class of macronutrients known as carbohydrates. We'll learn what a carbohydrate is and why carbohydrates are important to us. As we do this we'll focus on glucose, which is one of the simplest of the common carbohydrates as well as one of the most important.

A 5% solution of glucose, a carbohydrate also known as dextrose and blood sugar, provides nourishment through intravenous injection into the bloodstream.

QUESTION

Blood makes up about 8% of the body weight of a healthy adult. How many grams of glucose circulate through the body of a typical 110 pound person? ___________

14.2 A Case of Mistaken Identity

Unlike our nutritional fats and oils, all of which are esters of glycerol and which differ from one another entirely through the lengths and the degrees of unsaturation of their side chains, the carbohydrates come in a great variety of shapes and sizes. All carbohydrates, though, share certain key molecular characteristics.

1. Carbohydrates are composed exclusively of three elements: carbon, hydrogen, and oxygen.
2. Carbohydrate molecules themselves occur in various shapes and sizes, but the carbon atoms that form them are almost always strung along one next to the other in unbranched chains.
3. The ratio of hydrogen atoms to oxygen atoms in all carbohydrate molecules is almost always exactly 2:1, as it is in water.

This unvarying ratio generates molecular formulas for carbohydrates that suggested to the earliest workers in this field that these molecules are merely hydrates of carbon, or combinations of carbon and water. (The word *hydrate* and the latter portion of carbo*hydrate* come from a Greek word for "water.") The molecular formula of glucose for example, $C_6H_{12}O_6$, can be written as though the molecule were composed of six carbon atoms bonded to each other and also to six water molecules, as in $C_6(H_2O)_6$. Although this interpretation of the molecular formulas proved to be completely incorrect, the name *carbohydrate,* meaning "hydrate of carbon," has stuck. Now it applies not only to the carbohydrates themselves, but also to other, closely related compounds with hydrogen-to-oxygen ratios varying just a bit from 2:1.

Adding a little concentrated sulfuric acid to powdered sucrose produces heat, steam, and a black, brittle solid that resembles badly charred wood.

QUESTION

Adding concentrated sulfuric acid, a very strong acid and a very powerful *dehydrating* agent, to powdered table sugar effectively and dramatically dehydrates the sucrose, forming water and a black, brittle substance resembling badly charred wood. The reaction is vigorous and evolves considerable heat, enough heat, in fact, to convert the newly removed water into steam. What is the brittle, black solid formed from the sucrose by this dehydration? ________________

14.3 From Monosaccharides to Polysaccharides

A **monosaccharide** is the smallest molecular unit of a carbohydrate. Glucose is a monosaccharide.

Carbohydrates are easily sorted into several kinds of categories according to their size and also according to the functional groups they carry. (As we saw in Section 11.11, a *functional group* is a portion of the molecular structure that confers a characteristic chemical reactivity to a molecule.) The smallest, simplest carbohydrates, those that form the foundation of carbohydrate chemistry, are the **monosaccharides**. The root *-sacchar-* comes to us from the Latin *saccharum,* "sugar." We see it also in *saccharin,* the first commercially successful, synthetic sugar substitute. *Monosaccharide,* then, literally means "one sugar." Chemically, the monosaccharides are the smallest units of the carbohydrates. We can split any carbohydrate molecule into smaller and smaller units until we come to the monosaccharides that compose it. When we split apart a monosaccharide molecule, the products are almost never carbohydrates themselves. Glucose is a monosaccharide.

A **disaccharide** is a molecule formed from a combination of two monosaccharides. A **polysaccharide** is a molecule that exists as a chain of hundreds of monosaccharides.

Strings of monosaccharides, joined by covalent bonds, form larger and more complex carbohydrates, ranging in size from a combination of two monosaccharides, such as sucrose (table sugar), lactose (milk sugar), and related sugars, to the enormously long molecules of the edible starches of plants and the indigestible cellulose of dietary fiber. Join two monosaccharide molecules together chemically and you get a **disaccharide** (sucrose, for example); three give a trisaccharide; four, a tetrasaccharide; and so forth. Linking very large numbers of individual monosaccharides into very long chains gives **polysaccharides**, such as starch and cellulose. Molecules of these complex carbohydrates consist of chains containing 300 to often more than 1000 glucose molecules joined to each other, one after another, in long molecular strings.

In all of these cases, the carbon skeletons of the individual monosaccharides are connected through oxygen atoms, via carbon–oxygen–carbon bonds. While degrading the monosaccharides themselves into smaller molecules is a tricky and complex job that requires breaking the carbon–carbon bonds of their individual molecular skeletons, the more complex carbohydrate chains can be clipped easily by breaking the carbon–oxygen bonds that hold them together. Water does the job nicely through hydrolysis, especially if there's a little acid and perhaps a specific enzyme present. We'll have more to say about the catalytic action of enzymes in Section 14.12.

TABLE 14.1 Common Carbohydrates

Carbohydrate	Molecular Formula	Source or Origin	Monosaccharide(s) Produced on Hydrolysis
Monosaccharide			
Glucose (also known as blood sugar, grape sugar, and dextrose)	$C_6H_{12}O_6$	Blood, plant sap, fruit, honey	
Fructose (also known as levulose)	$C_6H_{12}O_6$	Plants, fruit, honey	
Galactose	$C_6H_{12}O_6$	From the hydrolysis of lactose	
Disaccharide			
Sucrose (also known as table sugar, beet sugar, and cane sugar	$C_{12}H_{22}O_{11}$	Sugar cane, sugar beets, maple syrup, and various fruits and vegetables	Glucose and fructose
Maltose (also known as malt sugar)	$C_{12}H_{22}O_{11}$	Partial hydrolysis of starch	Glucose
Cellobiose	$C_{12}H_{22}O_{11}$	Partial hydrolysis of cellulose	Glucose
Lactose (also known as milk sugar)	$C_{12}H_{22}O_{11}$	Makes up about 5% of milk	Glucose and galactose
Polysaccharide			
Starch		Potatoes, corn, various grains	Glucose
Cellulose		Cell walls of plants	Glucose

Table 14.1 presents some of the more common carbohydrates, their common names, and some of their chemical characteristics.

QUESTION

What monosaccharide(s) do you get from the hydrolysis of (a) table sugar, (b) lactose, (c) cellulose, (d) potato starch? ____________________

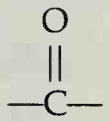
14.4 Glucose: An Aldohexose

It's useful to classify the monosaccharides themselves according to

- the lengths of their carbon chains, and
- which one of two important functional groups they contain.

We'll take the matter of chain lengths first. A monosaccharide with a molecular skeleton three carbons long is a *triose*. The suffix *-ose* tells us that we are dealing with a carbohydrate, while the prefix *tri-* indicates the number of carbons, three in this case. A *tetrose* is a four-carbon monosaccharide, a *pentose* contains five carbons, and a *hexose* contains six carbons. The *-ose* ending of these names comes from the word *glucose*, which was itself adopted as a chemical term (in 1838, by a committee of French scientists) from a Greek word for fermenting fruit juice or sweet wine, or simply for the quality of sweetness.

As for their functional groups, all common monosaccharides consist of a chain of carbons, all but one of which are bonded to a hydroxyl group (C—OH). The single exception is a carbon doubly bonded to an oxygen, thereby forming a carbonyl group (Section 10.7).

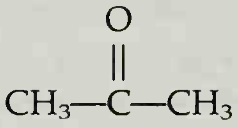


$$\overset{\displaystyle O}{\overset{\|}{—C—}}$$

carbonyl group

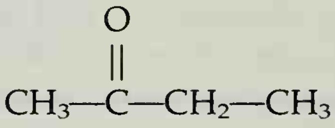
A **ketone** contains a carbonyl group bonded to two carbon atoms.

The two atoms (other than the oxygen) that are bonded directly to the *carbonyl carbon* determine whether it is part of an *aldehyde* or a *ketone*. In a **ketone**, both these atoms are carbons. Typical simple ketones include the solvents *acetone* and *methyl ethyl ketone*, which is also known by its more formal, chemical name, *2-butanone*. Both acetone and methyl ethyl ketone are liquids at room temperature. Acetone serves as the major solvent in some nail polish removers. (You can usually find it listed among the ingredients on the label.) Methyl ethyl ketone is a common component of nail polish, nail polish removers, and commercial paint thinners and removers.



$$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$$

acetone

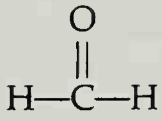


$$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_2—CH_3$$

methyl ethyl ketone
or
2-butanone

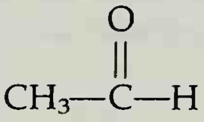
An **aldehyde** contains a carbonyl group bonded to at least one hydrogen.

In **aldehydes**, at least one of the substituents on the carbonyl carbon is a hydrogen. Among the simpler aldehydes are *formaldehyde* (in which *both* substituents are hydrogens), *acetaldehyde*, and *benzaldehyde*.



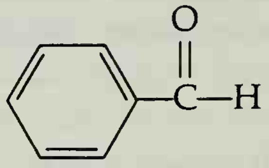
$$H—\overset{\displaystyle O}{\overset{\|}{C}}—H$$

formaldehyde



$$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—H$$

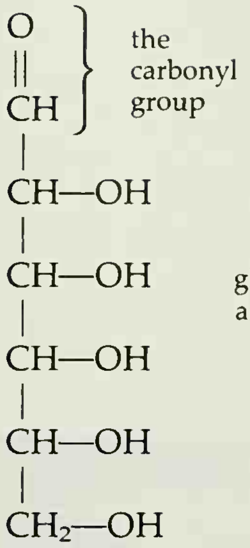
acetaldehyde



benzaldehyde

Formaldehyde itself is a water-soluble gas. A 37 weight percent solution in water, known as *formalin*, is an effective biological preservative and is used in preparing embalming fluids. Benzaldehyde, also known as oil of bitter almond, is useful as a food flavoring and is an ingredient of many perfumes.

All of the common monosaccharides contain one or the other of these two carbonyl groups. They are either polyhydroxy aldehydes or polyhydroxy ketones, or compounds very closely resembling polyhydroxy aldehydes and ketones. Monosaccharides with an aldehydic carbonyl group are the *aldoses*; those with ketonic groups are the *ketoses*. The classification of monosaccharides can indicate, simultaneously, both their carbon chain lengths and the kinds of substituents on their carbonyl groups. Glucose for example, with a six-carbon skeleton topped off by an aldehydic group, is an *aldohexose*. Here the prefix *aldo*- tells us that glucose contains the aldehyde carbonyl group (*aldehyde*, because there's a hydrogen bonded to the carbonyl group's carbon), the stem -*hex*- refers to the six carbons present, and the suffix -*ose* places the compound into the carbohydrate family.

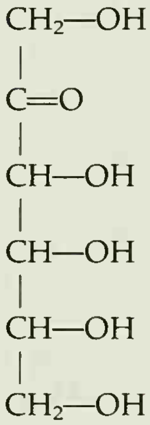


$$\begin{array}{l} \mathrm{O} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH_2{-}OH} \end{array}$$

glucose,
an aldohexose

QUESTION

Glucose, as we've just seen, is an example of an *aldohexose*. What would you call the category of monosaccharides that includes *fructose*?

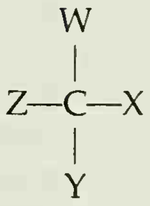


$$\begin{array}{l} \mathrm{CH_2{-}OH} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH_2{-}OH} \end{array}$$

fructose

14.5 Your Right Hand, Your Left Hand, a Mirror, . . .

Every monosaccharide molecule of every classification contains at least one carbon that bears a certain resemblance to one of your hands. As we saw much earlier, in Section 7.2, a carbon of an alkane or, more generally, any carbon bonded to four groups, lies in the center of a *tetrahedron*, a solid four-sided structure. With the carbon at its center, each of the four substituents lies at one of the four corners or apexes of the tetrahedron. If we have before us a carbon bonded to four different groups, such as the generalized molecule CWXYZ,



$$\begin{array}{c} \mathrm{W} \\ | \\ \mathrm{Z{-}C{-}X} \\ | \\ \mathrm{Y} \end{array}$$

we can represent the shape of the carbon and its four bonded groups as a tetrahedron, with C at the center of the three-dimensional figure and the substituents W, X, Y, and Z occupying the apexes (Figure 14.2).

All this is important to the chemistry of even the most ordinary of the sugars since

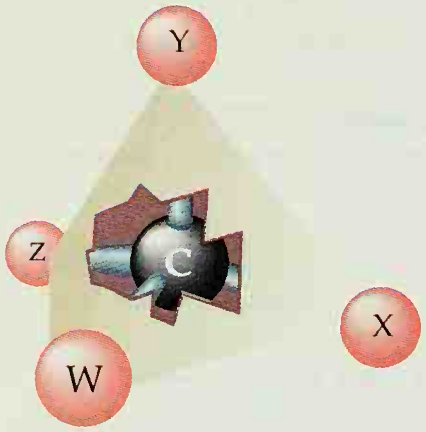
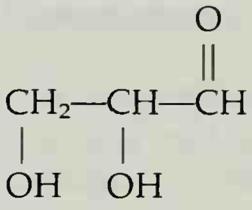


Figure 14.2
A tetrahedral carbon bonded to four different groups: W, X, Y, and Z.

- every carbohydrate molecule contains at least one of these CWXYZ carbons, and
- a carbon bonded to four different substituents confers certain extraordinary properties on the molecule, affecting especially its behavior toward light.

We'll examine the unusual behavior of the CWXYZ carbon through the aldotriose *glyceraldehyde*. As an aldotriose, glyceraldehyde is an aldehyde that contains three carbons and is a member of the carbohydrate family. This compound has no direct consumer applications whatever; its significance to us lies in its small size and its simplicity. It's a very good place to start.



$$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{CH}}$$

glyceraldehyde

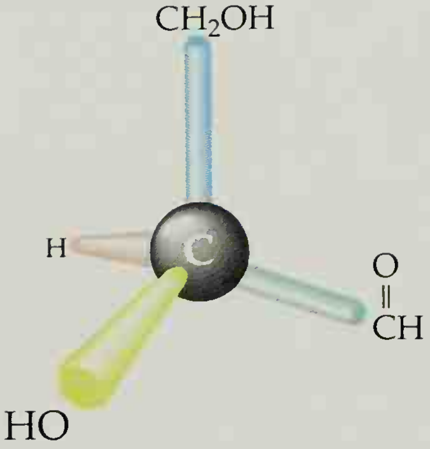
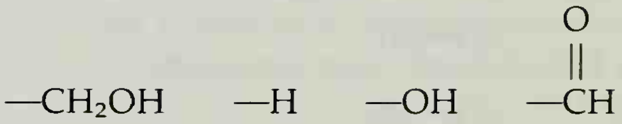


Figure 14.3
Glyceraldehyde stereochemistry.

With its central, tetrahedral carbon bonded to four different groups,



$$-CH_2OH \qquad -H \qquad -OH \qquad -\overset{\displaystyle O}{\overset{\|}{CH}}$$

glyceraldehyde clearly represents a CWXYZ molecule. The specific orientation in space of the four groups surrounding the central carbon represents the carbon's *stereochemistry* (Section 7.2; Fig. 14.3). This stereochemistry represents an important characteristic of a CWXYZ molecule since *any carbon bonded to four different groups* takes on a peculiar property also found in your right and left hands: *it is not superposable on its mirror image.* Thus the glyceraldehyde molecule of Figure 14.2 is not superposable on its mirror image. We can consider two structures to be identical, or superposable, if we can merge them in space so that each and every point on one of the structures coincides exactly with its equivalent point on the other structure. If such point-for-point merging in space is not possible, the two are *not* **superposable.**

Two structures are **superposable** if they can be merged in space so that each and every point on one of the structures coincides exactly with its equivalent point on the other structure.

Your right and left hands, for example, are not superposable. When you place your right hand before a mirror, the mirror produces an image that is essentially identical with your left hand. Just as your right hand cannot be superposed, point-for-point, on your left hand, your right hand cannot be superposed on its own mirror image. You can't fit your right hand into a left-hand glove, either.

Chiral molecules have the characteristic "handedness" of right and left hands. **Enantiomers** are nonsuperposable mirror images.

The three-dimensional glyceraldehyde molecule of Figure 14.2 can no more be superposed on its mirror image than your right hand can be superposed on its own mirror image, which corresponds to your left hand. Molecules with this property of "handedness" are called **chiral molecules,** from a Greek word meaning "hand." Chiral molecules exist as two isomeric structures that are alike in every way except for their stereochemistry and its consequences. Each of these two isomers, the "right-handed" and the "left-handed" molecules, is an **enantiomer** of the other. Together they form an *enantiomeric pair.* The two enantiomers of glyceraldehyde appear in Figure 14.4. Notice that

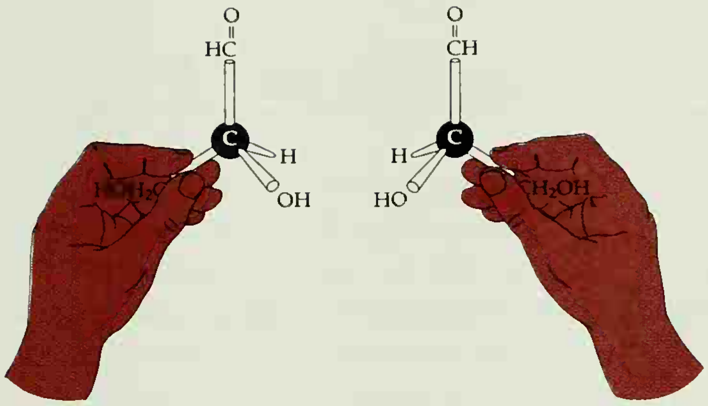


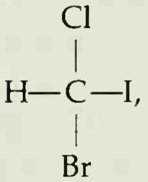
Figure 14.4
The two enantiomers of glyceraldehyde. The two molecules are nonsuperposable mirror images of each other.

they are mirror images of each other, like your right and left hands. Notice also that they are not superposable on each other, again like your right and left hands. Chiral molecules can affect light in a way we'll examine soon. But first, in the next section, we'll find a particularly simple and convenient way to represent their molecular structures.

We'll close here with a comment on an important structural requirement for chirality. We've seen that every carbon bonded to four different groups, as in CWXYZ, is chiral. Notice, though, that if two or more of these four substituents are identical, as in CWX*YY*, then the carbon *is* superposable on its mirror image and *cannot* be chiral. Remember that when we look at the substituents to determine whether any two are identical, we have to look at each substituent group as a whole, not simply at the four individual atoms bonded directly to the carbon.

A mirror turns a right hand into a left hand. (Or is it a left hand into a right hand?)

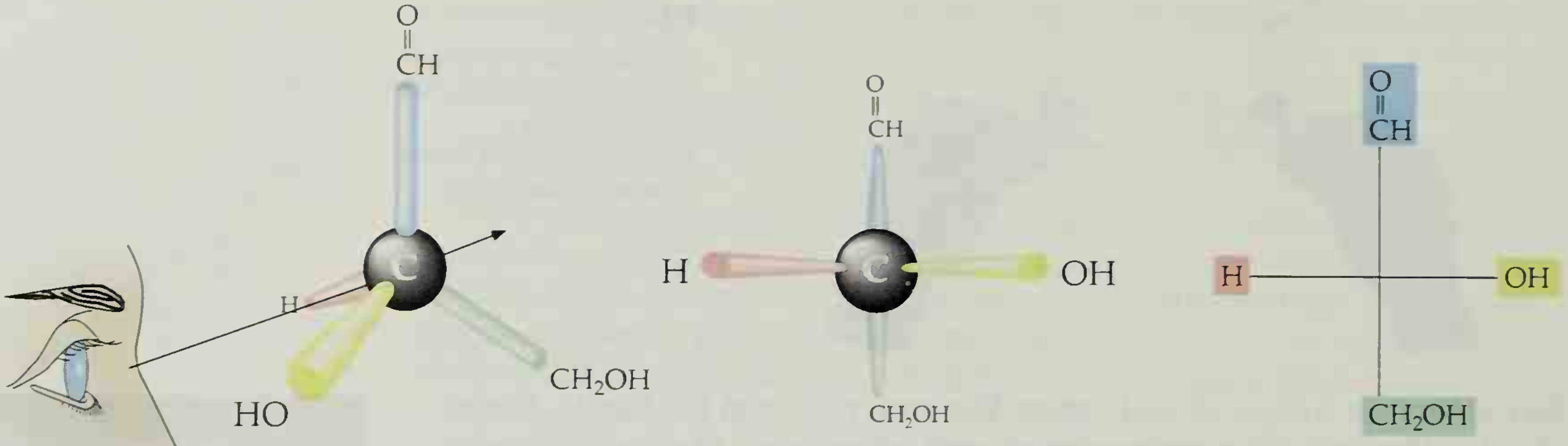
QUESTION

Which of the following are chiral: (a) a glove, (b) a shoe, (c) a tennis ball, (d) a molecule of methane, (e) the molecule  $\begin{array}{c} Cl \\ | \\ H{-}C{-}I \\ | \\ Br \end{array}$, (f) CH_2BrCl?

14.6 . . . A Human Skeleton, and . . .

Drawing the structure of a chiral molecule in as much detail as there is in Figure 14.2 is time consuming and requires a bit of artistic skill. A simpler and much more convenient approach to showing stereochemistry, the **Fischer projection**, appears in Figure 14.5. Emil Fischer, a German chemist, received the Nobel Prize in 1902, partly for his studies of the chemistry of sugars. To show clearly the stereochemistry of the chiral carbons in a sugar molecule, Fischer proposed that each chiral carbon be represented by a simple cross. Using glyceraldehyde as an example, we view the tetrahedral carbon of Figure 14.4 so that the carbon backbone is vertical, much like the spine of a human skeleton. The horizontal edge tying together the substituents at the front of the molecule now forms the rib cage of the skeleton. The chiral carbon itself lies at the intersection of the two lines.

A **Fischer projection** is used to show the stereochemistry of a chiral carbon.



Viewing this enantiomer of glyceraldehyde in this direction . . .

. . .produces this image.

Joining the groups at the rear by a vertical line and the groups at the front by a horizontal line produces a Fischer projection

Figure 14.5
The Fischer projection.

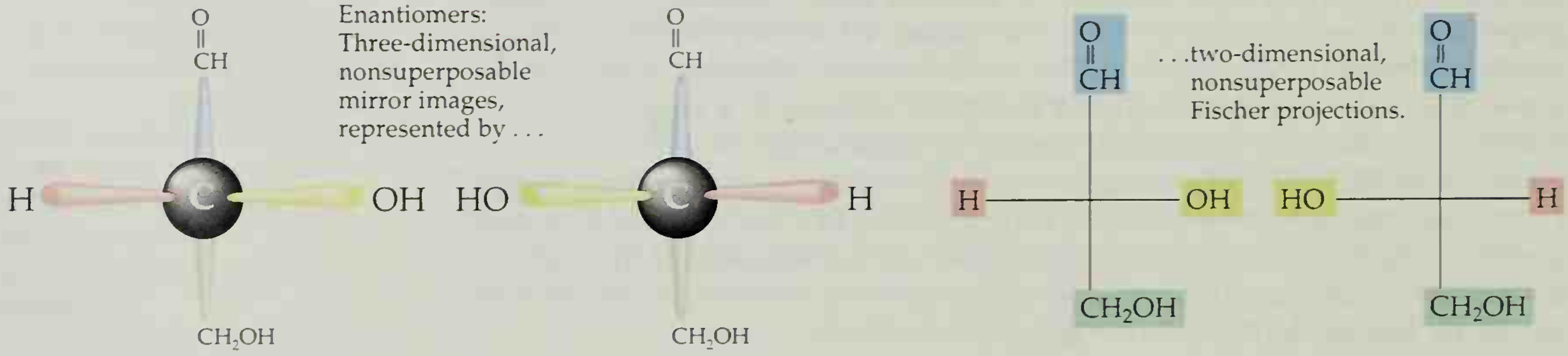
To construct the Fischer projection we simply draw a cross. The vertical line connects the carbons bonded to and behind the chiral carbon, while the horizontal line joins the substituents in front of the chiral carbon.

The utility of this projection comes not only from its simplicity and ease of use, but also from its close correspondence to the chiral molecules themselves. The Fischer projections of two enantiomers are themselves nonsuperposable mirror images and so these two-dimensional figures represent the three-dimensional chiral molecules very nicely (Fig. 14.6). Because of the way the Fischer projections are generated, we are not permitted to (mentally) remove them from the paper on which they're printed, nor are we permitted to rotate them except for a rotation of 180°, wholly within the plane of the paper. But we can slide them about on the paper to determine whether they represent structures that can or cannot be superposed. If the Fischer projections can be superposed, within the restrictions of movement we have just described, then the three-dimensional molecules they represent can also be superposed. The converse, of course, is also true.

QUESTION

Draw the Fischer projections of both enantiomers of $ClCH_2$—CHOH—CH_2OH and show that these projections cannot be superposed on each other. ____________

Figure 14.6
Fischer projections of enantiomers.



Enantiomers: Three-dimensional, nonsuperposable mirror images, represented by . . .

. . .two-dimensional, nonsuperposable Fischer projections.

14.7 . . . A Pair of Sunglasses

The most remarkable property that chirality confers on a molecule lies in its effect on polarized light. All light consists of waves with crests and troughs, much like the waves we see on the surface of water (Fig. 14.7). In water waves, any molecule of water, or any object floating on the water, moves largely up and down in a direction perpendicular to the direction in which the wave is traveling. While the wave that we are watching travels horizontally, the water itself oscillates vertically.

We can think of light in much the same way. According to one particularly useful physical model, a light beam moves along with its waves undulating, like water's waves, in a direction perpendicular to the direction of the light's travel. Unlike water waves, though, the undulations of light oscillate in *all* directions perpendicular to the direction of the beam. If we could place a sheet of some special material into a light beam's path so that we could watch these vibrations, we'd see something that looks like Figure 14.8. This represents ordinary or *unpolarized* light.

Polarized light differs from unpolarized light in one critical respect. Unpolarized light is made up of oscillations in *all* planes that include the beam's line of travel, but the oscillations of polarized light are limited to only one,

Polarized light is light consisting of oscillations in only one plane, which is known as the **plane of polarization**.

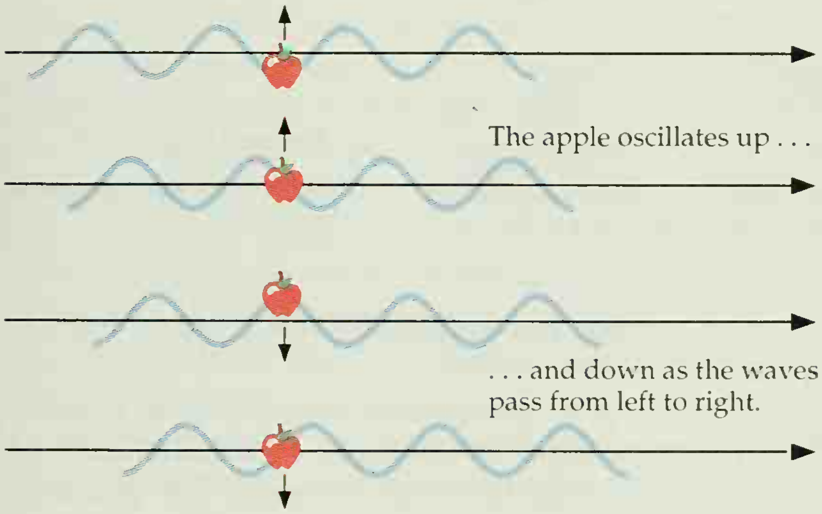


Figure 14.7
An apple bobbing in water.

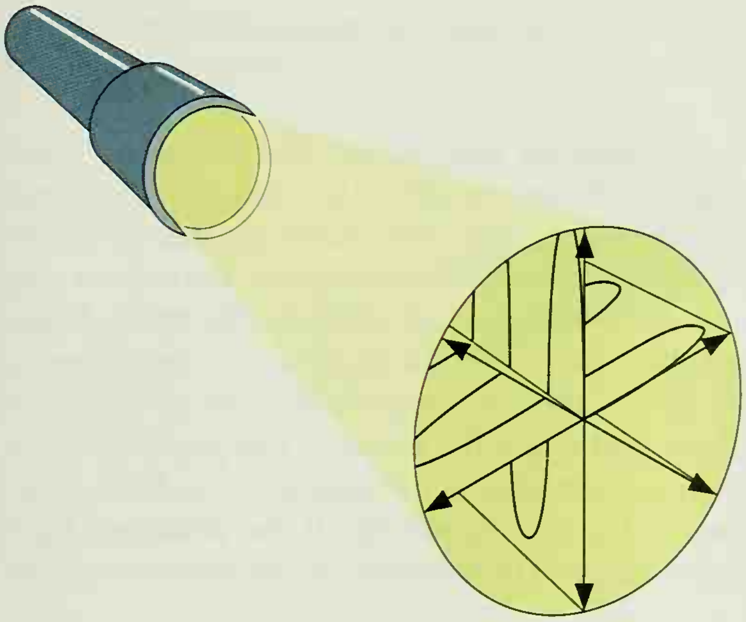
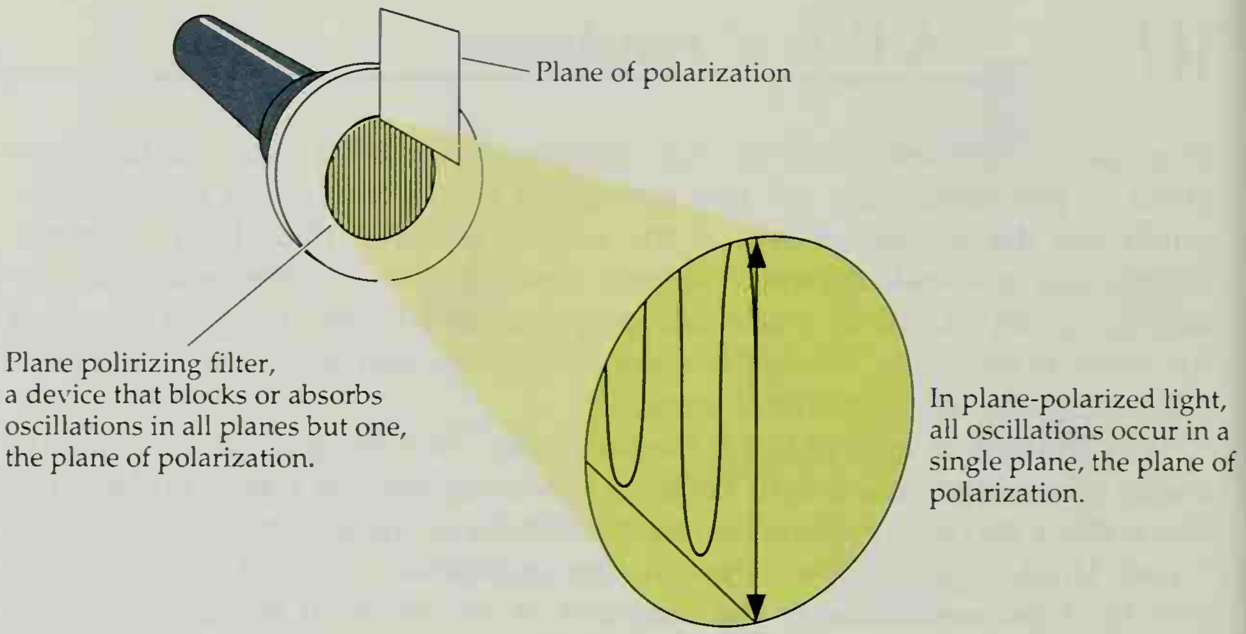


Figure 14.8
Unpolarized light.

Figure 14.9
Plane-polarized light.



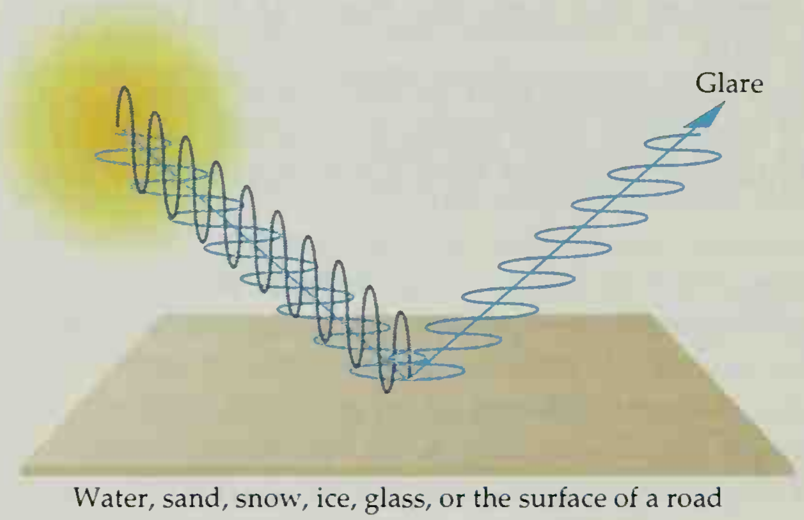


Figure 14.10
Reflected glare is plane-polarized light.

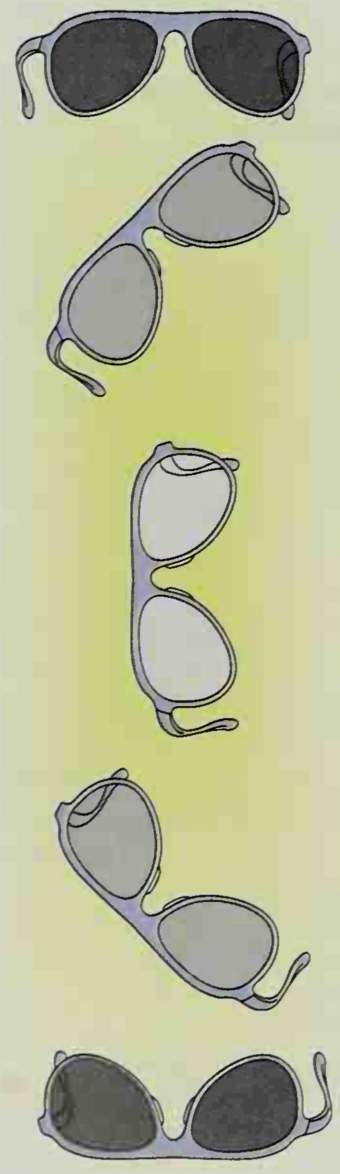


Figure 14.11
Polarizing sunglasses versus glare.

single plane, the **plane of polarization**. For emphasis, this form of light is sometimes called *plane-polarized* light (Fig. 14.9).

Several devices and some physical phenomena and processes can convert unpolarized light into plane-polarized light by blocking or removing all of the vibrations except for those occurring in what becomes the plane of polarization. Light reflected as glare from water, sand, snow, ice, roads, or other surfaces becomes polarized, with the plane of polarization parallel to the reflecting surface. Glare, then, is an example of plane-polarized light (Fig. 14.10).

To reduce glare we can wear polarizing sunglasses. The lenses of these sunglasses are, themselves, polarizing filters capable of blocking out all planes of vibration except one. Setting the lenses into the frames so that their polarizing planes are vertical orients them perpendicular to the horizontal surfaces that cause glare. The lenses now block out all of the horizontally polarized light that forms the glare, but allow vibrations in other directions to get through to our eyes. Hold a pair of these sunglasses in front of you, look through the lenses at surface glare, and rotate the glasses. You'll see the glare alternately appear and disappear as you swing the glasses in a circle (Fig. 14.11). That's because the lenses of the sunglasses let all the polarized light of the glare through only when the plane of polarization of the lenses matches

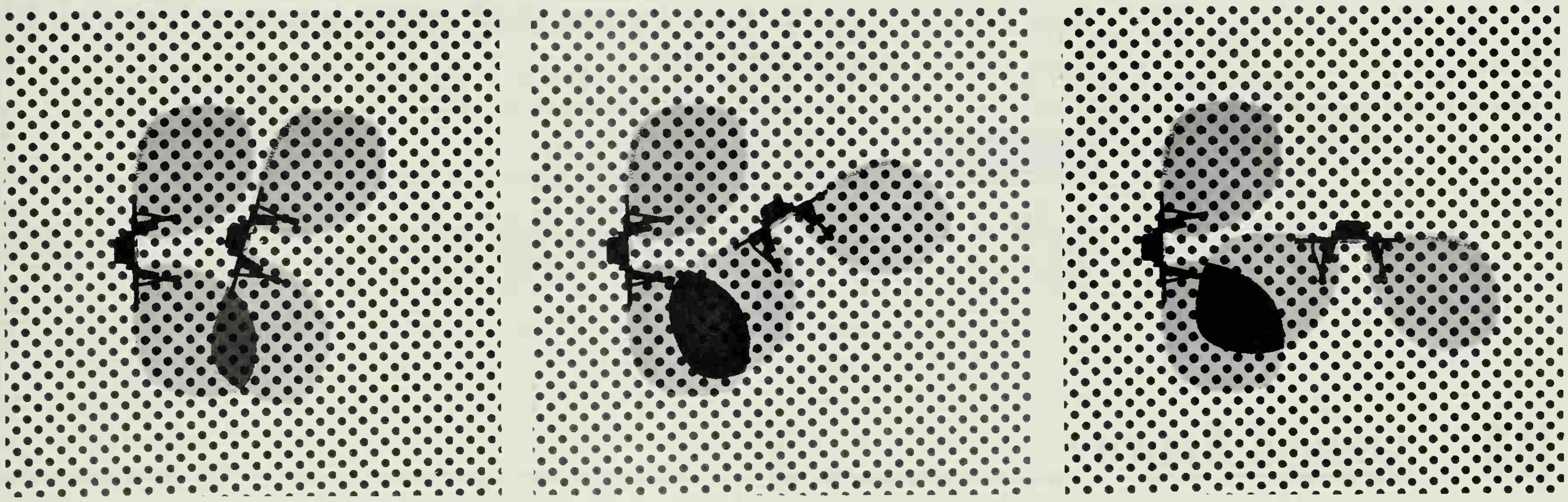


Figure 14.12
The effect of polarizing lenses on unpolarized light.

the direction of the light's oscillations. When the two planes are crossed, none of the glare gets through. As you rotate the lenses their plane of polarization also rotates, alternately matching the plane of the glare and crossing it.

In fact, you can block out virtually all light from any source of relatively low intensity by removing the lenses from the frame and crossing them as in Figure 14.12. With their planes of polarization crossed, the first lens effectively converts ordinary, unpolarized light into plane-polarized light and the second lens, with its plane of polarization perpendicular to that of the first lens, blocks out all the plane-polarized light coming through the first lens. The result is a very dark spot.

Place a hollow tube between the two lenses, fix the first lens into a permanent position, add a pointer and an angular scale to the nearer lens, introduce a few other refinements, such as a light source at the far end, and you have an instrument of immense value to the study of sugars, a *polarimeter* (Fig. 14.13). In the instrument you have just built, the fixed lens is called the polarizing filter and the other lens, which is still movable, is the analyzing filter.

In the next two sections we'll see how a polarimeter is used and how we get the common names *dextrose* for glucose, *levulose* for fructose, and *invert*

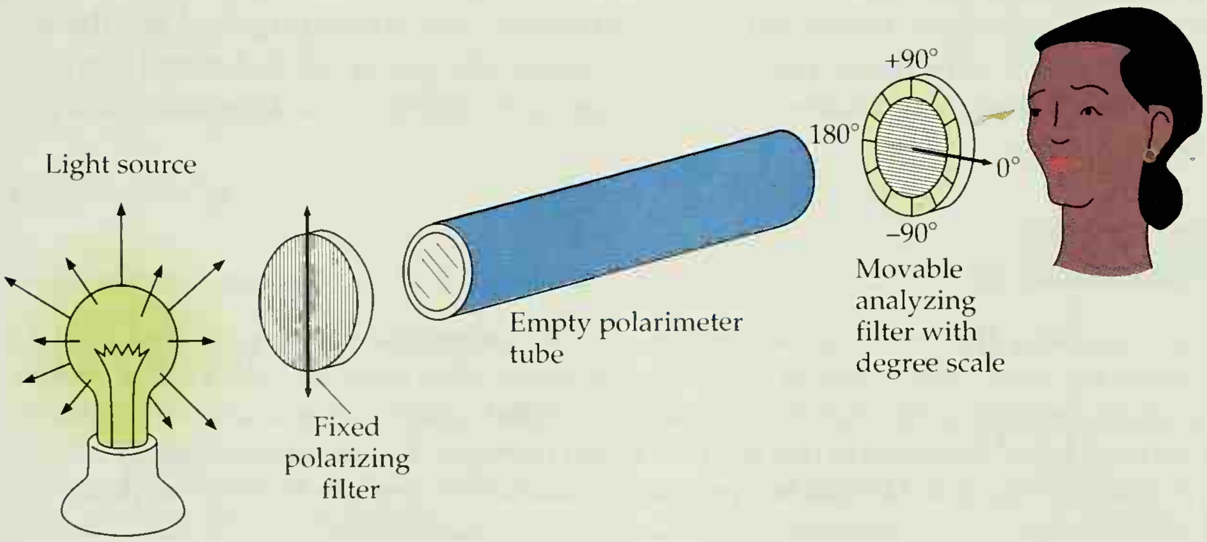


Figure 14.13
The essentials of a polarimeter.

sugar for the sugars of honey. All of these names come from the effect of these sugars on polarized light.

QUESTION

A pair of clear, colorless, untinted polarizing sunglasses would still reduce glare sharply, but they would reduce the intensity of other light only very little. Why?

14.8 Optical Activity

If you were to build a polarimeter like the one in Figure 14.13, and set the nearby movable analyzing filter with its plane of polarization exactly perpendicular to that of the fixed, polarizing filter, you would see only a dark or very dim field as you sight through the polarimeter tube.

But fill the hollow polarimeter tube with any substance made up of chiral molecules of a single stereochemistry, either one of the pure enantiomers of glyceraldehyde for example, and the image would brighten. *Chiral molecules have the remarkable property of rotating the plane of polarized light.* You would now readjust the analyzing filter by rotating it through a measurable angle to regain the darkest possible image.

The actual, quantitative angle through which you would have to rotate the filter depends on several factors, including the molecular structure of the chiral compound, its concentration (if you were using a solution), the temperature, and the length of the polarimeter tube. But under any specific set of conditions, the *direction* of rotation would depend only on which one of the two enantiomers you were examining. Under identical conditions, the two enantiomers of a chiral compound rotate the plane of polarized light to exactly the same degree, but in opposite directions. We call the enantiomer that requires the analyzing filter to be rotated clockwise **dextrorotatory**, from the Latin *dextra* for "right" (or, in a related sense, clockwise). In naming specific enantiomers, as we'll see in the next section, dextrorotation is often indicated by an algebraic "+." The other enantiomer, the one that generates a counterclockwise rotation, is **levorotatory**, from the Latin *laevus*, for "left" (counterclockwise). Levorotatory enantiomers are often indicated by the algebraic "−." Anything capable of rotating the plane of polarized light is **optically active**; substances that don't or can't produce such rotation are *optically inactive*.

An **optically active** substance is capable of rotating the plane of polarized light. A **dextrorotatory** substance rotates the plane to the right, or clockwise. A **levorotatory** substance rotates the plane to the left, or counterclockwise.

QUESTION

Knowing that the two enantiomers of a chiral compound rotate polarized light to exactly the same extent, but in opposite directions, what effect do you think a *mixture* of equal amounts of the two enantiomers of a chiral compound would have on plane-polarized light? Mixtures of this kind are called *racemates*. Is a racemate optically active? What term in Section 14.8 can be applied to a racemate to describe its effect on polarized light? ______

14.9 Glucose (Alias Dextrose), Fructose (Alias Levulose), and Invert Sugar

Glucose, an aldohexose, contains six carbons, four of which are chiral. The top, carbonyl carbon is not chiral and neither is the bottom one, which is bonded to two hydrogens along with an —OH group and the rest of the carbon chain. Each of these two carbons is *achiral*. Figure 14.14 shows the stereochemistry of each of the remaining four, chiral carbons.

Drawing the mirror image of the Fischer projection of Figure 14.14 reveals that glucose can exist as two enantiomers and that it must, therefore, be optically active. Since virtually all naturally occurring glucose consists exclusively of the dextrorotatory enantiomer, glucose is also known as *dextrose*. Similarly, since almost all naturally occurring fructose (Fig. 14.15) is levorotatory, *levulose* is another name for this monosaccharide. To emphasize the optical activity of these naturally occurring monosaccharides, glucose is often referred to as (+)-glucose and fructose as (−)-fructose. As we saw earlier, the algebraic signs contained within the parentheses refer to the direction of rotation.

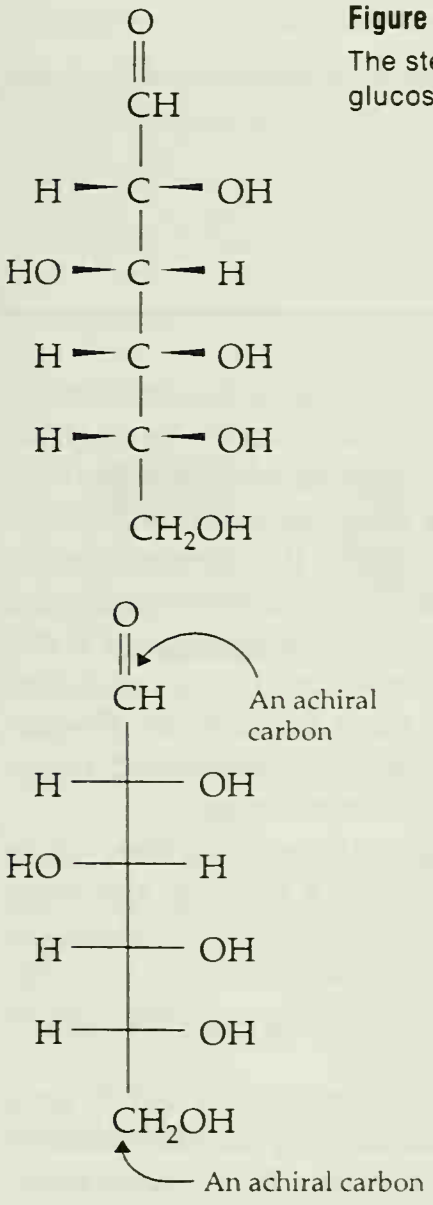


Figure 14.14
The stereochemistry of glucose.

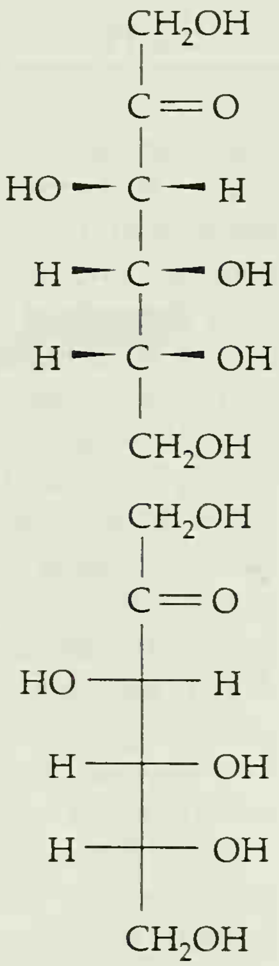


Figure 14.15
The stereochemistry of fructose.

Under identical conditions, (−)-fructose rotates plane-polarized light through a larger angle, counterclockwise, than (+)-glucose does in a clockwise direction. In a mixture of equal amounts of the two, (−)-fructose overpowers the rotatory power of (+)-glucose to produce a small, net levorotation.

As we saw in Table 14.1, sucrose is a disaccharide composed of one glucose unit linked to one fructose. The hydrolysis of sucrose, a dextrorotatory carbohydrate itself, thus yields equal quantities of the two monosaccharides, (+)-glucose and (−)-fructose, which form a levorotatory mixture because of the greater rotational power of the (−)-fructose.

Honey is largely invert sugar, a mixture of glucose and fructose.

This difference in the direction of rotation results in a clear inversion in the sign of rotation as sucrose hydrolyzes. We can observe this phenomenon by placing an aqueous solution of (+)-sucrose in a polarimeter tube and adding a little acid. First we'd observe dextrorotation because of the sucrose. Then, as the sucrose hydrolyzes to equal quantities of (+)glucose and (−)-fructose, we'd see the rotation slowly decrease, become zero, and finally turn into levorotation as the (−)-fructose takes over. Because of the inversion in the sign of rotation that accompanies this hydrolysis, the product—a mixture of equal amounts of (+)-glucose and (−)-fructose—is called **invert sugar**. Invert sugar is the major component of honey.

Invert sugar is a mixture of equal quantities of glucose and fructose.

QUESTION

How many of glucose's six carbons are chiral? How many of fructose's six carbons are chiral? ______

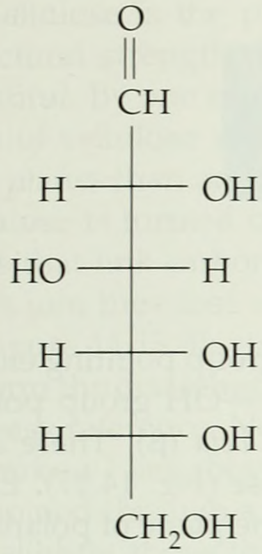
14.10 Cyclic Monosaccharides

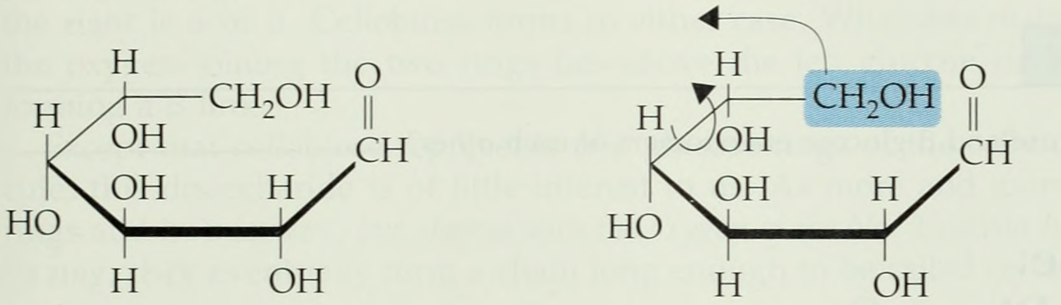
Our discussion of the chemistry of carbohydrates began with the implication that monosaccharides are all simple, straight-chain compounds. As they actually exist, though, the pentoses (five-carbon monosaccharides) and the hexoses (six-carbon monosaccharides) almost always occur as cyclic molecules. They form rings by adding one of their —OH groups to the carbon–oxygen double bond of the carbonyl group. For glucose this addition, shown in Figure 14.16, produces a ring of six atoms: the first five carbons of the hexose chain and the oxygen of the reactive —OH group. Ring formation of this kind occurs simply because it transforms the molecule into a more stable form. Chemically, these six-membered rings (and, in some cases, five-membered rings) are more stable than the straight chains of the monosaccharides.

It's customary to draw the cyclic monosaccharides as though we were viewing them almost edge-on, much as you see in Figure 14.16. With the rings drawn like this, the —H and —OH substituents that extended to the right and to the left in the Fischer projections now point upward and downward. The direction from which the —OH adds to the carbonyl group determines which one of two possible cyclic structures forms.

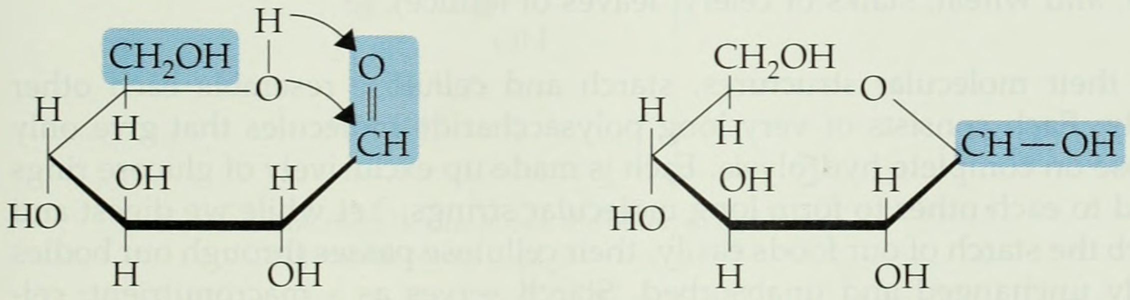
Since the carbonyl group itself is planar, with the carbon bonded to only three groups, the carbonyl carbon can't be chiral as long as the molecule remains in the form of an aldehyde or a ketone. (Anything that's two-dimen-

Figure 14.16
Ring formation in glucose.


Glucose


A glucose molecule on its side, showing the arc of the carbon skeleton. Notice that the — OH groups alternate above and below the ring in the same order as they alternate to the right and left in the Fischer projection.

Rotation around the bond, as shown, places the — CH_2OH group above the ring and places the — OH in the position to...


... add to the carbonyl group, forming a six-membered ring.

sional or planar is always superposable on its own mirror image.) But when the —OH group does add, as in Figure 14.16, the carbonyl carbon not only becomes tetrahedral, but it now bears four different substituents:

An —OH group
—H
The oxygen of the ring
A carbon of the ring

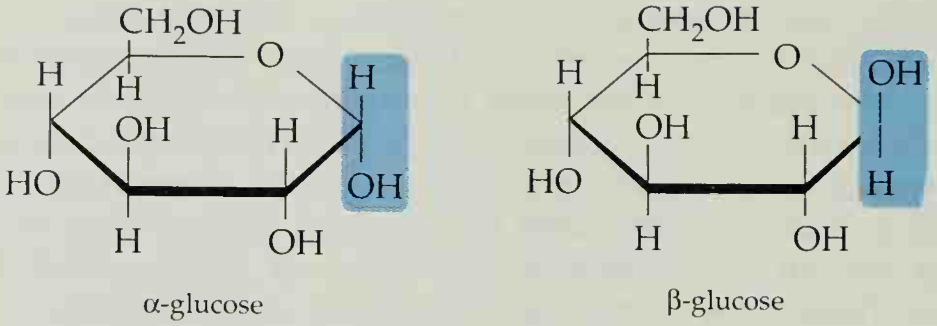


Figure 14.17
The two glucose rings.

This carbon is now chiral and can hold its new —OH group pointing either up or down as we normally view the ring. If the new —OH group points down, we have an *alpha* (α) ring; if it's up, the ring is *beta* (β). There are, then, *two* cyclic forms of glucose: α-glucose and β-glucose (Fig. 14.17). Each one happens to be dextrorotatory, although they rotate the plane of polarized light to different extents.

QUESTION

Are α-glucose and β-glucose enantiomers of each other? ____________________

14.11 Starch and Cellulose: You Eat Both, You Digest One

The existence of these two forms of glucose, α and β, explains nicely the difference between the two polysaccharides that make up an important part of our diet:

- The *starch* of the seeds and roots of plants (wheat, corn, and potatoes).
- The *cellulose* of their more fibrous structures (bran or seed husks of oats, rye, and wheat; stalks of celery, leaves of lettuce).

In their molecular structures, starch and cellulose resemble each other closely. Each consists of very long polysaccharide molecules that give only glucose on complete hydrolysis. Each is made up exclusively of glucose rings joined to each other to form long molecular strings. Yet while we digest and absorb the starch of our foods easily, their cellulose passes through our bodies largely unchanged and unabsorbed. Starch serves as a macronutrient; cellulose provides us with dietary fiber, sometimes called roughage or indigestible carbohydrate. This difference between the two polysaccharides originates in their molecular structures: starch is made up exclusively of rings of α-glucose; cellulose is composed exclusively of rings of β-glucose.

In forming any of the larger carbohydrates, ranging from the simple disaccharides of sucrose and lactose to the polysaccharides of starch and cellulose, individual cyclic molecules of monosaccharides combine and join together through the loss of water molecules. We'll now see how this combination occurs and how it produces the important difference between starch and cellulose. We'll look first at cellulose since it provides us with the simpler example.

Cellulose is the principal component of plant cells. It gives plants their structural strength. While cellulose doesn't occur in animals, it is certainly plentiful. By one estimate, growing plants produce something like 100 billion tons of cellulose worldwide each year. There's probably more cellulose on this planet than any other single organic compound. The molecular chain of cellulose is formed of molecules of β-glucose, joined together through oxygens that link carbon 1 of one of the rings with carbon 4 of another. As the rings join they lose a molecule of water.

Figure 14.18 illustrates a combination of this sort as two glucose rings join to form the disaccharide *cellobiose*. The ring carbons are numbered in the figure for easy reference. Notice that the ring on the left is β-glucose since the oxygen on carbon 1 lies above the ring. As a result the two glucose rings of cellobiose are joined through a β link. As they are shown in the figure, one of the rings lies slightly above the other, in a different horizontal plane. In the formation of the disaccharide cellobiose it doesn't matter whether the glucose ring on the right is α or β. Cellobiose forms in either case. What *does* matter is that the oxygen joining the two rings lies above the left glucose ring, thereby forming a β link.

Except that cellobiose represents two glucose rings of the cellulose molecule, this disaccharide is of little interest to us. As more and more glucose rings add in this way, *but always with the oxygen of the No. 1 carbon lying above its ring*, they eventually form a chain long enough to be called cellulose (Fig.

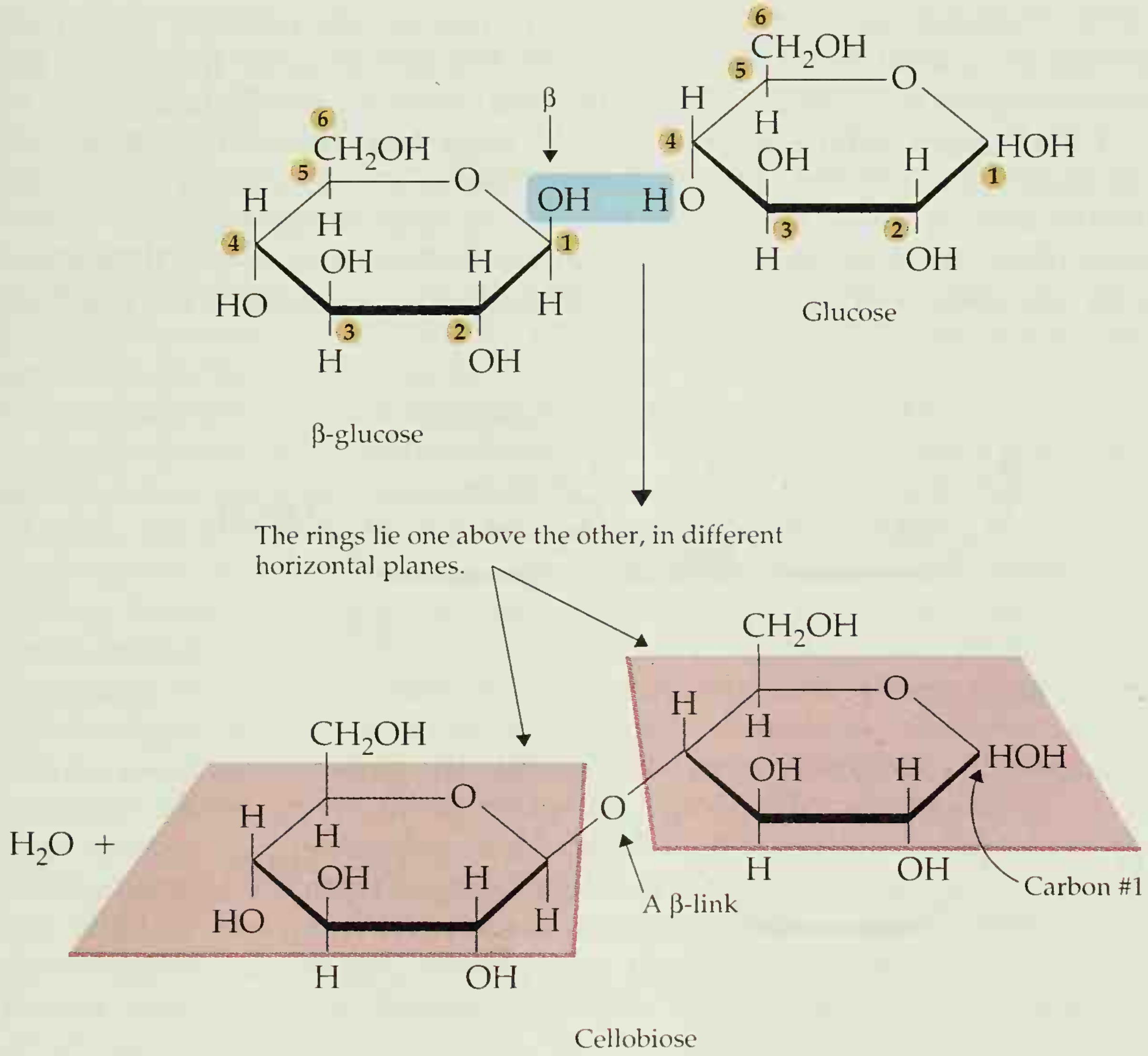


Figure 14.18

Two glucose molecules (one of them β-glucose) combine to form cellobiose and water.

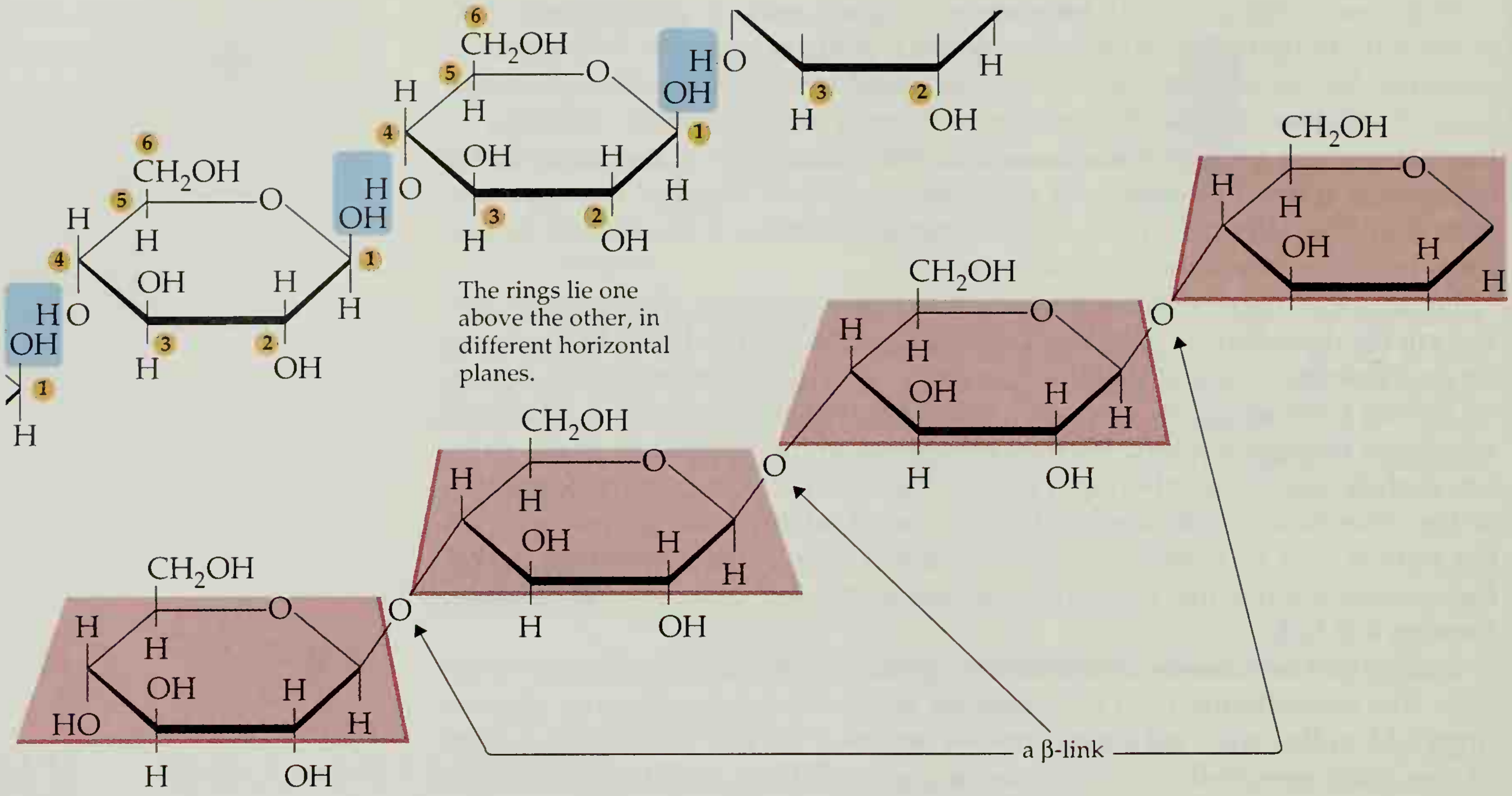


Figure 14.19

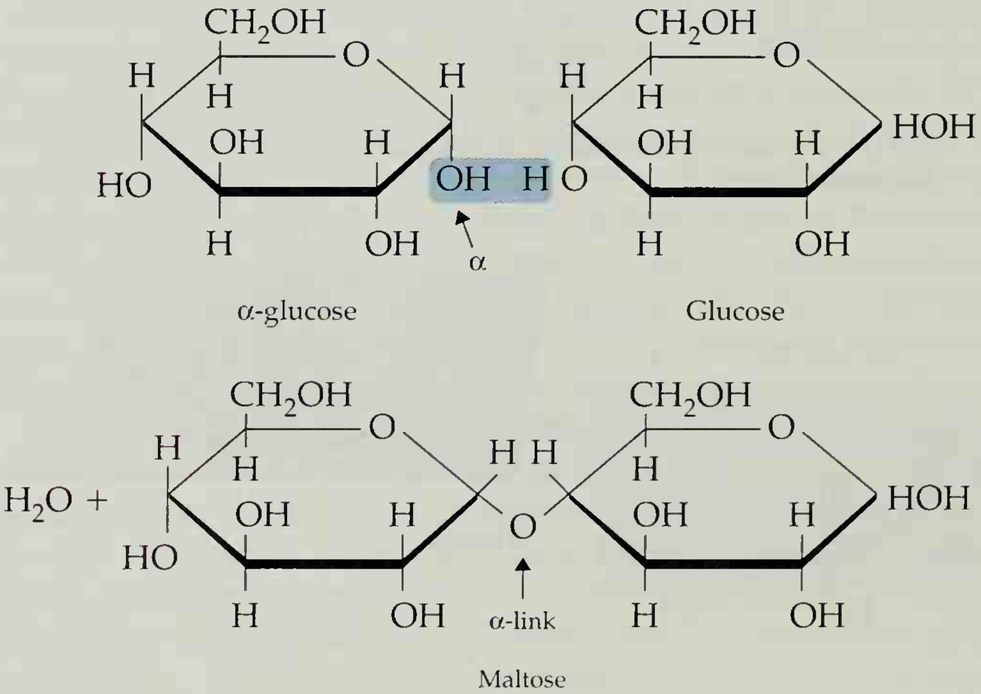
Beta-glucose and the chain of the cellulose molecule.

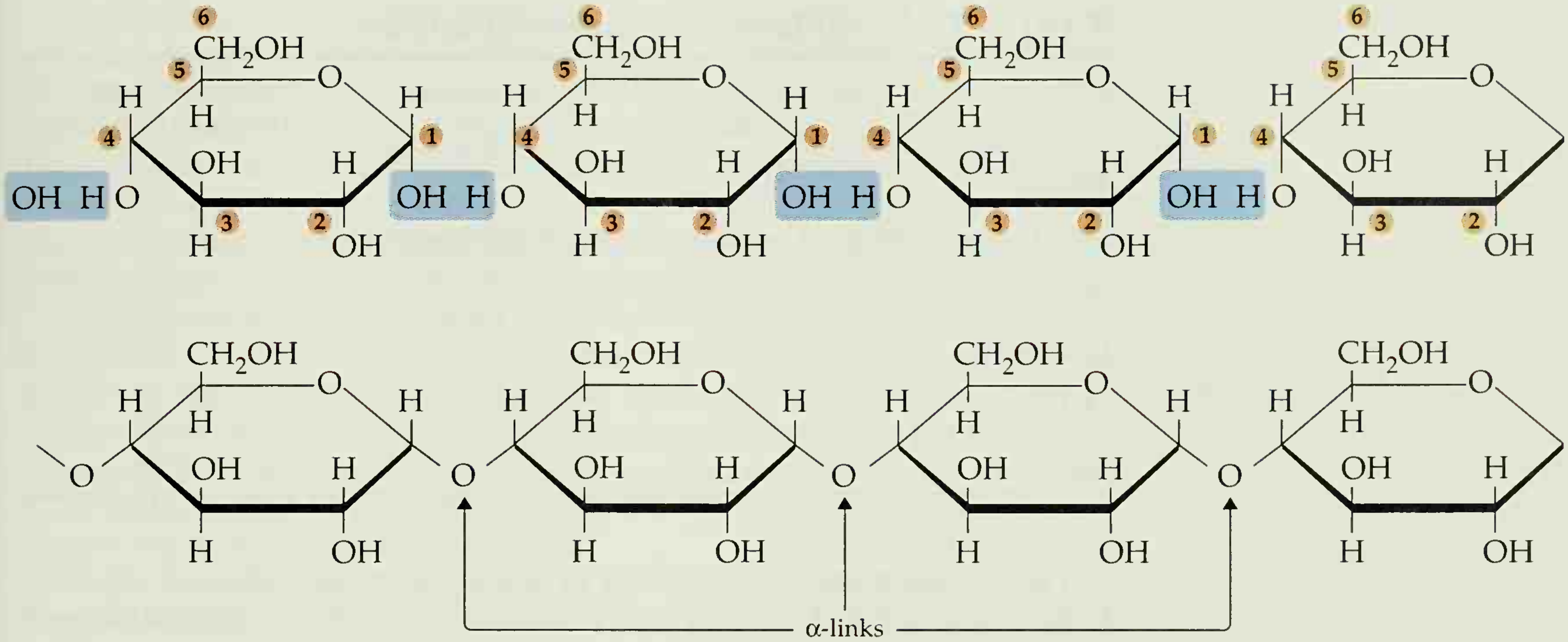
14.19). Cellulose molecules vary in length from several hundred to several thousand consecutive glucose rings, depending on its source. In cellulose all of the oxygens that link one ring to the next are in the β orientation.

If the oxygen joining the two glucose rings is in the α orientation, the resulting link is α and the disaccharide that forms is *maltose* (Fig. 14.20). Note that because of this α orientation the glucose rings of this figure lie in the same plane. As with cellobiose, the maltose that's formed here is of interest to us only because of its relationship to the larger polysaccharide. The addition

Figure 14.20

Two glucose molecules (one of them α-glucose) combine to form maltose and water.





The rings all lie in the same plane.

Figure 14.21

Alpha-glucose and the chain of the starch molecule.

of more α-glucose rings in this same way eventually produces starch (Fig. 14.21). In starch, all of the linking oxygens are α.

Unlike cellulose, starch consists of two different kinds of polysaccharide molecules. A long, unbranched, linear chain with links exclusively between the No. 1 carbon of one ring and the No. 4 carbon of the next, as in Figure 14.21, is called *amylose*. These amylose molecules are strings of α-glucose rings averaging several hundred glucose rings each. The chains of another type of starch, *amylopectin*, run several hundred thousand glucose rings long, with branches occurring from carbon 6 at about every 25th glucose ring. These branches lead to still other α-glucose chains of varying length. The amylose molecule looks like a long string with plenty of twists and turns; the amylopectin resembles the branch of a tree. The relative proportions of amylose and amylopectin in food starches vary, with the starches of our cereals running about three parts amylopectin to one part amylose.

Starch differs from cellulose in another way as well, through a curious phenomenon that lets us tell easily which is which. Let a few drops of tincture of iodine fall on some pure cellulose and nothing much happens. Try it with some celery. You find that the iodine solution retains its usual red-brown color as it soaks into the fibrous stalk. Starch is another matter. It turns blue-violet or black when the iodine touches it. That's why in our opening demonstration the potato, which is rich in starch, turned the iodine nearly black but the apple didn't. The apple has plenty of cellulose (as does the potato) and it's sweet because of its low-molecular-weight carbohydrates. But because of its low starch content the apple hardly affected the iodine's color.

In addition to differing from each other, both starch and cellulose can be distinguished from many mono- and disaccharides by taste. Neither starch nor cellulose has much taste, while many naturally occurring mono- and disaccharides are distinctly sweet. Table 14.2 lists the relative sweetness of several mono- and disaccharides, with table sugar (sucrose) assigned a rating of 100 for comparison.

Two polysaccharides of food: the starch of potatoes and the cellulose of cabbage.

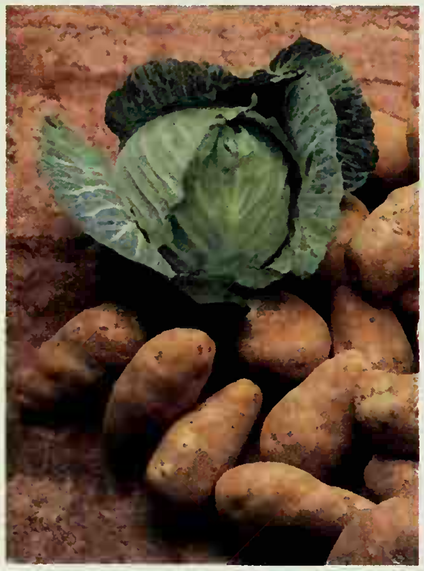


TABLE 14.2 Relative Sweetness of Sugars

Sugar	Sweetness (Relative to Sucrose)
Fructose	173
Invert sugar (mixture of equal parts glucose and fructose)	130
Sucrose	100
Glucose	74
Maltose	32
Lactose	16

There's one more polysaccharide of interest to us here, *glycogen*. This carbohydrate is similar to amylopectin in molecular structure except that its molecules are more highly branched and smaller, with fewer glucose rings. Animals manufacture and store glycogen to serve as a reservoir of readily available glucose. Deposited largely in the liver and muscles, the glycogen molecule can be quickly cleaved to individual glucose molecules that provide the body with a constant supply of energy. Because of its storage in the animal body as a readily available source of glucose, glycogen is sometimes called "animal starch." We don't store much glycogen, though. We use up the liver's supply each night as we sleep and must replenish it the next day. A longer fast causes us to eat into our reserves of fat.

QUESTION

Describe how we can distinguish cellulose and starch on the basis of (a) the molecular structure of each, (b) the chemical behavior of each, (c) the way our body uses each.

14.12 How We Digest Carbohydrates: The Secret of Fiber

While any of the monosaccharides, glucose or fructose for example, easily penetrates the intestinal wall to enter the bloodstream, neither disaccharides nor the larger carbohydrates normally get through the intestinal barrier. They are too large. To assimilate these larger carbohydrates, from maltose and sucrose to starch, we must first clip them down to their component monosaccharides, which are able to pass through the intestinal wall and into the bloodstream. As we've seen, in forming the larger carbohydrate molecules the individual monosaccharide rings connect to each other with loss of a molecule of water. To reverse this process, to cleave the disaccharides and the polysaccharides to their component monosaccharides, we must return the water to the molecules through hydrolysis (Section 11.11).

Our bodies carry out this hydrolysis through the catalytic action of our digestive *enzymes*. Enzymes, you'll recall, act as biological catalysts that allow chemical reactions to take place more rapidly or under milder conditions than they might otherwise, but are not consumed themselves. In cleaving the nutrient polysaccharides quickly and efficiently in the relatively mild chemical environment of our digestive systems, these molecular catalysts act very much like the platinum and palladium catalysts that help remove unburned hydrocarbons from automobile exhausts (Section 8.9).

An enzyme that enables us to digest both maltose and starch is *maltase*, which our bodies produce in sufficient quantities to allow us to digest the starch we eat. As you might infer from this single example, an enzyme's name usually resembles the name of the substance it acts on. For the simple disaccharides, just replace the *-ose* ending of the sugar with *-ase* to get the name of the enzyme that hydrolyzes the disaccharide. Maltase helps us hydrolyze the link of maltose and starch.

We've seen that the combination of two glucose units through a β link produces *cellobiose*, which resembles two links of the cellulose chain. Since we don't produce any of the digestive enzyme that hydrolyzes the β linkage, **cellobiase**, we can't digest cellobiose or cellulose.

For humans, starch constitutes a *digestible carbohydrate*, while cellulose is one of the *indigestible carbohydrates* that form a large part of the **fiber, bulk** or **roughage** of our diets. Grass, leaves, and other plant material, all of which are indigestible in our own intestines, provide metabolic energy to cows, goats, sheep, and other ruminants, and to termites and similar insects, simply because the digestive systems of these animals harbor microorganisms that produce the needed cellobiase. We humans don't have the required enzyme, and so we can't live on grass and wood.

The **fiber, bulk**, or **roughage** of our foods is largely cellulose, a carbohydrate we find indigestible because of our lack of the enzyme **cellobiase**.

Foods rich in fiber include fruits, vegetables, bran, and nuts. For good health it's recommended that these be part of our daily diets. Dietary fiber seems to reduce the risk of cancer, especially cancer of the colon. How and why dietary fiber might have this beneficial effect are uncertain. One bit of speculation holds that the secret of fiber may lie in its mechanical effect on our large intestine. Fiber absorbs much water as it passes through us and it assumes considerable bulk. This bulk may stimulate the intestine and promote a rapid transit of the fibrous bulk through and out of our bodies. If this rapid passage of fiber also speeds the elimination of other, cancer-causing substances, then their contact time with intestinal tissue is shortened as well, and their opportunity for acting on intestinal tissue and generating cancer is diminished.

On the other hand, another possibility may simply be that as we increase the proportion of fiber-containing foods in our diets we necessarily decrease the proportion of meats and other fatty foods. Since diets high in fats seem to be associated with cancer (Chapter 13, Perspective), this hypothesis could as easily account for the protective effect of fiber.

QUESTION

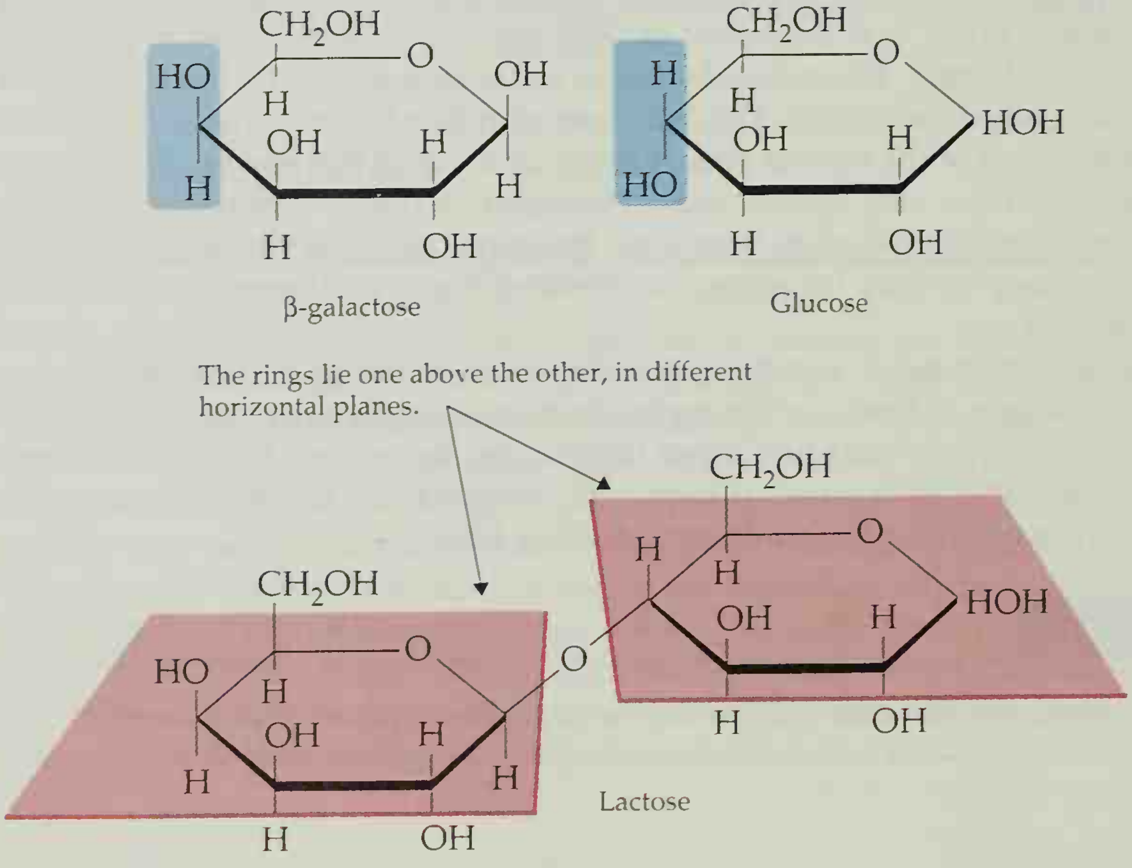
How would you name the enzyme that helps us digest lactose (milk sugar)?

14.13 Why Large Quantities of Milk, Cheese, and Ice Cream, Can Cause Digestive Problems in Two Adults out of Three

Lactose (from the Latin *lac*, for "milk"), the principal carbohydrate of milk (Table 14.1), offers a good example of the problems we can encounter through defects in our enzyme-catalyzed digestive processes. Lactose is a disaccharide that consists of a *galactose* ring joined to a glucose ring through a β link. The monosaccharide galactose differs only subtly from glucose, through the stereochemistry of carbon 4. If the —OH on carbon 4 of the monosaccharide ring points down, we have glucose; if it points up, it's galactose (Fig. 14.22). Since virtually no disaccharide of any kind gets through the intestinal wall and into the bloodstream, we need the enzyme *lactase* to hydrolyze lactose into its components, galactose and glucose. The more milk and milk products we consume, the more lactase we need.

Normally, there's plenty of lactase in the digestive systems of infants and children. That's fortunate, since nursing babies get about 40% of their calories from the lactose of their mother's milk. By and large, older children have more than enough lactase to digest all the lactose of the milk, cheese, ice cream, and other dairy products they eat. But gradually, as we grow from infancy to adolescence, most of us lose the ability to produce lactase in large quantities, and so we're largely "lactase deficient" as adults. In this condition we produce very small amounts of lactase, too little to handle more than a glass or two of milk at a time. It's been estimated that about 70% of the world's adult population, or about two out of three adults throughout the world, have very low levels of lactase in their digestive systems. More specifically, estimates for the percentage of lactase deficient adults range from about 3%

Figure 14.22
Galactose, glucose, and lactose.

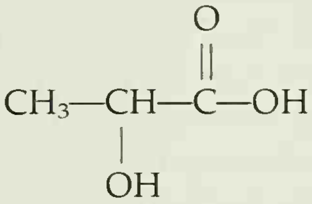


The rings lie one above the other, in different horizontal planes.

for Scandinavians and northern Europeans to 80 to 100% for some Asians. In North America the estimates for adults run from 5 to 20% for the white population to 70% for the nonwhite population.

Without enough lactase in the digestive fluids, the lactose of milk and milk products isn't hydrolyzed effectively. Whenever large quantities of this disaccharide are consumed, much of it, unhydrolyzed and unabsorbed, passes along the intestinal path to a region where it undergoes fermentation to gases such as carbon dioxide and hydrogen and to lactic acid, a bowel irritant. The combination easily produces gastric distress and diarrhea.

Milk and milk products are rich in the disaccharide lactose.



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH$$

lactic acid

Not everyone is lactase deficient and, for those who are, the amount of lactose needed to cause distress varies considerably. Nonetheless, gastric problems produced by drinking large amounts of milk or eating large quantities of cheese and ice cream could result from the simple inability to hydrolyze a β linkage tying a galactose ring to a glucose ring in the disaccharide lactose.

QUESTION

What is the single variation in molecular structure that differentiates cellobiose (Fig. 14.18) from lactose (Fig. 14.22)? ______________________________

14.14 Enzymatic Locks and Molecular Keys

It's clear from what we've seen in this chapter that our digestion of carbohydrates requires the presence of specific enzymes. (We can extrapolate this to the digestion of triglycerides and proteins, our other macronutrients, as well.) We've seen that biological enzymes allow certain chemical reactions, including those of our digestive processes, to occur under the relatively mild conditions present within living systems. We've also seen that enzymes can be highly specific in their actions. Maltase, for example, the enzyme that allows the easy hydrolysis of the α linkage of starch, has no effect on the hydrolysis of the β linkage of cellobiose or cellulose.

A similar sort of situation occurs with lactase, the enzyme that aids in the digestion of lactose. As we see in Figure 14.22, the link joining the two monosaccharide rings of lactose has the β geometry, as it does in the cellobiose molecule in Figure 14.18. Yet lactase, like maltase, has no effect on the hydrolysis of cellobiose or cellulose. As you saw when you answered the question at the end of Section 14.13, the only difference in molecular structure that distinguishes lactose from cellobiose lies in the stereochemistry of carbon 4 of the ring shown to the lower left in the two figures. The —OH group lies above the ring in lactose, below in cellobiose.

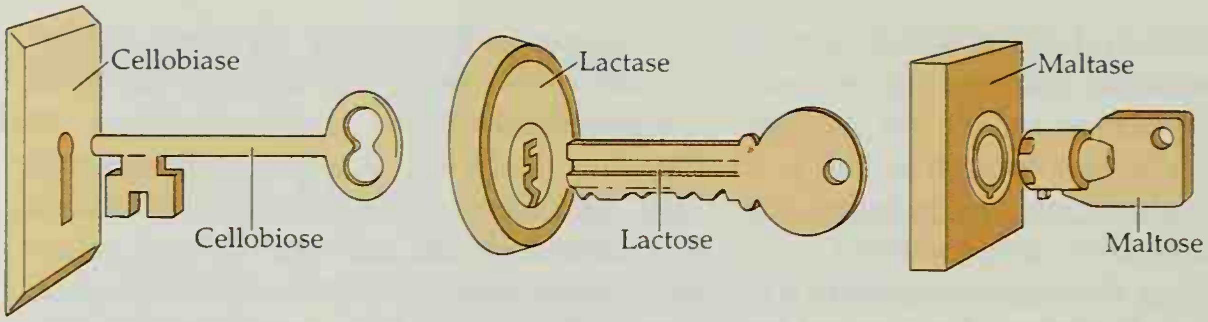


Figure 14.23 The lock-and-key analogy of enzyme action. Each key fits only its own lock.

To account for major differences in enzyme activity caused by small differences in molecular structure, a "lock and key" analogy has evolved. Enzymes are huge protein molecules (Chapter 15) with intricate and well-defined shapes. For effective catalytic activity, the molecule on which the enzyme works must fit into the convolutions of the enzyme's shape much as a key must fit into a lock. When the key's shape matches exactly the tumblers of the lock, the lock opens. Any change in the key's shape or any change in the tumblers, and the combination fails. In this sense, the cellobiose, lactose and maltose keys fit only their own, respective, enzymatic locks (Fig. 14.23).

PERSPECTIVE: Can This Textbook Help End World Hunger?

Our examination of carbohydrates and of the enzymes that allow us to digest them raises an intriguing question: Would it be possible to eliminate human starvation by introducing cellobiase into our diets in a convenient, economical, and safe way? If humans could cleave the long cellulose chains into readily absorbable glucose, we might then be able to survive on grass, leaves, the bark of trees, and even paper. With a good source of cellobiase at hand, you might have a new option for a textbook at the end of a course: You might be able to put it between two pieces of bread, along with some lettuce and tomato, and enjoy it as a nutritious lunch.

As for the question of ending human starvation by introducing cellobiase into our diets so that we might be able to digest and metabolize the cellulose of plant parts and plant products, the answer is "it depends." (This same answer also applies to so many other questions that involve the interaction of chemistry, society, and the welfare of individuals.) If starvation could be ended merely by adding energy (calories) to our daily diets—energy that would provide the minimal number of calories needed for basal metabolism, for example—then the answer would be "yes." But healthful and sufficient diets require more than calories. As we'll see in Chapter 15, they require, among other things, proteins (more specifically, proteins containing certain *essential amino acids*) to help form the physical structures of our bodies and our enzyme systems. Healthful diets require, too, certain minerals and vitamins, sometimes in amazingly small quantities each day, to keep the chemical reactions of life running smoothly. (We'll examine these in more detail in Chapter 16.) What's more, for good health our diets even require the very indigestible dietary fiber that's made up of the β links we *can't* turn into energy. If we could digest the β-linked polysaccharides as well as those that are α-linked, roughage and fiber would disappear from our diets and our large intestines would suffer the consequences, including, perhaps, higher rates of cancer.

Diets that provide sufficient energy do, indeed, protect against starvation. Yet the case against foods that provide *only* energy, to the exclusion of other nutrients, has been made so well that we now recognize many foods that are rich in calories but not in vitamins and minerals as "junk foods," filled with "empty calories." We'll have more to say about this in Chapter 17.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

______ are compounds of carbon, hydrogen, and oxygen, usually in a ratio of two hydrogens to one oxygen. Among the simplest, those called ______ , are glucose (an ______) and ______ (a ______). Other common names for glucose include "blood sugar," so named because of its presence in the blood, and ______ , which has its origin in the direction that glucose rotates ______ . Common ______ include both maltose and cellobiose, in which two ______ rings combine with each other, and ______, a disaccharide that's known as "milk sugar" and that consists of a ______ ring joined to a glucose ring. Our most common ______ are ______ , an important foodstuff that consists of long chains of glucose rings joined to each other through ______ , and ______, which also consists of long chains of glucose rings. These are joined to each other through ______ . We can digest starch because our bodies produce the enzyme ______ , but fiber constitutes an indigestible carbohydrate in our diets since we lack ______. Those of us who suffer from a deficiency of ______ find that milk and milk products produce gastrointestinal distress.

α links
β links
aldohexose
carbohydrates
cellobiase
cellulose
dextrose
disaccharides
fructose
galactose
glucose
ketohexose
lactase
lactose
maltase
monosaccharides
plane-polarized light
polysaccharides
starch

2. Identify or define each of the following: (a) an aldehyde, (b) a chiral molecule, (c) dextrose, (d) invert sugar, (e) optical activity, (f) sucrose.

3. Give an alternative name for each of the following: (a) blood sugar, (b) grape sugar, (c) milk sugar, (d) cane sugar, (e) the principal carbohydrates of honey.

4. Give the names of chemical compounds that consist of a carbonyl group bonded to (a) two methyl groups, (b) one methyl group and one hydrogen, (c) two hydrogens, (d) one methyl group and one ethyl group, (e) one phenyl group and one hydrogen.

5. Name (a) an aldohexose, (b) a different aldohexose, (c) a ketohexose, (d) an aldotriose.

6. Classify each of the following as a monosaccharide, a disaccharide, or a polysaccharide: (a) amylose, (b) glucose, (c) lactose, (d) sucrose, (e) cellulose, (f) galactose, (g) cellobiose, (h) fructose.

7. What is the linguistic origin of each of the following words, or of the italicized portion: (a) glucose (b) mono*saccharide*, (c) *dextro*rotatory, (d) chiral, (e) *lac*tose, (f) carbohydrate?

8. Suppose you have some pure cellulose and some pure starch in separate containers, but you don't know which is which. What simple test could you perform to decide which is the starch and which is the cellulose?

9. Of what value is glycogen to us?

10. Name some foods that contain large amounts of indigestible carbohydrate.

11. Cows, sheep, and goats can digest grass and the leaves and stems of plants. Why can't we?

12. Describe two ways that diets high in fiber may help protect against cancer of the large intestine.

13. Describe the difference between amylose and amylopectin.

14. Name or describe the four major parts of a polarimeter and describe the function of each.

15. Given a molecular structure, how can you identify any chiral carbons that may be present?

16. Name an aldehyde that is not a carbohydrate but that is commercially useful and describe its use.

17. Name a ketone that is not a carbohydrate but that is commercially useful and describe its use.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

18. Each chiral carbon of a molecule can exist in a right-handed form and in a left handed form. How many different isomers that differ only in the stereochemistry of their chiral carbons can there be of a compound containing (a) one chiral carbon? (b) two chiral carbons? (c) three chiral carbons?

19. Can you arrive at a formula that will give you the number of different isomers that can exist for a compound that contains *n* chiral carbons?

THINK, SPECULATE, REFLECT AND PONDER:

20. Which of the following alcohols, if any, are chiral: (a) methyl alcohol, (b) ethyl alcohol, (c) *n*-propyl alcohol, (d) isopropyl alcohol?

21. Draw the Fischer projections of the two enantiomers of $CH_3—CHOH—CH_2—CH_3$.

22. Is the following statement true or false? Explain. "All of the carbohydrates of our diets provide us with 4 Cal per gram."

23. Is (+)-fructose an enantiomer of (−)-fructose? Explain.

24. Is (+)-glucose an enantiomer of (−)-fructose? Explain.

25. Draw the structure of a compound that can be classified as a ketotriose. How many chiral carbons does it have?

26. Glucose molecules exist primarily as rings rather than straight chains. Why?

27. What is the name of the enzyme our bodies use to hydrolyze table sugar?

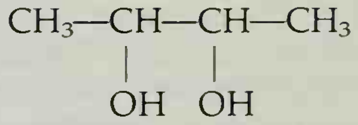
28. Suppose you have a pair of heavily tinted sunglasses, but you don't know whether they contain polarizing lenses. What simple experiment could you perform to find out?

29. Suppose you have symptoms that you think may be caused by your sudden development of a lactase deficiency. You make an appointment with a physician to have the symptoms diagnosed, but meanwhile you make a small change in eating habits so that you can gain some evidence to confirm or deny your suspicions. What do you do to obtain this evidence, and how do you interpret it?

30. What is the major biological function of the glucose that circulates in your blood? Suppose you learn that your body will soon stop generating the enzymes needed to hydrolyze disaccharides, such as sucrose and the higher carbohydrates as well, and that medical assistance will be unavailable for several days. What would you do to ensure a sufficient concentration of glucose in your body?

31. How would your diet be different if your body generated cellobiase but neither maltase nor any other enzyme that could catalyze the hydrolysis of the linkage of carbohydrates? (a) What foods, rich in carbohydrates, would you eat for energy? (b) What foods would you eat for roughage?

32. Draw Fischer projections of all the possible stereoisomers of 2,3-butanediol:



$$CH_3—\underset{\underset{\displaystyle OH}{|}}{CH}—\underset{\underset{\displaystyle OH}{|}}{CH}—CH_3$$

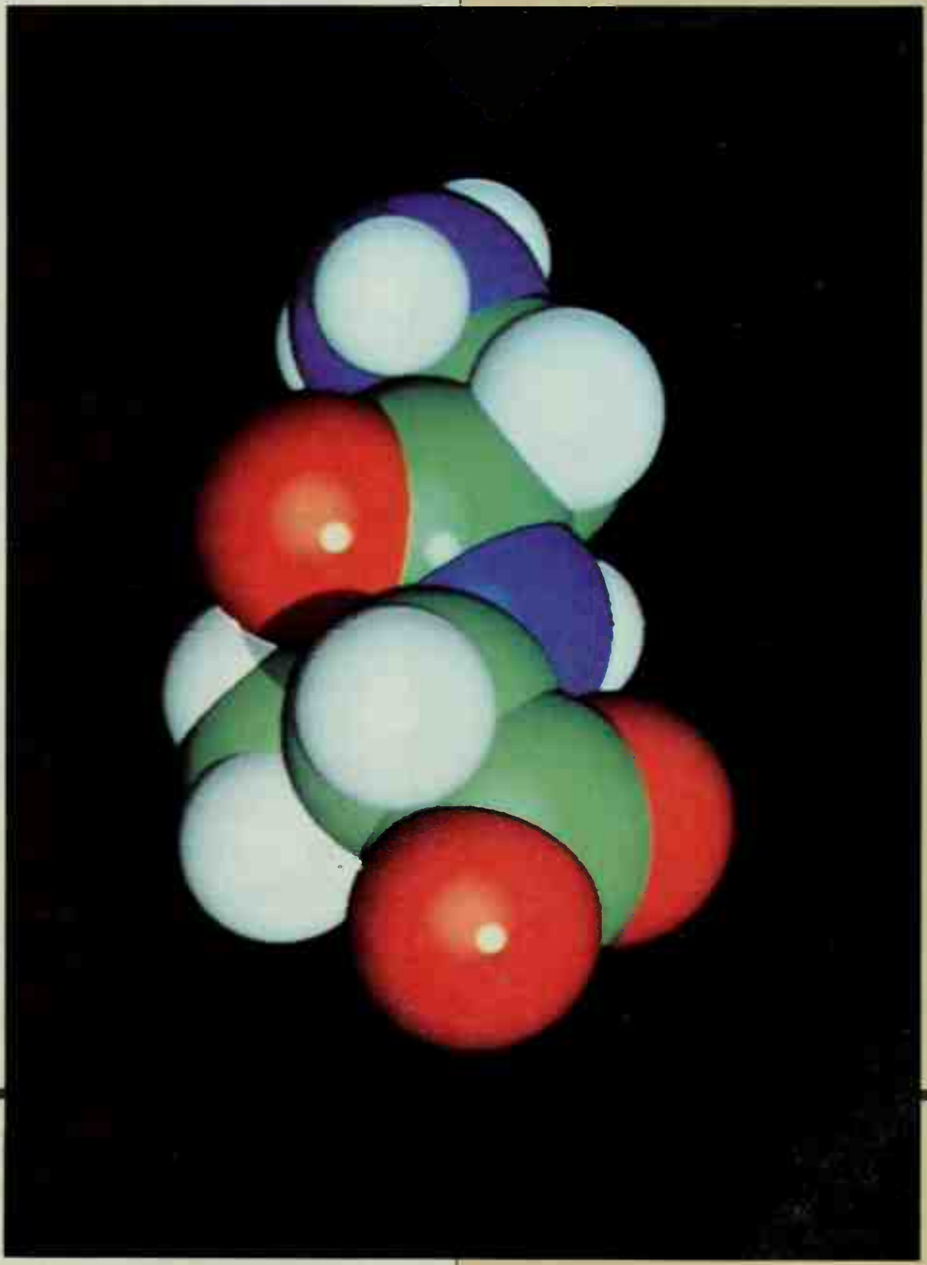
a. How many stereoisomers of 2,3-butanediol are there?
b. Does an enantiomeric pair exist among these stereoisomers?
c. Is there a stereoisomer that *does* contain chiral carbons but whose Fischer projection *is* superposable on itself (after a rotation of 180°)?

Stereoisomers that do contain (two or more) chiral carbons but that are nonetheless superposable on themselves are called *meso* compounds. *Meso* compounds are optically inactive.

15

Proteins

FIRST AMONG EQUALS



A molecule of glycylalanine, a dipeptide.

Heating denatures the protein of egg white.

How to Turn an Egg White White

You can turn an egg white white by heating it. Actually, the clear, gelatinous part of a raw egg, the part we call the "white" (as distinct from the yolk), isn't white at all. It's colorless. You can make it turn white by heating it or by doing a few other simple things we'll describe here.

An egg white is a combination of about 90% water and 10% proteins, the subject of this chapter. Within the raw egg, the proteins of this mixture are distributed in small globules throughout the water. As they occur naturally here in the egg white and throughout the tissues and fluids of plants and animals, proteins are in their native state. That is, their molecules take the particular shapes and forms suited to each protein's function within the organism. In the egg white each long protein molecule folds and wraps around itself to form a small sphere. It's the dispersal of groups of these spheres through the water of the white that produces its characteristic transparency and gelatinous texture.

But heat an egg white and the protein molecules begin unfolding and assuming other shapes in a process called *denaturation*. (We'll have more to say about denaturation later. For now, we'll recognize it simply as an unfolding of the polymeric string of a molecule of native protein.) As a result of the denaturation, the proteins of the egg white begin assembling into combinations with each other. The clear "white" turns white and becomes firm. The longer you cook an egg, the greater the change in the proteins. The white becomes more opaque and firmer as you progress from soft boiled to poached, and fried. Throughout the heating the proteins of the white are transformed from native proteins into denatured proteins.

You can denature some of proteins of the white even without using heat. Break open a raw egg and separate the white from the yolk. (We'll use only the white here.) Put the white into a small glass and sprinkle a little table salt on it. Within a few minutes you'll see the egg white turn opaque and coagulate around the salt grains. The salt is denaturing the protein. You can do the same thing with some baking soda, which is the common name of sodium bicarbonate, $NaHCO_3$. Its a basic substance and it raises the pH of the protein enough to denature it.

Figure 15.1

Adding rubbing alcohol, a mixture of isopropyl alcohol and water, to egg white denatures the protein and causes the egg white to curdle.

An even more dramatic effect involves use of the scientific method. Divide an egg white between two different glasses. Put about a tablespoon of rubbing alcohol into one of the glasses and swirl it slightly. The egg soon begins to turn white and coagulate, as if it were being heated. You'll recall from Section 9.9 that rubbing alcohol is a solution of 70% isopropyl alcohol and 30% water. Is it the isopropyl alcohol or the water that's denaturing the egg protein?

We can answer this question with the portion of the white in the other glass. Since we can't easily obtain pure isopropyl alcohol to determine its effect on the protein, we're left with an examination of water's effect. Add about a teaspoon of water, roughly the same amount of water as is in a tablespoon of rubbing alcohol, to the white in the other glass. This may produce a little coagulation, but not nearly on the scale produced by the rubbing alcohol. We conclude that it was the isopropyl alcohol, not the water, that denatured the protein of the egg white (Fig. 15.1).

In this chapter we'll examine proteins in detail. We'll learn what they are made of, how they behave, what foods provide them, and why they are important to us.

15.1 First among Equals

Proteins themselves form the third of the three classes of macronutrients. The word itself comes to us from a 19th-century Dutch chemist and physician, Gerardus Mulder. In 1838 he wrote of discovering a substance he believed to be the chemical essence of all life and that (he thought) permeates all parts of every living thing. To reflect what he imagined to be its fundamental importance, he chose its name from the Greek word *proteios*, for "primary" or "first." Although proteins do, indeed, occur in every living cell, Mulder's enthusiasm and the limits of chemical science in the early 19th century over-

Proteins form our nails, skin, and hair and provide them with their strength.

stated the case for proteins as the fundamental chemical substances of all life. Yet proteins are, indeed, vital to our lives and furnish us with virtually every atom of nitrogen that's found in our tissues.

While our brain, nerves, and muscles depend on the carbohydrate glucose for energy, and while we might be as immobile as plants if it weren't for the compact storehouse of energy that fat provides, it's protein that gives the very shape to our bodies. Proteins form our hair and our nails. Along with water, they are the principal substances of our muscles, organs, blood, and skin. They are the collagen of our connective tissue that holds our bones together in a cohesive skeleton and wraps our bodies in flesh. They are the molecules of our enzymes, those catalysts that promote the chemical reactions that digest our food, provide us with energy, and manufacture the tissue of our bodies. Even the secret of life itself seems to be sealed in a protein molecule.

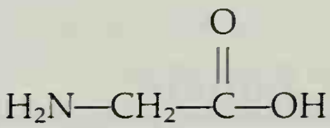
QUESTION

What chemical element is supplied to our bodies by proteins but not by carbohydrates, fats, or oils? ______________________________

15.2 Amines and Amino Acids

Like the extended carbohydrate molecules of starches and cellulose, proteins consist of extremely long, threadlike chains. In protein molecules these chains range in molecular weight from about 10,000 to well over 1,000,000 amu. For comparison, the molecular weight of a typical fat molecule runs between 500 and 1000 amu. Unlike the more common carbohydrates, though, with individual links consisting of one or another of only three different monosaccharides (glucose, fructose, and galactose), the protein molecules—at least those important to human life—are formed from an assortment of some 20 different *amino acids*. (Some authorities recognize as many as 23 amino acids in human proteins: others hold that the additional three are simply variants of the central set of 20. We'll stay with the fundamental 20 in this discussion.)

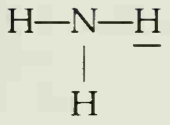
By whatever criteria we may use, though, the simplest of all the amino acids is *glycine*.



$$H_2N—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—OH$$

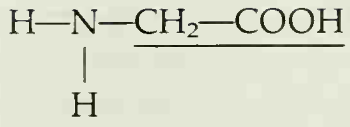
glycine

The amino acids themselves, these individual links of the protein chain, are unusual molecules containing within their own structures two functional groups of contradictory properties. We see in glycine a methylene group, $—CH_2—$, bonded to both an acidic *carboxyl* group ($—COOH$, which can also be written as $—CO_2H$) and a basic *amino* group ($—NH_2$). The glycine molecule could be constructed by replacing one of the hydrogens of a basic ammonia molecule with an acidic $—CH_2—COOH$ unit,



$$\mathrm{H{-}\underset{\underset{H}{|}}{N}{-}\underline{H}}$$

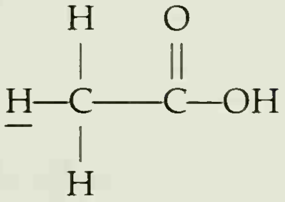
ammonia



$$\mathrm{H{-}\underset{\underset{H}{|}}{N}{-}\underline{CH_2{-}COOH}}$$

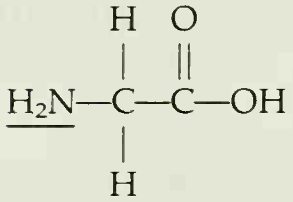
glycine

or by replacing one of the methyl hydrogens of acetic acid with a basic —NH_2 group.



$$\mathrm{\underline{H}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

acetic acid



$$\mathrm{\underline{H_2N}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

glycine

We've already seen that molecules bearing a carboxyl group as their only functional group are acids (Section 10.17). Molecules bearing only the amino function are **amines** and are bases. We can think of amines as molecules in which one or more of the hydrogens of an ammonia molecule, NH_3, have been replaced with an alkyl group (Section 11.14). Replacing one of ammonia's hydrogens with a methyl group, for example, gives us methylamine, $CH_3{-}NH_2$.

An **amine** is an organic base whose molecules bear the *amino* group, —NH_2.

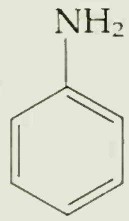
Generally, amines are less basic than ammonia. They are not commonly found in consumer products. For many of us our most frequent contact with amines comes through the odor of the sea and of fresh seafood. Since amines are released by all decaying animal flesh, the continual cycle of birth and death of marine organisms provides a constant supply of amines to seawater and to the air above the oceans. These amines are partly responsible for the characteristic odor of the sea and its inhabitants. This macabre aspect of amine chemistry is reflected by the common names of two amines, *cadaverine* (from *cadaver*, "a dead body") and *putrescine* (from *putrefy*, "to decay with an odor"). Both of these amines occur in decaying animal tissues. Putrescine not only serves as a mark of decay, but is indispensable to life as well. It is essential to the growth of cells and occurs in all thriving animal tissue. Typical amines appear below.

$CH_3{-}NH_2$

methylamine

$CH_3{-}CH_2{-}NH_2$

ethylamine



aniline

$H_2N{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2$

putrescine, also known as 1,4-diaminobutane

$H_2N{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2$

cadaverine, also known as 1,5-diaminopentane

Typical Amines, Organic Bases

Amines are bases as defined by Brønsted and Lowry (Section 10.4) and by Lewis (Section 10.5). Like all bases, including sodium hydroxide and ammonia, amines can combine with an acid to form a salt.

$$NaOH + HCl \longrightarrow Na^+Cl^- + H_2O$$

sodium hydroxide → sodium chloride

$$NH_3 + HCl \longrightarrow NH_4^+Cl^-$$

ammonia → ammonium chloride

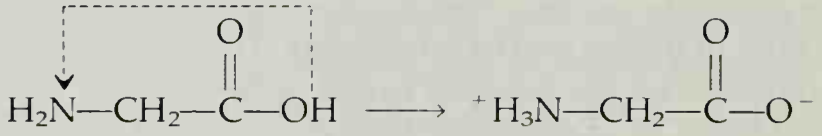
$$CH_3{-}NH_2 + HCl \longrightarrow CH_3{-}NH_3^+Cl^-$$

methylamine → methylammonium chloride

Since amino acids bear both the carboxyl group of carboxylic acids (and therefore can act as acids) and the amino group of amines (and therefore can act as bases), the amino acids have properties of both amines (the organic bases) and acids. That's why they are called **amino acids** and that's why they show some unusual chemical behavior.

An **amino acid** is a compound whose molecules carry both a carboxyl group and an amino group. Amino acids have properties of both acids and bases.

With both acidic and basic functional groups present in the same molecule, amino acids possess properties of both an acid and a base in a single covalent molecule. As in any other acid, the —COOH group can release a proton to a base; as in any other base, ammonia for example, the $-NH_2$ group can accept a proton. What's more, the overall proton transfer can occur internally, with the —COOH losing its proton to the $-NH_2$ of the very same molecule. The product of this internal neutralization is an ion bearing both a positive (cationic) and a negative (anionic) charge. It's known as a *zwitterion* from the German words meaning "hybrid", "doubled" or "twinned."



$$H_2N{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \longrightarrow {}^+H_3N{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-$$

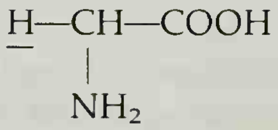
un-ionized glycine zwitterion of glycine

QUESTION

Write a balanced chemical equation for the reaction of glycine (a) with HCl and (b) with NaOH. For simplicity, assume that the glycine molecule is un-ionized; that is, *not* in the form of its zwitterion.

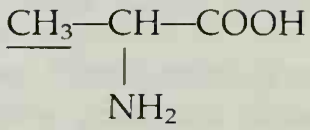
15.3 The α-Amino Acids

The other amino acids, larger and structurally more complex than glycine, carry longer carbon chains and, in most cases, additional functional groups as well. In *alanine*, for example, a methyl group replaces one of the hydrogens of the $-CH_2-$; in *serine* a $-CH_2-OH$ group replaces the hydrogen.



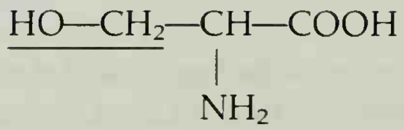
$$\underline{H}{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}COOH$$

glycine



$$\underline{CH_3}{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}COOH$$

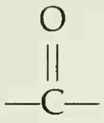
alanine



$$\underline{HO{-}CH_2}{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}COOH$$

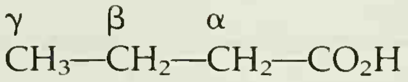
serine

In every case, from glycine onward to the largest and most complex amino acid of proteins, the nitrogen of the amino group bonds to the acid's α-*carbon* (*alpha-carbon*), the carbon that also bears the carboxyl group. Although we customarily number the carbons of a chain sequentially, as the IUPAC system instructs (Section 7.7), the Greek alphabet offers us a convenient alternative for specifying positions in organic molecules. In discussing the structure and chemistry of compounds bearing a carbonyl group,



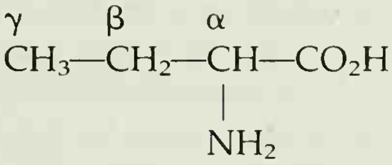
$$\overset{\overset{\displaystyle O}{\|}}{-C-}$$

(such as carboxylic acids, aldehydes (Section 14.4), and ketones), it's useful to refer to the carbon bonded directly to the carbonyl group as the α-*carbon*. The next carbon becomes the β-*carbon* (*beta-carbon*), next to that is the γ-*carbon* (*gamma-carbon*), then the δ-*carbon* (*delta-carbon*), and so on, down the chain and through the Greek alphabet. Since we can view amino acids as carboxylic acids that contain an amino group on their carbon chains, we can use this same system in naming them.



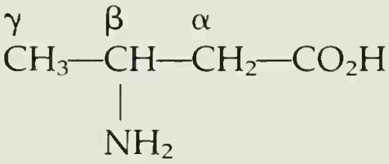
$$\overset{\gamma}{CH_3}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-CO_2H$$

Greek Letter Designations of the Carbons of Butyric Acid



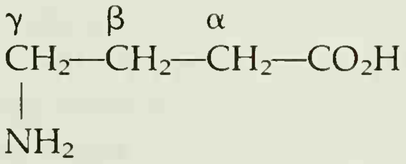
$$\overset{\gamma}{CH_3}-\overset{\beta}{CH_2}-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\alpha}{CH}}-CO_2H$$

α-aminobutyric acid



$$\overset{\gamma}{CH_3}-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\beta}{CH}}-\overset{\alpha}{CH_2}-CO_2H$$

β-aminobutyric acid



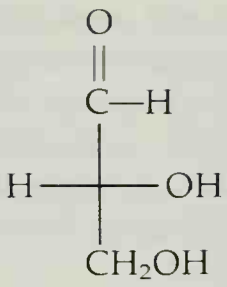
$$\underset{\underset{\displaystyle NH_2}{|}}{\overset{\gamma}{CH_2}}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-CO_2H$$

γ-aminobutyric acid

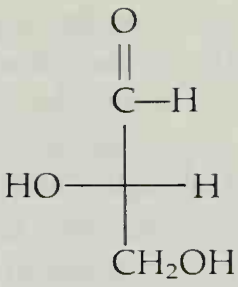
Greek Letter Names of the Aminobutyric Acids

All but one of the amino acids that occur in protein contain an α-carbon bearing four different groups, and so all (except one) are chiral (Section 14.5). Moreover, the chiralities of virtually all of these naturally occurring α-amino acids give their Fischer projections a common characteristic. With the carbonyl group at the top, the amino group lies to the left. This particular characteristic places them in a category of chiral compounds known as the L-*series*. This is a series of chiral compounds in which, with the carbonyl at the top, the hydrogen lies to the right and the functional group—an amino group or a hydroxyl group—lies to the left. Reverse the two, place the hydrogen to the left and the other group to the right, and you have the D-*series*.

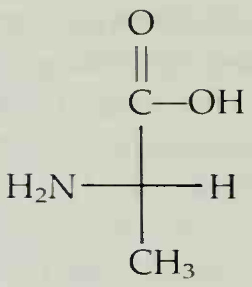
At any rate, all of the chiral amino acids that form protein molecules do belong to the L-series. (The designations D- and L- come from the two enantiomers of glyceraldehyde, the one that's dextrorotatory and the one that's levorotatory.)



D-glyceraldehyde



L-glyceraldehyde



L-alanine
(The chiral amino acids
of protein
all have this same
kind of chirality)

QUESTION

Name the single, naturally occurring -amino acid that is achiral (not chiral).

15.4 Essential Amino Acids

Since all of the amino acids found in protein are α-amino acids, we can view each one of them as a variant of glycine in which an α-hydrogen is replaced by some other substituent. Table 15.1 presents the 20 amino acids of human protein, with emphasis on the structural group that differentiates each from the others. The table also gives the common abbreviations for the amino acids and specifies whether each is a necessary part of our diets. The question of whether any one of these amino acids *must* be part of the foods we eat, or whether we can form it within our own bodies as we need it, is important in assessing the quality of the proteins in our diet.

The **essential amino acids** are the amino acids that our bodies cannot synthesize from other chemicals and that we must obtain from our foods. The **nonessential amino acids** are the amino acids our bodies can synthesize from other chemicals.

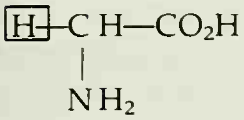
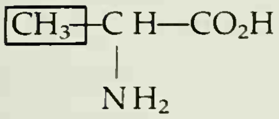
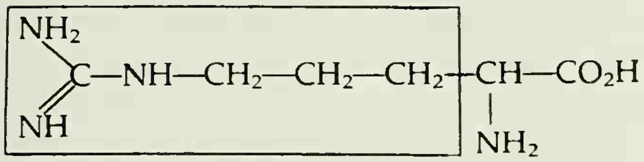
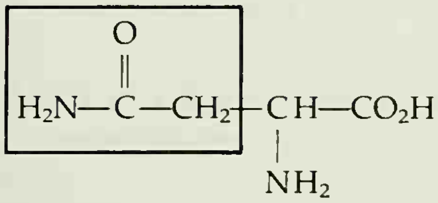
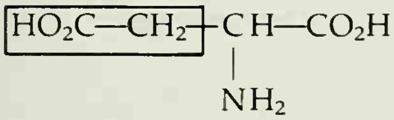
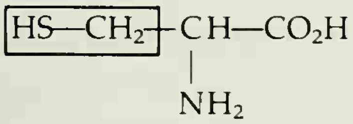
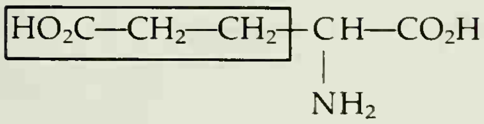
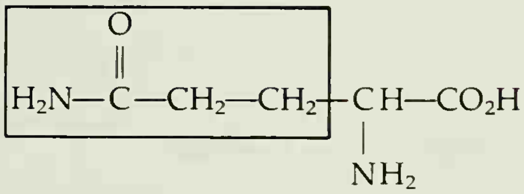
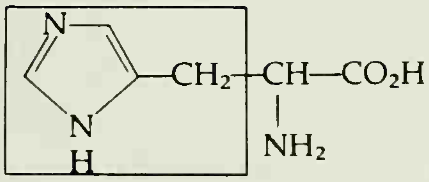
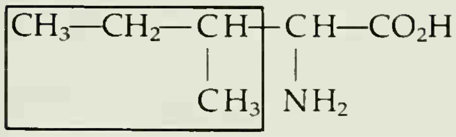
Of these 20 amino acids, our bodies lack the ability to synthesize about half, the **essential amino acids**. These we must get from the proteins of the foods we eat so that we can use them in forming our own bodily protein. The remainder, those that our own bodies can produce as they are needed, are the **nonessential amino acids**.

The dividing line between the two classes isn't always completely clear. As shown in Table 15.1, eight of the amino acids appear to be essential for everyone; two more, arginine and histidine, probably can be generated in an adult's body but not in the body of a young child. What's more, a couple of the nonessential amino acids seem to be able to substitute for at least a portion of two essential amino acids. Cysteine seems to be able to take up part of the slack left by a deficiency of dietary methionine (another sulfur-containing amino acid), while tyrosine stands in, at least partially, for phenylalanine.

QUESTION

What is the difference between an essential amino acid and a nonessential amino acid? Name two in each category.

TABLE 15.1 The 20 Amino Acids of Human Protein

Structure	Name	Abbreviation	Dietary Requirement[a]
 $\boxed{H}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Glycine	Gly	Nonessential
 $\boxed{CH_3}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Alanine	Ala	Nonessential
	Arginine	Arg	Essential for infants
 $\boxed{H_2N-\overset{\overset{\displaystyle O}{\Vert}}{C}-CH_2}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Asparagine	Asn	Nonessential
 $\boxed{HO_2C-CH_2}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Aspartic acid	Asp	Nonessential
 $\boxed{HS-CH_2}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Cysteine	Cys	Nonessential
 $\boxed{HO_2C-CH_2-CH_2}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Glutamic acid	Glu	Nonessential
 $\boxed{H_2N-\overset{\overset{\displaystyle O}{\Vert}}{C}-CH_2-CH_2}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Glutamine	Gln	Nonessential
	Histidine	His	Essential for infants
 $\boxed{CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{\vert}}{C}H}-\underset{\underset{\displaystyle NH_2}{\vert}}{C}H-CO_2H$	Isoleucine	Ile	Essential

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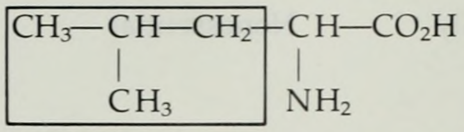
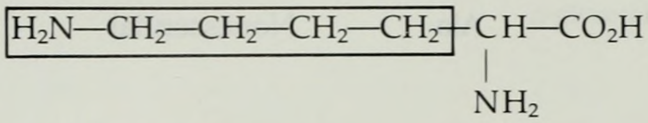
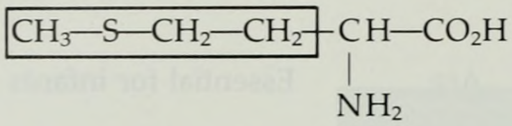
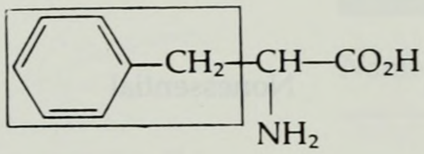
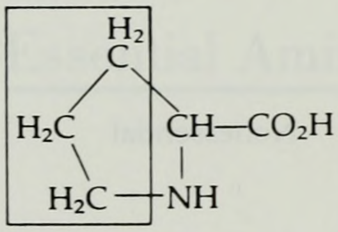
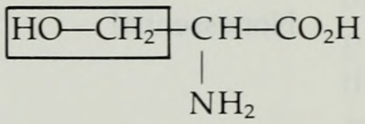
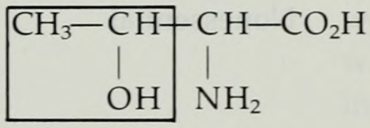
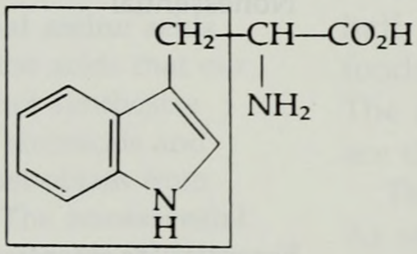
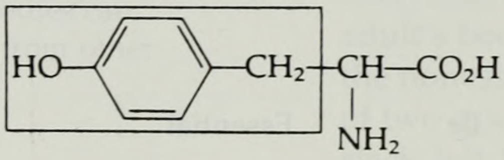
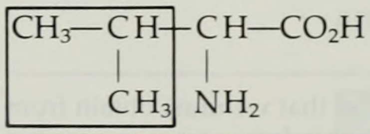
[a] The essential amino acids are those that our bodies cannot synthesize from other chemicals and that we must obtain from our foods. The nonessential amino acids are those that our bodies can produce from other chemicals.

TABLE 15.1 (*continued*)

Structure	Name	Abbreviation	Dietary Requirement[a]
 $\boxed{CH_3-\underset{CH_3}{CH}-CH_2}-\underset{NH_2}{CH}-CO_2H$	Leucine	Leu	Essential
 $\boxed{H_2N-CH_2-CH_2-CH_2-CH_2}-\underset{NH_2}{CH}-CO_2H$	Lysine	Lys	Essential
 $\boxed{CH_3-S-CH_2-CH_2}-\underset{NH_2}{CH}-CO_2H$	Methionine	Met	Essential
	Phenylalanine	Phe	Essential
	Proline	Pro	Nonessential
 $\boxed{HO-CH_2}-\underset{NH_2}{CH}-CO_2H$	Serine	Ser	Nonessential
 $\boxed{CH_3-\underset{OH}{CH}}-\underset{NH_2}{CH}-CO_2H$	Threonine	Thr	Essential
	Tryptophan	Trp	Essential
	Tyrosine	Tyr	Nonessential
 $\boxed{CH_3-\underset{CH_3}{CH}}-\underset{NH_2}{CH}-CO_2H$	Valine	Val	Essential

[a] The essential amino acids are those that our bodies cannot synthesize from other chemicals and that we must obtain from our foods. The nonessential amino acids are those that our bodies can produce from other chemicals.

15.5 The Quality of Our Protein

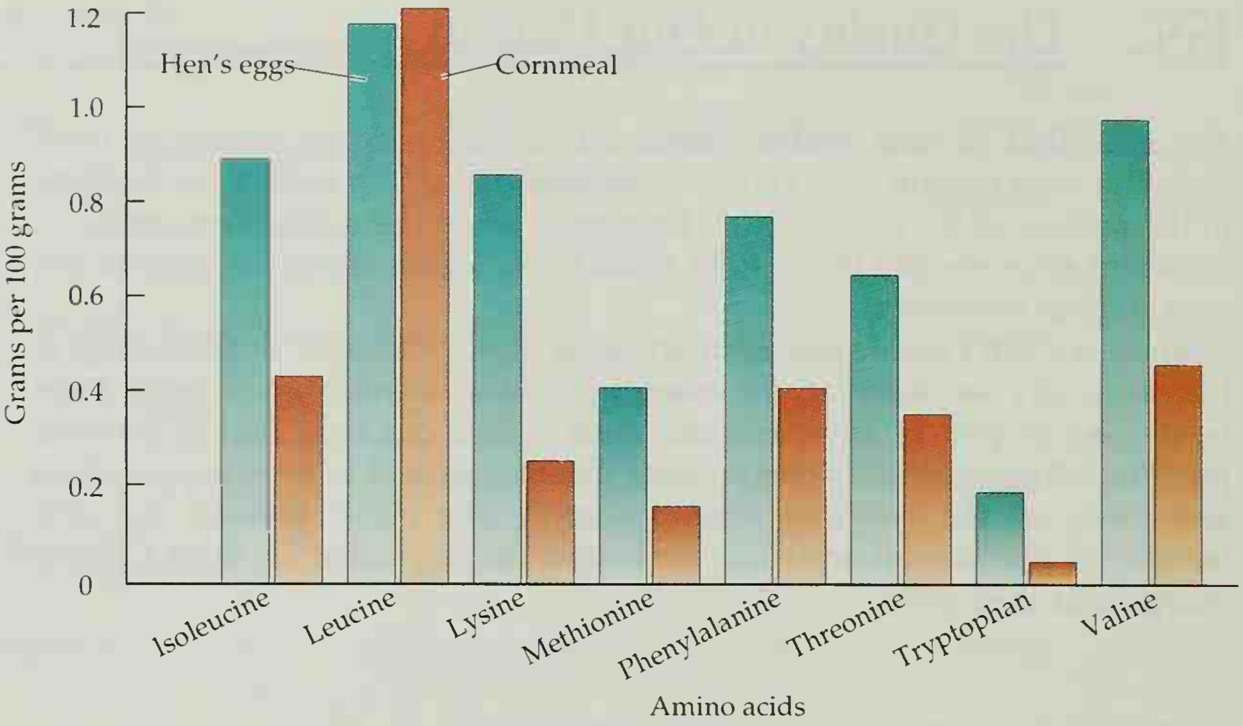
The quantities of total protein contained in various foods appear in Table 15.2. But total protein isn't enough. The essential amino acids must be there in the protein of the food we eat. They must all be there, simultaneously, in sufficient amounts and in the right ratios if our bodies are to use them in our own protein formation.

Since we can't store significant amounts of any of them for future use in the same way we store fat, for example, all the essential amino acids must be present as part of any particular meal. When our cells start to produce proteins, all the necessary components must be present in good supply, then and there, or the synthesis simply doesn't take place. Instead, the cells metabolize the unused acids that do happen to be present for the 4 Cal/g of energy that they yield.

TABLE 15.2 Protein Content of Foods

Food	Percent Protein (average or range)
Cheese	Cream cheese 9 ↔ 36 Parmesan
Peanuts	27
Chicken	21
Fish	Flounder 15 ↔ 21 Sardines
Beef	Hamburger 16 ↔ 20 Round
Eggs	13
Wheat flour	13
White flour	11
Cornmeal	9
Lima beans	8
Milk	Whole 4 ↔ 8 Condensed
Rice	8
Peas	7
Corn	4
Dates	2
Potatoes	2
Bananas	1
Carrots	1
Orange juice	1

Figure 15.2
Grams of the essential amino acids per 100 g of hens' eggs and of cornmeal (approximate values).



Complete or **high-quality protein** contains all the essential amino acids in about the same ratio as they occur in our own proteins. **Incomplete** or **low-quality protein** is deficient in one or more of the essential amino acids.

To do us any good, then, the proteins of our foods must provide us with substantial amounts of all the essential amino acids, and in about the same ratio as they occur in our own proteins. The dietary proteins that provide us with something close to that ratio are the **complete** or **high-quality proteins**; those deficient in one or more of the nutrients are the **incomplete** or **low-quality** proteins.

Of all common foods, eggs furnish substantial amounts of the essential amino acids in a proportion closest to the human average. They provide us with the highest-quality dietary protein. This shouldn't surprise us since chickens are vertebrates, not so very far removed biologically from humans, and each egg must contain all of the amino acids that eventually become the protein of a whole chick. In Figure 15.2 we see the amounts of each of the eight amino acids known to be essential for adults, as they occur in the protein of hens' eggs (and in the protein of cornmeal as well, for comparison in a few moments). All this, incidentally, isn't meant to suggest that eggs are the perfect food. Their very high cholesterol content (Section 13.3) limits their use by people who must avoid this substance.

The high-quality protein of eggs furnishes us with essential amino acids in nearly the same ratios found in human protein. The low-quality protein of cornmeal is deficient in several essential amino acids, especially lysine, methionine, and tryptophan.

To sum up, then, the ratio of the essential amino acids in any particular food is every bit as important as the actual quantities of each. Although the cornmeal in Figure 15.2, for example, contains almost as much total protein as eggs, and even a bit more leucine per 100 g, this grain serves as a comparatively poor source of dietary protein. Much of its leucine is lost through conversion to energy since cornmeal's deficiencies in the other essential amino acids don't allow very much protein formation. Most other grains and grain products also provide inferior dietary protein.

QUESTION

Assuming that the composition of egg protein accurately reflects our own, which essential amino acid is present in human protein in the smallest quantity? ______

15.6 The Vegetarian Diet

Finding the actual content of the essential amino acids in various foods and comparing their ratios with those found in eggs can be laborious and tricky. The approach used in Figure 15.3 makes the comparisons easier. Each bar in this figure reflects the amount of the amino acid (in a particular food protein) as a percentage of that amino acid's contribution to egg protein. A bar that reaches to 100% represents an amino acid that's present in the same ratio to the others as it is in eggs. For any particular foodstuff that contains all the essential amino acids in exactly the same ratio as egg protein (or human protein) and is therefore of the same nutritional quality as egg protein, all of the bars representing the amino acids would reach exactly to the 100% mark. Bars that rise above the 100% mark represent amino acids present in excess. Like the leucine of cornmeal, they would be converted to energy instead of being incorporated into a protein. Bars falling below 100% represent amino acids present in smaller ratios than in egg protein. Since, as we saw in the previous section, all of the necessary amino acids must be present for protein formation to occur, deficiencies in any of the essential amino acids in our diets limit the amount of protein our bodies can form. For each food protein, the essential amino acid that falls farthest from the mark serves to limit the amount of human protein that can be formed from the entire combination.

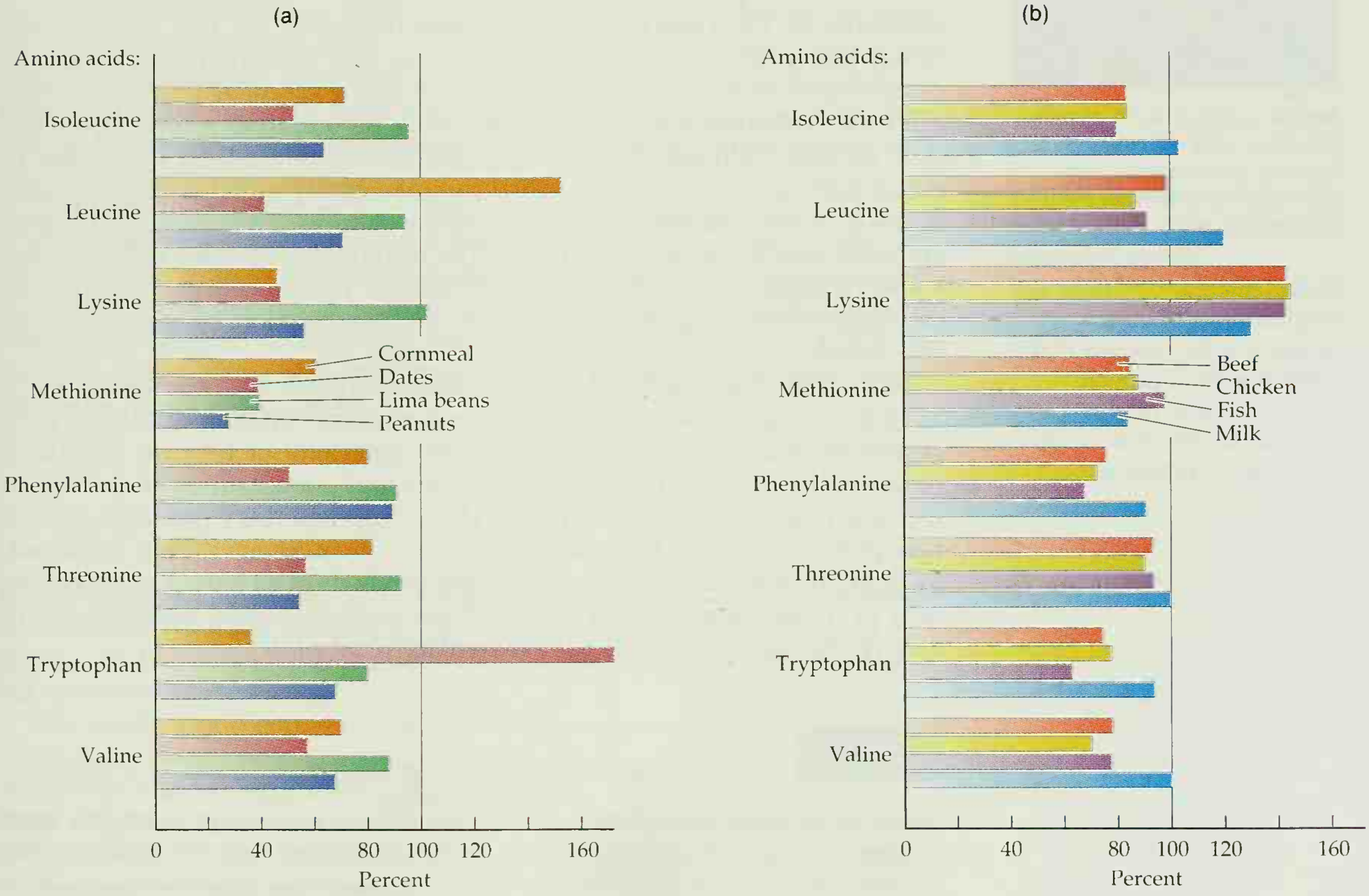


Figure 15.3
Essential amino acids of the typical plant (a) and animal (b) proteins as compared with egg protein.

Dates, lima beans, cornmeal, and peanuts represent plant foods that are deficient in one or more essential amino acids and that furnish low-quality protein.

Animal products such as milk, fish, beef, and chicken typically provide more high-quality protein than do plant products.

Complementary proteins are combinations of incomplete or low-quality proteins that, taken together, provide about the same ratio of essential amino acids as do high quality proteins.

For this reason that particular essential amino acid is sometimes known as the *limiting amino acid* in any particular food protein.

In Figure 15.3a we see clearly the deficiencies of lysine, methionine, and tryptophan in cornmeal. Deficiencies, especially of lysine and methionine, show up here for other common food grains as well. Fruits are also very poor sources of complete dietary protein, and most vegetables and other plant products aren't much better. Only peanuts, of the common plant foods, provide substantial amounts of all the essential amino acids (except methionine). Although dates appear to contain a large proportion of tryptophan, Table 15.2 shows that their total protein content is very low. So while the ratio of tryptophan to all of the other amino acids is quite high, none of them, including tryptophan, is present in substantial quantities.

It shouldn't surprise us that animal foods in general—beef, poultry, seafood, dairy products, and, of course, eggs—provide plenty of high-quality protein (Fig. 15.3b) while plants serve as poorer sources. The bodies of animals and the materials they produce to nourish their young are all chemically and biologically more nearly akin to our own physical bodies than are the inhabitants of the plant kingdom.

While the high quality proteins of meat, milk, and eggs provide us with our most efficient sources of the essential amino acids, they are by no means absolutely necessary to a healthful and perfectly satisfactory diet. After all, we're looking for only 8 to 10 essential amino acids, regardless of what sort of dietary proteins or combination of proteins furnish them. Consuming a combination of proteins from two or more different foods at the same meal can make up for a marked lack of protein quality in any one of the foods. When the foods are combined at one meal, the proteins they provide, in combination, can serve as a rich source of all the essential amino acids and can be indistinguishable from a high-quality protein from a single foodstuff such as beef. Different low-quality proteins that complement each other to mimic high-quality protein are called **complementary proteins** and are found in many of the traditional dishes of various cultures. The breakfast of cereal and milk provides a good illustration. The plentiful lysine of the milk provides a nice complement to the lysine deficiencies of our cereals. Another set of complementary proteins comes in the combination of peanut butter and bread.

Beef, veal, pork, and other meats are among our best sources of high-quality protein. Those of us who abstain from them (whether because of their potentially hazardous saturated fats and cholesterol or because of ethical, religious, or other dietary restrictions) can find good sources of protein in fish and poultry, as we see in Figure 15.3b. Eggs and dairy products provide rich protein for diets from which all forms of meat have been banished. Vegetarians who refuse to eat any animal products at all have a much harder time of it, but they can still obtain all the essential amino acids by careful dietary choices that include complementary plant proteins.

QUESTION

According to Table 15.2, peanuts provide about twice the amount of protein, gram for gram, as eggs. Yet (except for their cholesterol content) eggs are a better source of dietary protein than peanuts. Why? ____________________

15.7 Amides

The entire process of eating, digesting, absorbing, and metabolizing food can be summed up like this: Our bodies take apart the macronutrients of the food we eat

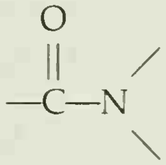
- To derive energy from them, and
- to use their elements and molecular fragments to build the substances we need for growth and for the operation and repair of our bodies.

That, aside from the alleviation of hunger and the sheer pleasure it can give us, is what eating is all about.

In building and maintaining our physical bodies we construct our own complex molecules of fats, carbohydrates, and proteins. Aside from differences in the length and unsaturation of side chains, there's not much variation in the fat molecules that we eat or those that we form in our bodies. Similarly, the polysaccharides of our food and our bodies are, for the most part, strings of glucose molecules that vary a bit in length and in the particular spots where one ring connects to another. But our proteins, those of our food and of our bodies, are another matter. The diversity of our protein structures is almost incomprehensible.

Up to now we've been considering what amino acids we need for protein formation, and how we get them. Now let's look briefly at how we use them to construct the complex protein molecules that compose and regulate our bodies. In fashioning their various protein molecules, our bodies link the individual α-amino acids, both the essential and nonessential, into enormously long sequences, much as individual monosaccharides join with each other to form polysaccharides.

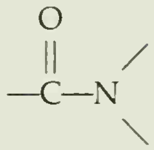
As a simple illustration of this combination, we can imagine two molecules of glycine joining together to form a new (and very short) molecule of *glycylglycine*. In this process, the —OH of the carboxyl group on one glycine molecule and one of the amino hydrogens of another leave as a water molecule (Fig. 15.4). The two glycines join through a covalent bond connecting the carbonyl carbon of one of them with the nitrogen of the other, thereby forming an **amide** functional group



$$-\overset{\displaystyle O}{\overset{\|}{C}}-N\begin{smallmatrix}/\\ \backslash\end{smallmatrix}$$

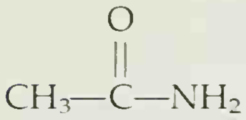
When this amide functional group links two amino acids, it's called a *peptide bond* and the resulting compound, glycylglycine for example, is known as a *peptide*. We'll examine both peptides and the peptide bond in more detail in the next section.

Amides are compounds containing the **amide** functional group,



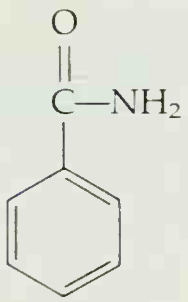
$$-\overset{\displaystyle O}{\overset{\|}{C}}-N\begin{smallmatrix}/\\ \backslash\end{smallmatrix}$$

This amide group occurs in a variety of other organic compounds as well, compounds having no connection whatever with the amino acids or proteins. Acetamide and benzamide are simple examples.



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$$

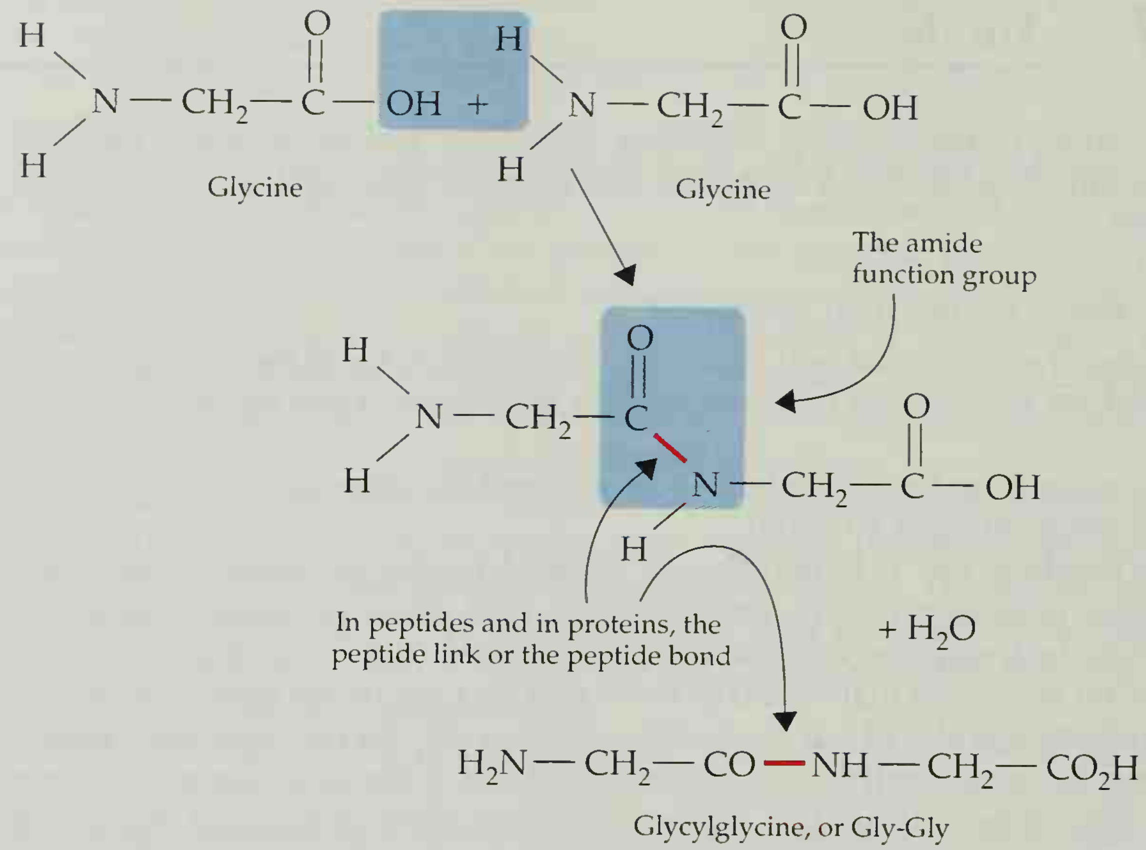
acetamide

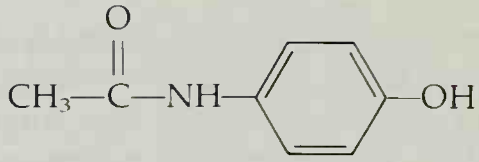


benzamide

More important to us as consumers are the more complex amides such as *acetaminophen*, which is the *analgesic* or painkiller of such over-the-counter medications as Datril and Tylenol.

Figure 15.4 Peptide formation.



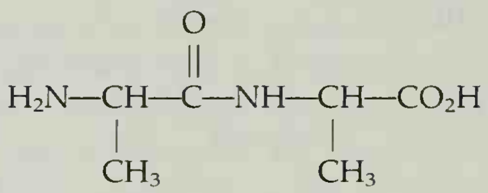


acetaminophen

In acetaminophen, which is an amide despite the "amino" of acet*amino*phen, we see an example of an *N-substituted* amide, a compound in which one of the hydrogens of the amide nitrogen has been replaced by an organic group.

QUESTION

What name would you give to the following compound? (Refer to Table 15.1.)



$$H_2N—\underset{\displaystyle CH_3}{\underset{|}{CH}}—\overset{\displaystyle O}{\overset{\|}{C}}—NH—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CO_2H$$

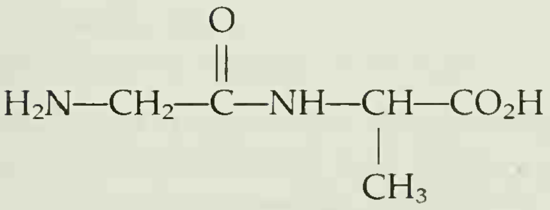
15.8 Peptide Links and Primary Structures

Because of its short chain and very small molecular size, glycylglycine simply doesn't qualify as a protein. Relatively short chains of amino acids, connected through these amide groups, are called *peptides*; the carbon-nitrogen bond that connects them is the **peptide link** or the **peptide bond**. A sequence of two amino acids forms a **dipeptide**, as we've seen in glycylglycine; three, joined by two peptide links, make up a **tripeptide**; four, joined by three peptide links, make up a **tetrapeptide**; and so on. Chains of 10 or more amino acids are **polypeptides**. It's only when the molecular weight of a polypeptide exceeds about 10,000 amu that it becomes a **protein** (Fig. 15.5).

A **peptide bond** or a **peptide link** is a carbon-nitrogen bond that links two amino acids. The resulting compound is a **dipeptide**, a **tripeptide**, a **tetrapeptide**, and so on, depending on the total number of amino acids joined by peptide links. **Polypeptides** consist of chains of 10 or more amino acids. **Proteins** are polypeptides with molecular weights greater than about 10,000 amu.

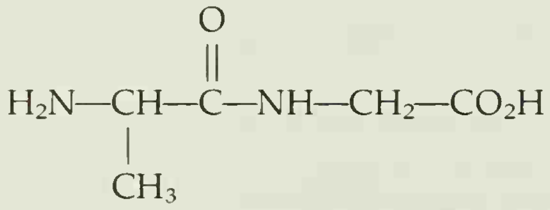
To understand how many different polypeptides and proteins can be formed from only the 20 amino acids in Table 15.1, let's first find how many dipeptides we can construct from just two amino acids, alanine and glycine. We've seen two of the dipeptides already, glycylglycine and the alanylalanine of the question at the end of the preceding section. (In writing the molecular structures of the peptides, it's customary to place the amino acid with the free amino group on the left and the one with the free carboxyl group on the right, and to name the various amino acids from left to right.)

Two additional dipeptides are glycylalanine and alanylglycine or, using the abbreviations in Table 15.1, Gly-Ala and Ala-Gly. These are, indeed, two different compounds. Notice that the part of the structure bearing the carboxyl functional group (—CO_2H) comes from an alanine molecule in Gly-Ala, but from a glycine molecule in Ala-Gly.



$$\mathrm{H_2N{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CO_2H}$$

glycylalanine, Gly–Ala



$$\mathrm{H_2N{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2{-}CO_2H}$$

alanylglycine, Ala–Gly

With just two amino acids, then, we can devise four different dipeptide chains: Ala-Ala, Ala-Gly, Gly-Gly, and Gly-Ala. As we increase the number of amino acids that we can use and as we lengthen the chain that we build with them, the number of different peptides that result grows almost beyond comprehension.

To grasp the enormous variety of polypeptide and protein structures that can exist, let's consider a simple analogy. We'll represent each amino acid by a letter of the alphabet and, in something resembling a game of anagrams, determine how many words can be formed by rearranging the sequence of letters. With *N*, for example, representing alanine, and *O* representing glycine, (and limiting ourselves to using each letter once and only once in each word) we can form the two words NO (for alanylglycine) and ON (for glycylalanine).

NO ON

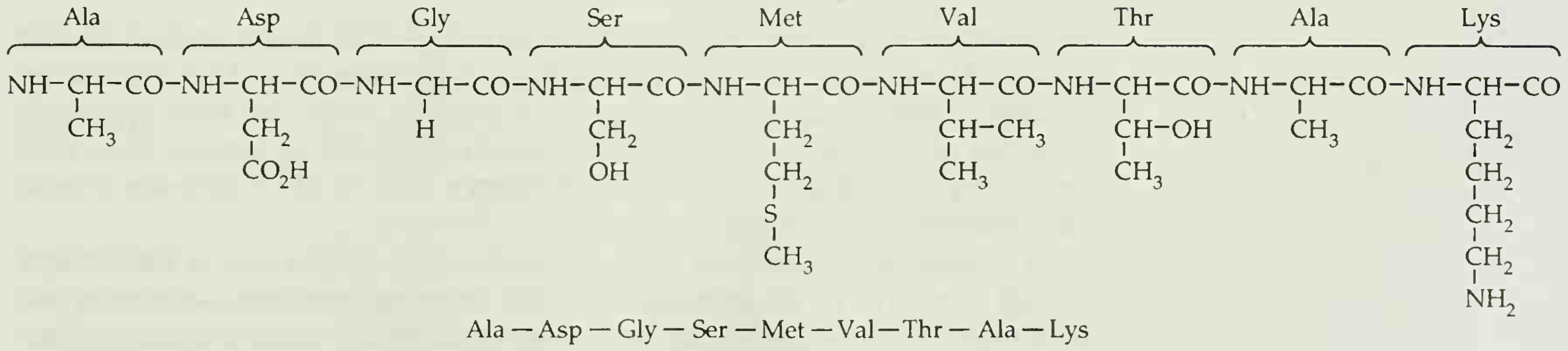


Figure 15.5
A typical segment of the chain of a polypeptide or a protein.

In the next step, let the three letters A, E, and T represent three different amino acids. With these we can generate the four words ATE, EAT, TEA, and ETA (the seventh letter of the Greek alphabet), and two more nonsense words, AET and TAE, for a total of six three-letter combinations.

AET
ATE
EAT
ETA
TAE
TEA

Adding an M to our supply gives us a total of 24 four-letter words, including such English words as MEAT, TEAM, MATE, and TAME and a long list of nonsense combinations, such as AEMT and EMTA.

AEMT
AETM
AMET
AMTE
ATEM
ATME
EAMT
EATM
EMAT
EMTA
ETAM
ETMA
MAET
MATE
MEAT
META
MTAE
MTEA
TAEM
TAME
TEAM
TEMA
TMAE
TMEA

The sequence of amino acids each of these words represents is called the *primary structure* of the peptide. By using each of four different amino acids once and only once in the chain, we can generate 24 different tetrapeptides, each with its own, unique primary structure. Of course, we're limiting ourselves here by using each of four different amino acids just once in the sequence. We could form far more by omitting one or more of the amino acids and using any of the others more than once.

QUESTION

You are given a kit of three amino acids, labeled A, B and C. (a) How many different *dipeptides* can you form using each amino acid no more than once in any dipeptide? (b) How many different dipeptides can you generate from these three amino acids if there's no restriction on the number of times each can appear in the primary structure? ____________________

15.9 The Secret of Life, or Why Shakespeare Could Have Been the Greatest Chemist of Them All

Now we can leap ahead to the entire assortment of 20 amino acids of human protein. If we were to assign a letter to each of these 20 and limit ourselves to constructing as many 20-letter words as possible, with each letter appearing once and only once in every sequence much as we did in Section 15.8, we'd have more than 2,430,000,000,000,000,000 (or 2.43×10^{18}) different words, each representing a different protein.

Of course, this is only an analogy, and a very simple one at that. We've limited ourselves to 20 amino acids in the primary structure, with each acid used once and only once. Our bodies don't have any such limitations. Peptides and proteins of any length can be formed, and any of the 20 amino acids can be dropped from any particular primary structure, or repeated here and there anywhere in the sequence. And yet each of the enormously long and unimaginably intricate peptide chains that our bodies do, in fact, produce is a rational, chemical "word" that performs a specific and important function in sustaining our lives. If the "word" is "misspelled," if just the right sequence of just the right amino acids isn't present in the polypeptide, the results can be tragic.

Insulin, for example, is a hormone important to the metabolism of glucose. Insufficient production of insulin by the pancreas results in the condition of ineffective glucose metabolism known as *diabetes* or, more specifically, *diabetes mellitus* (Section 14.1). Insulin itself is a polypeptide composed of 51 amino acids, with pairs of cysteines joined, here and there in its primary structure, through sulfur–sulfur bonds (Fig. 15.6). When the human body synthesizes insulin, it forms the molecule shown in Figure 15.6, with exactly that sequence of amino acids and no other.

In creating the proteins that keep us going, then, our bodies are as elegant chemically as Shakespeare himself. Combining the 26 letters of the English alphabet, along with spaces, commas, semicolons, periods, and other punctuation marks, Shakespeare created *Hamlet, Macbeth, Julius Caesar, The*

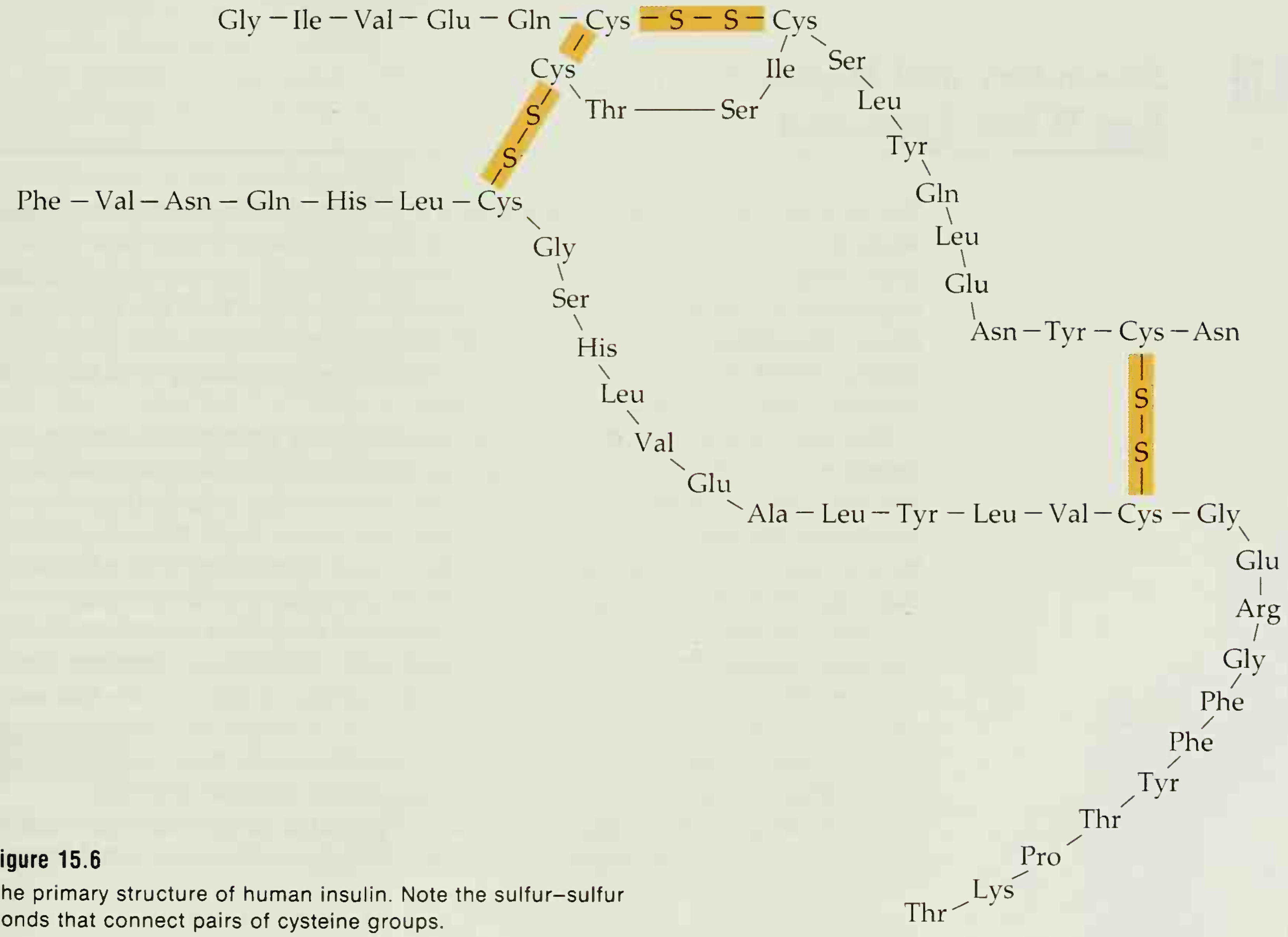


Figure 15.6

The primary structure of human insulin. Note the sulfur–sulfur bonds that connect pairs of cysteine groups.

Taming of the Shrew, Twelfth Night, and all of his other plays, and all of his sonnets. Just as each of his written words works toward making his plays and sonnets sound and read just right, each peptide or protein formed by a healthy body works toward making it grow and function effectively.

In the chemical and biological mechanics of how we do all this, of how we dissect the molecules of the plants and animals that we take as food, and recombine them into the proteins and the other substances that form and govern our human bodies, in all this lies the secret of life itself. It is a secret that science is illuminating slowly, painstakingly, step by step. With each discovery we learn more clearly how living things form, how they grow and take their own shapes, how they use their foods to sustain them. We are coming to understand how, through the operations of the genetic code of the DNA molecule, all living things pass their undiscovered mysteries along to generations yet unborn and unimagined. It is a story that lies far beyond this brief examination of the extraordinary chemistry of our most ordinary things.

QUESTION

What is the name of the hormone needed for the effective metabolism of glucose? What is the common name of the condition that results from a deficiency in the production of this hormone and the resulting ineffective metabolism of glucose

15.10 Secondary and Higher Structures—Egg White Explained

We've seen that the primary structure of a protein, the sequence of the amino acids in its molecular chain, determines what protein it is and how it functions. Beyond this primary structure, though, there is another characteristic important to the functioning of the protein: the shape that the long chain takes. This shape determines how well the protein can do its job. Two of the shapes found in proteins, *fibrous* and *globular,* are particularly well suited to several of the functions proteins perform.

Our hair and nails, and the claws of animals, for example, are tough and strong because they are formed of fibrous proteins. Their strength comes from the organization of their protein molecules into parallel strands that entwine much like strands of fiber that are twisted into strong rope. Fibrous proteins have primary structures that cause them to align themselves with each other this way, providing strength to the parts of the body that they form.

Other peptide molecules remain largely aloof from their neighbors, twisting and coiling their own strands back into themselves, forming small spheres. These globular proteins take shapes similar to the micelles that soap and detergents form in water (Section 11.7). As a result they move around easily in the bloodstream and other fluids, available to do their chemical work where they are needed. Enzymes are examples of globular proteins.

These shapes taken by the primary structures of proteins are called *secondary structures.* In some proteins the secondary structure is a coil that looks much like a long spring bent back on itself repeatedly. These coils can twist about to form even more complex shapes, the *tertiary* and *quaternary* structures.

Among the forces that hold together the secondary and higher structures of fibrous and globular proteins are **hydrogen bonds**. These are very weak bonds formed by the attraction of

- a nitrogen, oxygen, or halogen atom for
- a hydrogen atom that's bonded to a different nitrogen, oxygen, or halogen atom.

Hydrogen bonds are very weak individually, although the cumulative effect of many of them acting in concert can hold the shape of a secondary structure nicely in place.

A **hydrogen bond** is a weak chemical bond formed through the attraction of a nitrogen, oxygen, or halogen atom for a hydrogen bonded to a different nitrogen, oxygen, or halogen atom.

In polypeptides and proteins these hydrogen bonds form between the oxygen of a carbonyl carbon that's part of a peptide link and the hydrogen atom on a nitrogen of a different peptide link, either at another point in the chain or on some other molecule. We'll have more to say about the formation of hydrogen bonds and their importance in protein molecules when we examine the proteins of hair in Chapter 21. For the moment it's important simply to understand that they are weak bonds and that the accumulation of these hydrogen bonds along a polypeptide chain is what holds the primary structure in the shape of the secondary and higher structures. The hydrogen bonds of the protein of egg white, for example, hold the long molecules in their globular form, giving the white its characteristic consistency and transparency.

As we saw in our opening demonstration, proteins that are in their native state, those occurring in plants and animals such as the proteins of egg white, have secondary structures well suited to the functions they perform. Heating an egg white, as we do when we cook the egg, overcomes the hydrogen bonds that hold the protein in its secondary structure and allows the molecule to unravel, still keeping its original primary structure. When the protein of the white unravels it comes in contact with other protein molecules, which have also unraveled from their globular shapes. These denatured proteins now gather into shapes more like those of fibrous proteins and form the familiar tough white of the cooked egg. Adding salt or the isopropyl alcohol of rubbing alcohol to the protein, as we did in our opening demonstration, also disrupts the sequence of hydrogen bonds in the native protein and denatures it. Cooking an egg, then, is one way to denature the native proteins of an egg white. The heat breaks the hydrogen bonds that hold its molecules in their native secondary and higher structures. The proteins then regroup in other ways that produce the texture and appearance of the cooked egg.

QUESTION

Why don't the proteins of an egg white return to their original clear, colorless, gelatinous form as the cooked egg cools? ______________________________

15.11 Sickle Cell Anemia, Kwashiorkor, and High-Density Lipoproteins

To illustrate the important and complex roles that proteins play in maintaining our health, well-being, and life, we'll look at *sickle cell anemia*, a genetic defect that produces a painful and fatal form of anemia; *kwashiorkor* (kwash-e-OR-kor), a potentially fatal condition that results from the absence of essential amino acids from the diet; and high-density lipoprotein, a combination of proteins and triglycerides that helps remove cholesterol from our bodies.

An illustration of the importance of even a single amino acid in a protein chain occurs in sickle cell anemia, a genetic disease that destroys the blood's capacity to carry oxygen to the cells. The disease occurs principally in people of West African ancestry. It gets its name from its distortion of the red blood cells from their normal disklike form into the shape of a sickle. Hemoglobin, the protein of the red blood cells that carries oxygen from the lungs to the tissues, consists of 574 individual amino acid units strung out in two pairs of polypeptide chains. During hemoglobin's synthesis within the body, each amino acid is placed at a specific point within these chains. Sickle cell anemia results from a genetic error that places valine rather than the required glutamic acid at a precise point within one of the pairs. As a result of this small structural change, the hemoglobin molecule loses its ability to carry oxygen effectively. Its shape distorts, producing the characteristic sickle shape of the red blood cell.

Kwashiorkor develops from severe cases of protein deficiency, resulting from the virtually complete absence of essential amino acids from the diet. The word *kwashiorkor* comes from the language of Ghana, a country on the west coast of Africa. There, nursing infants receive sufficient protein from their mother's milk for good health and growth. With the coming of a second child, though, the first is commonly weaned and placed on a diet consisting almost exclusively of readily available fresh fruits, which are poor in protein, and plants, such as potatoes, that are rich in carbohydrates but are also poor in protein. This new diet contains only small quantities of protein, and low-quality protein at that. The first-born soon suffers from a severe protein deficiency and develops a variety of symptoms including a swollen abdomen, loss of color from the hair, patchy and cracked skin, loss of appetite, and general listlessness. Death often follows. The word *kwashiorkor* originated as the name of an evil spirit that, tradition held, afflicted the first child after the second was born. While kwashiorkor occurs principally in the tropics, its effects can be found worldwide.

High-density lipoproteins (HDLs) wrap themselves around cholesterol and carry it through our blood. Cholesterol itself (Section 13.3) is a waxy substance with very little tendency to dissolve in water. It's a hydrophobic substance (Section 11.6). To transport it through the blood, our bodies wrap packets of cholesterol in a sheath of proteins and varying amounts of triglycerides that present a more hydrophilic surface to the water of the blood. The resulting bundle, known as a **lipoprotein**, resembles the micelles of detergents.

A **lipoprotein** is a combination of a protein with cholesterol and triglycerides, in varying proportions, that carries these substances through the blood.

The lipoproteins are classified by their density: the HDLs are high-density, the LDLs are low-density, and the VLDLs are very-low-density lipoproteins.

The density of the lipoprotein appears to affect the fate of the cholesterol it carries. While only about a quarter of the cholesterol of the blood is carried in the form of HDLs, these high-density lipoproteins seem to have a protective effect on the body. They appear to remove cholesterol from deposits on the walls of arteries and transport it to the liver for disposal. LDLs and VLDLs, on the other hand, seem particularly effective in depositing cholesterol on arterial walls. There also seems to be a dietary connection here. Studies have connected large amounts of saturated fats in the diet with formation of the LDLs and VLDLs, while polyunsaturated fats seem to stimulate formation of the HDLs.

QUESTION

Name (a) a genetic disease produced by an error in the primary structure of a protein, (b) a condition produced by a marked deficiency of essential amino acids in the diet, and (c) the structures that carry cholesterol through the blood. ____________

PERSPECTIVE: Protein And Health

As with Gerardus Mulder (Section 15.1), our first contact with proteins might lead us to believe that they are, indeed, the foremost chemicals of life. Proteins build the tissues of our organs and our muscles. All our enzymes are proteins. For tasks including

- digesting food
- carrying oxygen to our tissues
- growing hair and nails
- healing cuts, wounds, and broken bones, and
- fighting off the invading microorganisms of disease

we depend on proteins. "Surely," we might think, "the more protein we eat, the better our lives."

Not quite. Remember that in many ways proteins are just another macronutrient, furnishing the same 4 Cal/g as carbohydrates. We don't use them as brain fuel, as we do glucose, nor store them as readily portable supplies of energy, as we do fats. While protein is being processed by our digestive systems, our bodies look at it as a collection of amino acids, to be used as needed.

If there's no demand for the special talents of the protein molecules we can make from them—if we aren't ill, recovering from surgery, running short of insulin or some other enzyme, or under some sort of physical stress such as pregnancy—we use them for energy or convert them to body fat as we do with our other macronutrients. We can't simply decide that this morning's fried eggs are going into muscle tissue, or antibodies, or hair. If there's no demand for muscle tissue, generated by exercise, or for antibodies, generated by an invasion of microorganisms, or for some other specialized molecules only the amino acids can form, we either use them for energy or store them by converting them to fat.

How much protein do we need? As a general recommendation, only about 10 to 15% of our calories should come from protein. (Estimates for the remainder of our calories vary, but 20 to 25% has been recommended as a healthful maximum from fats and oils. For good health, most of our calories ought to come from the large carbohydrate molecules of starches.) For now we can say that, as a rough rule of thumb, most Americans consume at least twice as much protein as they need. Of course, the term *most* isn't the same as *all*. There are special demands and stresses brought on by illness, on the one hand, and pregnancy and lactation, on the other. Because of the need to repair and create tissue, these stresses require extra quantities of protein. Other groups who may not be getting enough include dieters with severely restricted food intake and those who simply can't obtain sufficient protein because of poverty or disability.

While both plants and animals can supply us with protein, each source provides its own advantages. Animal protein is high quality protein, rich in the essential amino acids. Yet animal protein brings with it cholesterol and the saturated fatty acids of animal fat. Vegetable protein spares us these, but by and large it's poor in some vital minerals, notably calcium, iron, and zinc. On the other hand, plant protein is less expensive than animal protein and supplies us with fiber as a bonus. For most of us, fortunately, the answer is simple: a varied diet including our major sources of protein—fish, poultry, vegetables, and legumes, along with milk, milk products, and some eggs—supplies us with adequate amounts of the nutrient.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

Dietary ______ provides us with the ______ we need to form our bodily enzymes and structures such as skin, hair and nails. In generating our own protein, we use some 20 amino acids. Those we can form ourselves, through chemical reactions that take place in our own bodies, are called ______ amino acids. An example of this type of amino acid is ______ . Those we cannot form but must obtain from our foods are the ______ amino acids. An example of this type of amino acid is ______ . With the single exception of ______ , all of the naturally occurring amino acids are ______ and are classified as members of the ______ .

The actual sequence of the amino acids along a protein or polypeptide chain represents the chain's ______ . In this structure the individual amino acids are joined to each other through ______ links, which are incorporated within the ______ functional groups of simpler molecules. Two amino acids joined together in this way form a ______ , three form a ______ , and so on, up to chains of nine amino acids. Beyond nine and up to molecular weights of about 10,000, the chains are known as ______ ; beyond that size they are classified as proteins.

alanine
amide
amino acids
chiral
dipeptide
essential
glycine
leucine
L-series
nonessential
peptide
polypeptides
primary structure
protein
tripeptide

2. Define, identify, or explain each of the following:

a. α-amino acid
b. acetaminophen
c. amine
d. HDL
e. high-quality protein
f. insulin
g. kwashiorkor
h. LDL
i. sickle cell anemia
j. zwitterion

3. What happens when a protein is denatured?

4. Describe four ways to denature the protein of egg white.

5. What's the difference between a globular protein and a fibrous protein?

6. Name three foods that provide large amounts of high-quality protein.

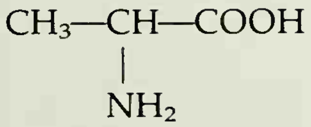
7. Why do animal products generally provide better quality protein than plant products?

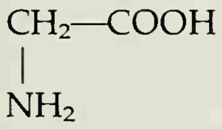
8. Which, if any, of the following are essential amino acids for adults: (a) tryptophan, (b) valine, (c) isoleucine, (d) serine, (e) leucine?

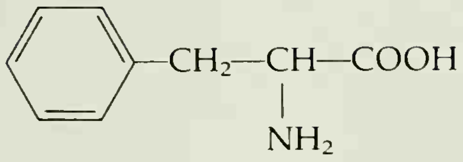
9. What amino acids are essential for children but not for adults?

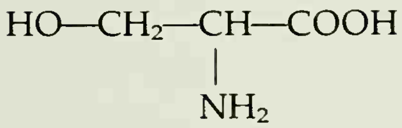
10. Why do vegetarians who avoid all animal products, including eggs, milk, and cheese, have to be particularly careful about their choice of the foods they eat?

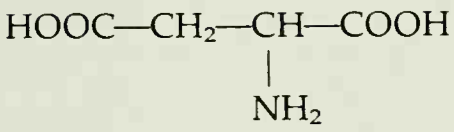
11. Name each of the following α-amino acids:

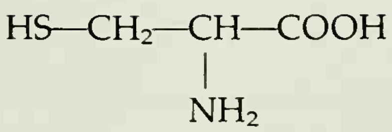
a.

$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

b.

$\underset{\displaystyle NH_2}{\underset{|}{CH_2}}-COOH$

c.


d.

$HO-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

e.

$HOOC-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

f.

$HS-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

12. Give the molecular structures of each of the following α-amino acids: (a) glutamic acid, (b) threonine, (c) arginine, (d) tyrosine.

13. In what way are cysteine and methionine different from the other amino acids in Table 15.1?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

14. With no restrictions on how many times you may use each, how many *tripeptides* can you generate from *two* different amino acids? Using the abbreviations for alanine and glycine, write the primary structures of all the tripeptides these two amino acids could form.

15. With no restrictions on how many times you may use each, how many *tripeptides* can you generate from *three* different amino acids? Using the abbreviations for lysine, methionine, and phenylalanine, write the primary structures of all the tripeptides these three amino acids could form.

THINK, SPECULATE, REFLECT, AND PONDER

16. Write a chemical reaction in which alanine, (a) acts as a base; (b) acts as an acid.

17. Most of the proteins that occur in blood serum (the fluid portion of the blood) are globular proteins. Why do you think this is so?

18. Explain the significance of the *limiting amino acid* in food protein.

19. What is the limiting amino acid in (a) cornmeal, (b) lima beans, (c) peanuts?

20. Of the following foods, which one is the best source of dietary lysine: bananas, carrots, corn, dates, fish, orange juice, potatoes?

21. Is each of the following statements true or false? Explain your answers.

a. The combination of cereal and milk provides complementary protein.
b. The combination of eggs and cornmeal provides complementary protein.

22. Is each of the following statements true or false? Explain your answers.

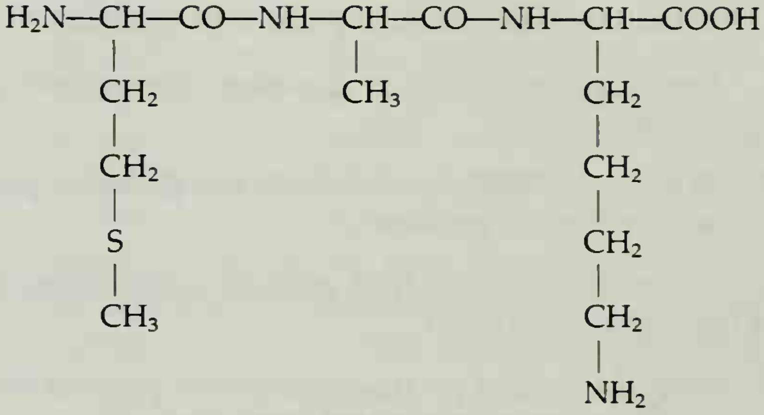
a. If, without changing any other aspect of your daily living, you eat more fatty foods, you will gain weight because the additional triglycerides of your diet will add adipose tissue to your body.

b. If, without changing any other aspect of your daily living, you eat more foods rich in high-quality protein, you will gain weight because the additional amino acids will add muscle tissue to your body.

23. Figure 13.3a reveals that the protein of lima beans contains a larger percentage of the essential amino acids than does the protein of peanuts. Yet peanuts are generally considered to be a better source of protein than lima beans. Explain why.

24. Table 15.2 shows that peanuts contain about 27% protein. Yet Figure 15.3a shows that they contain very little of the essential amino acid methionine. Suppose someone suggested a diet in which peanuts provided for all of your protein needs. According to this diet, you would eat enough peanuts every day so that even with methionine as the limiting amino acid, you would get enough methionine to allow the syntheses of all the needed proteins in your body. How would you respond to this suggested diet? Describe your reasoning.

25. Give the primary structure of the following peptide by using the abbreviations of the amino acids it contains.



$$\begin{array}{ccccccccccccccccc}
H_2N & - & CH & - & CO & - & NH & - & CH & - & CO & - & NH & - & CH & - & COOH \\
 & & | & & & & & & | & & & & & & | & & \\
 & & CH_2 & & & & & & CH_3 & & & & & & CH_2 & & \\
 & & | & & & & & & & & & & & & | & & \\
 & & CH_2 & & & & & & & & & & & & CH_2 & & \\
 & & | & & & & & & & & & & & & | & & \\
 & & S & & & & & & & & & & & & CH_2 & & \\
 & & | & & & & & & & & & & & & | & & \\
 & & CH_3 & & & & & & & & & & & & CH_2 & & \\
 & & & & & & & & & & & & & & | & & \\
 & & & & & & & & & & & & & & NH_2 & &
\end{array}$$

26. Is the compound in Problem 25 a monopeptide, a dipeptide, a tripeptide, or a tetrapeptide?

27. How many peptide bonds does the compound in Problem 25 contain?

28. Name and draw the molecular structure of the compound represented by the abbreviation Val-Pro-Gly.

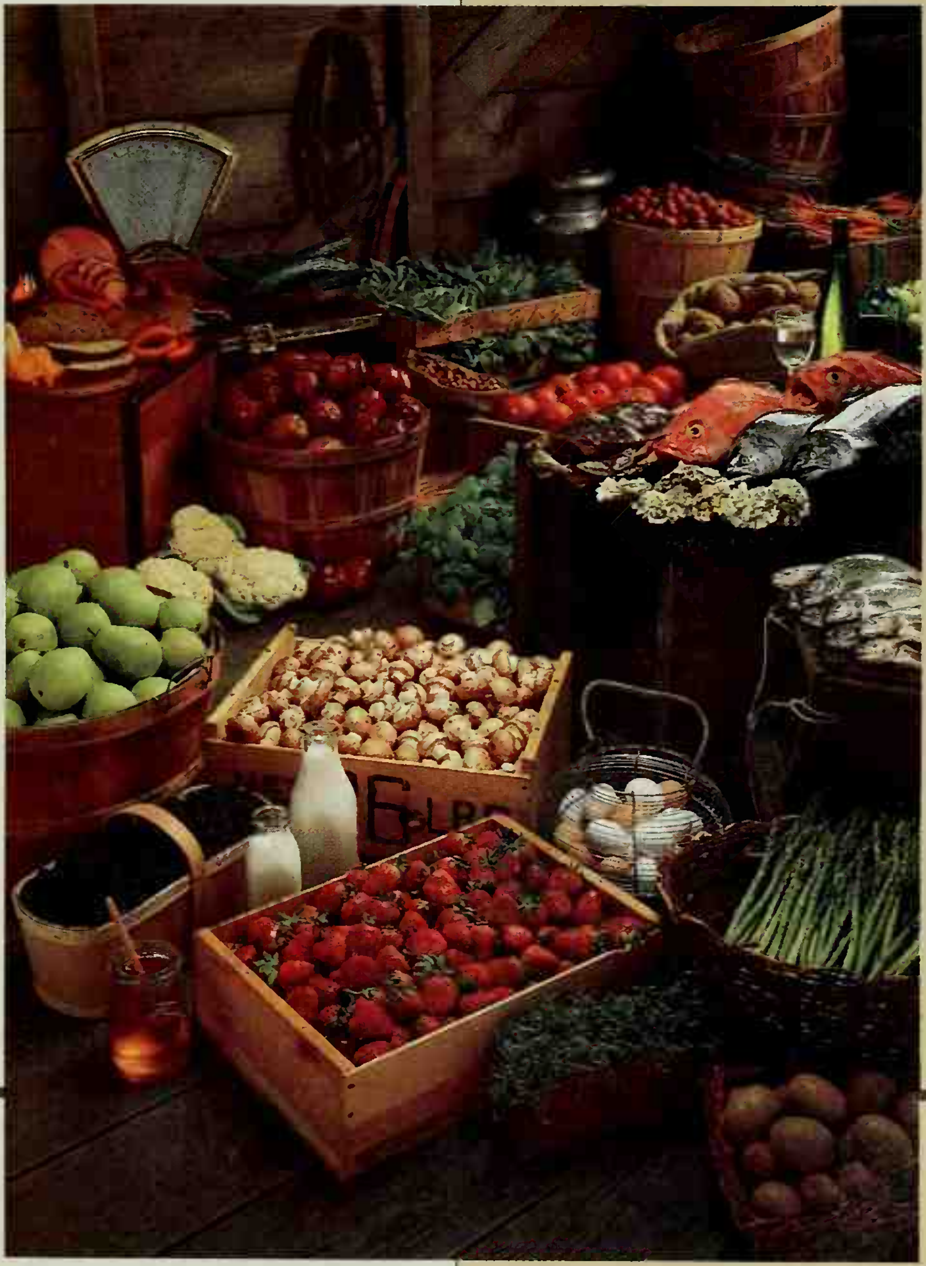
29. Name an amino acid in Table 15.1 that has more than one chiral carbon.

30. Would you expect a zwitterion to be a good electrolyte? Explain.

Mineral and Vitamins

16

THE VITAL ACCESSORIES



A variety of foods furnishes a healthful balance of vitamins and minerals.

A drop of iodine on a tablet of Vitamin C.

The Power of Vitamin C

When we think of vitamin C we think of oranges, and with good reason. Oranges are rich in vitamin C. A half cup of orange juice, 4 oz, contains about 62 mg of the vitamin. That's enough to carry most of us through the day. Citrus fruit generally is rich in this vitamin. Other foods containing plenty of vitamin C include broccoli, brussel sprouts, cantaloupe, cauliflower, collard greens, green beans, and potatoes.

Many of us regard vitamin C as a natural component of healthful foods that protects us against illness. That's one way of looking at it. But vitamin C is also a chemical, consisting of a highly organized arrangement of protons, neutrons, and electrons, capable of reacting in well-defined ways with other chemicals. It's a combination of carbon, hydrogen, and oxygen atoms held together by covalent bonds, with the molecular formula $C_6H_8O_6$ and the chemical name *ascorbic acid*.

We can see it in action with a little water, tincture of iodine, household bleach, and two vitamin C tablets. We've used tincture of iodine before, in our examination of redox reactions in Chapter 6 and in our investigations of the vegetable oils of Chapter 13 and the carbohydrates of Chapter 14. As we saw in the table of standard reduction potentials in Chapter 6, iodine is a good oxidizing agent, capable of being reduced to iodide ions as it oxidizes other chemicals (Table 6.1). Iodine is especially useful here because we can see clearly the loss of color as the red-violet molecular I_2 is reduced to colorless I^- anions by the vitamin.

You can see the vitamin's chemical prowess in either of two ways. In one approach, simply put a drop of the iodine solution on the surface of a vitamin C tablet. (A 250 mg tablet of the pure vitamin works nicely.) Watch closely, because the iodine quickly loses its color. The molecular iodine, I_2, is rapidly reduced to colorless iodide ions, I^-, by the powerful reducing activity of the vitamin. As part of this redox reaction (Chapter 6), the iodine oxidizes the vitamin C to a different compound.

After the color of the iodine has disappeared, add a drop or two of liquid bleach to the tablet. You'll see its surface darken immediately as the chlorine of the bleach reoxidizes the iodide ions back to molecular iodine. We saw something like this happen in the opening demonstration of Chapter 6, when we used galvanized tacks to decolorize iodine. In this current demonstration, the vitamin C is behaving chemically much like the zinc tacks of Chapter 6.

You can also carry out this demonstration by dropping the tablet into about a quarter cup of water. You don't have to wait until the tablet dissolves. Swirl the tablet in the water for a few moments and then add a few drops of iodine. After the color disappears, add a few drops of the bleach. You'll see the color reappear, as it did with the dry tablet (Fig. 16.1). The speed of the appearance of the color depends on the temperature of the water, the amounts of iodine and bleach you add, and other factors. You may want to try this a few times to see the effects of different water temperatures and other conditions.

(After the red-violet color of the iodine reappears, both with the dry tablet and with the solution of vitamin C in water, it fades away again after a short time. This results from continued oxidation of the I_2 to still other, colorless substances by the household bleach. You can demonstrate that this is happening by adding a drop or two of the tincture of the iodine solution to a little liquid bleach. The color of the iodine rapidly fades in the bleach because of this continued oxidation. The nature of this oxidation of I_2 by the bleach does not affect the results we obtain from the vitamin C or our discussion of them.)

You can use the scientific method in this demonstration to prove an important point. When you add the bleach to the vitamin C, after the original color has disappeared, you see a return of color. How do we know this comes from a reaction of the bleach with the iodide ions? Could the color now be coming from a reaction of the bleach with the vitamin C itself? We can answer this question by using a *control*, an experiment identical to the first in every way but a critical one. For the control experiment add a bit of liquid bleach to a fresh vitamin C tablet untouched by iodine. There's no color this time. We interpret this observation as proving that the color you saw on adding the bleach to the first tablet must have come from a reaction of the bleach with iodide ions that were present, not from a reaction with the vitamin. You can perform this same test with a tablet in a little water.

We'll have more to say about the ease of oxidation of vitamin C later in this chapter.

Figure 16.1
The color of iodine fades as Vitamin C reduces I_2 to I^-. The color reappears as Cl_2 oxidizes I^- to I_2. No color appears when we add the bleach to Vitamin C.

16.1 Beyond the Macronutrients

In the previous few chapters we've seen that the macronutrients, along with fiber and water, make up the bulk of the food we eat. While the macronutrients supply us with energy and with the materials of our physical bodies, they alone can't keep us healthy and well nourished. To use them effectively we need the accessory actions of still other chemicals, the minerals and vitamins that come to us in food along with fats, oils, carbohydrates, and proteins.

Micronutrients are the components of food that we need in very small amounts for life and good health.

Commercially available mineral and vitamin supplements.

Food, in short, is more than simply a mixture of macronutrients, fiber, and water. Minerals help form our bones, our teeth, and our blood, maintain the balance of fluids inside and outside our cells, produce our stomach acid, and keep the body's machinery running smoothly. Vitamins make possible the production of energy from the macronutrients and the formation of coherent body tissues.

In classifying all these components, it's customary to combine the minerals and vitamins into the class **micronutrients**. These substances don't give us any significant amounts of energy directly through their own conversion into energy (Chapter 12). Nor, except for the calcium and phosphorus of our bones and teeth, do they provide the raw material for tissue formation. We do need them, though, usually in minuscule amounts, so that we can convert the macronutrients into energy and into the materials of the body. In this chapter we'll examine the minerals and vitamins of our food. We'll see what they are, where they come from, and what they do for us.

16.2 The Major Minerals, from Calcium to Magnesium

Minerals are chemical elements we need for life and good health that are not part of the macronutrients.

The classification **minerals** includes all the nutritional chemical elements of our foods, except for carbon, hydrogen, nitrogen, oxygen, and (by some definitions) sulfur, all five of which come to us with the macronutrients. Of all the minerals, calcium is the most abundant in our bodies, ranking fifth among all of our atoms, just behind hydrogen, oxygen, carbon and nitrogen (see Fig. 2.5). Between 1.5 and 2.0% of your body weight comes from calcium, and more than 99% of all this calcium lies in your bones and teeth. To translate this into more concrete terms, if you weigh 70 kg (154 pounds), you're carrying around some 1.0 to 1.5 kilograms of calcium in your skeleton and in your mouth.

Next in rank comes the element phosphorus. Although calcium is the major mineral of our bones and teeth, it takes about half a gram of phosphorus to pack each gram of calcium firmly into the bony lattices and hold it there. Add the smaller amounts of phosphorus in our soft tissues to that of our skeletons, and a 70 kg person owns a total of almost a kilogram of the element.

We have smaller amounts of potassium, chlorine, sodium, and magnesium inside us, in that order. These elements form the major ions of the fluids in and around our cells. (The fluids within the cells are *intracellular*; those outside, are *extracellular*.) Potassium, the principal cation inside the cells, governs the activity of the cellular enzymes. Sodium, which is the dominant cation outside the cells, keeps the water content of the intracellular and extracellular fluids in a healthy balance. Both sodium and potassium cations regulate the distribution of hydrogen ions throughout our bodies and thereby keep the acidities of our various fluids within their normal ranges.

Along with these alkali metal cations, chloride anions also help regulate fluid balances and, in combination with protons, provide the hydrochloric acid of our gastric juices. They also serve to balance the electrical charges of the various cations.

Calcium, phosphorus, and magnesium are the major minerals of teeth and bones.

Sodium and potassium play major roles in regulating the water balance of the body, including the formation and secretion of sweat.

Magnesium plays many parts, several of them secondary roles. It's second to calcium as the hard mineral of bones and teeth, and second to potassium in regulating chemical activities within the cells. Magnesium helps control the formation of proteins inside the cells and the transmission of electrical signals from cell to cell.

QUESTION

Is the sodium ion more likely to be found in the intracellular fluid or in the extracellular fluid? What class of compounds would you expect to be a major source of dietary sulfur? ______

16.3 Trace Elements, from Iron on Down

Together, just 11 elements—the carbon, hydrogen, nitrogen, oxygen, and sulfur of the macronutrients and water, and the calcium, phosphorus, potassium, chlorine, sodium, and magnesium of the minerals—compose well over 99% of the mass of all living matter. All the remaining elements necessary for good health make up the category of **trace elements**. Generally, we consider as trace elements those needed in our diets at levels of less than 100 mg (0.100 g) per day. We'll examine the quantitative daily requirements more closely in the next section.

The **trace elements** are the dietary elements we need at levels of less than 100 mg per day.

Among the more important of the trace elements are iron, fluorine, zinc, copper, selenium, manganese, iodine, molybdenum, chromium, and cobalt, arranged here in decreasing order of the amount of each in an adult body. They function in various ways, with most of them incorporated into the structures of enzymes, hormones and related molecules, or acting in conjunction with vitamins.


A deficiency of iodine can lead to an enlargement of the thyroid gland, a condition known as *goiter.*

Table salt is available with added iodide ion, usually as potassium iodide, KI, and without this micronutrient.

Iron, for example, forms a critical part of the hemoglobin molecule of red blood cells. It's the iron of the hemoglobin that bonds to oxygen acquired as the blood passes through the lungs, and that carries the oxygen throughout the body. Fluorine, as the fluoride anion, helps harden the enamel of teeth, making them resistant to decay. Many communities add fluoride salts to drinking water supplies to protect the teeth of children. A compound of fluorine, often sodium fluoride, is listed among the ingredients of most anticavity toothpastes. Zinc is important to growth, to the healing of wounds, and to the development of male sex glands. A deficiency of iodine leads to enlargement of the thyroid gland of the neck, a condition known as a *goiter*. A single cobalt atom is incorporated into every molecule of vitamin B_{12}.

Other trace elements play various roles in the body. Because of the abundance of some of them in our diets, our knowledge of their actions in human bodies sometimes comes from studies of deficiencies artificially produced in the diets of animals. Deficiencies of copper produce symptoms ranging from changes in hair color to anemia and bone disease. Manganese is essential for healthy bones, a well-functioning nervous system, and reproduction. Chromium plays an important part in the metabolism of glucose.

QUESTION

About 0.01% of potassium iodide is added to the sodium chloride sold as "iodized salt." What health benefit does this provide? ______________________

16.4 How Much Is Enough? The RDAs, Part I: Minerals

Granted that we need quite a variety of minerals in our foods, where do we find them and how much of each do we need? The more common dietary sources of minerals are well known and appear in Table 16.1. The question of how much we need can be more of a problem.

To answer this question, the National Academy of Sciences and the National Research Council, organizations of distinguished U.S. scientists and

TABLE 16.1 Dietary Sources of Minerals

Mineral	Source
Calcium, Ca[a]	Milk and dairy products such as cheese and ice cream; fish, such as sardines, eaten with their bones; broccoli and other dark green vegetables; legumes
Chlorine, Cl[a]	Table salt
Chromium, Cr[b]	Brewers' yeast; meat (except fish); whole grains
Cobalt, Co[b]	Most animal products, including meat, milk, and eggs
Copper, Cu[b]	Liver and kidneys; shellfish; nuts; raisins; dried legumes; drinking water in some areas
Fluorine, F[b]	Drinking water (in some regions); tea; fish, eaten with their bones
Iodine, I[b]	Iodized salt; seafood; bread
Iron, Fe[b]	Liver and other red meats; raisins; dried apricots; whole-grain cereals; legumes; oysters
Magnesium, Mg[a]	Whole-grain cereals; nuts; green vegetables; seafood
Manganese, Mn[b]	Nuts; whole grains and cereals; leafy green vegetables; dried fruits; roots and stalks of vegetables
Molybdenum, Mo[b]	Animal organs; cereals; legumes
Phosphorus, P[a]	Nearly all foods
Potassium, K[a]	Nearly all foods, especially meat, dairy products, and fruit
Selenium, Se[b]	Various foods, including grains, meat, and seafood
Sodium, Na[a]	Table salt
Sulfur, S[a]	Dietary proteins of meat, eggs, dairy products, grains, legumes
Zinc, Zn[b]	Meat; eggs; seafood (particularly oysters); dairy products; whole grains

[a] A major element of our micronutrients.

[b] A trace element of our micronutrients.

engineers, publish every few years the recommendations of their Food and Nutrition Board. These are summarized as the Recommended Dietary Allowances, or RDAs, and, as stated in the publication, are "the levels of intake of the essential nutrients considered, in the judgment of the Food and Nutrition Board on the basis of available scientific knowledge, to be adequate to meet the known nutritional needs of practically all healthy persons." The RDAs are, in brief, the average daily amounts of various nutrients that, in the opinion of a group of well-informed scientists, most of us should consume to maintain good health. They're considered to be at least adequate for nearly everyone and certainly more than enough for most of us.

There are also a few important things that these RDAs are *not*. First, they certainly don't cover every single vitamin and mineral we need for good health. As a result, we couldn't expect to keep in good condition by mixing

TABLE 16.2 Selected Recommended Dietary Allowances (RDAs) for Minerals[a]

		Weight		Height		Ca	P	Fe	Mg	Zn	I	Se
Gender	Age	kg	lb	cm	ft'in"	(mg)	(mg)	(mg)	(mg)	(mg)	(μg)[b]	(μg)[b]
Both	0–0.5	6	13	60	2'	400	300	6	40	5	40	10
	0.5–1	9	20	71	2'4"	600	500	10	60	5	50	15
	1–3	13	29	90	2'11"	800	800	10	80	10	70	20
Men	15–18	66	145	176	5'9"	1200	1200	12	400	15	150	50
	19–24	72	160	177	5'10"	1200	1200	10	350	15	150	70
	25–50	79	174	176	5'10"	800	800	10	350	15	150	70
	51+	77	170	173	5'8"	800	800	10	350	15	150	70
Women	15–18	55	120	163	5'4"	1200	1200	15	300	12	150	50
	19–24	58	128	164	5'5"	1200	1200	15	280	12	150	55
	25–50	63	138	163	5'4"	800	800	15	280	12	150	55
	51+	65	143	160	5'3"	800	800	10	280	12	150	55
—Pregnant						1200	1200	30	320	15	175	65
—Lactating												
(First 6 months)						1200	1200	15	355	19	200	75
(Second 6 months)						1200	1200	15	340	16	200	75

[a] Condensed version of Recommendations by the Food and Nutrition Board of the National Academy of Science, National Research Council. Published in 1989.

[b] 1 μg (one microgram) = 10^{-6} g = 10^{-3} mg.

up a daily porridge of all the substances they cover, in the exact quantities they recommend, and consuming the stuff as our only source of micronutrients. The daily recommendation for chromium, for example, hasn't yet been established, and so this metal isn't on the RDA list. Yet we seem to need it for the effective metabolism of glucose. (To provide a bit of guidance for chromium and a handful of other minerals and vitamins lacking specific RDAs, the Food and Nutrition Board also publishes a supplementary list of daily ranges of these micronutrients it considers to be safe and effective.)

It's foolhardy, moreover, to believe that every last substance we need for good nutrition is now well established. Nor are these recommendations meant to cover the more extreme nutritional requirements that result from illnesses or unusual genetic makeups. Although they're surely suitable for virtually all of us, they simply don't apply to everyone.

The RDAs provide an excellent guide to good nutrition, obtained through a well balanced and diversified diet. A condensed version of recent mineral RDAs appears in Table 16.2. Notice that the RDA for any particular nutrient depends on a person's gender, weight, age, and height, and on such conditions as pregnancy and lactation. We'll have more to say about these variables in Section 16.11.

QUESTION

What is the difference, as reflected by the RDAs in Table 16.2, between the mineral requirements of (a) men and women aged 15 to 18? (b) Men and women aged 19 to 24? (c) Men 15 to 18 and men 19 to 24? (d) Women 15 to 18 and women 19 to 24?

16.5 Vitamins

We also need small amounts of vitamins in our diets, just as we require minerals. But despite the nutritional similarities, there are important chemical differences between the two. First, the dietary minerals are simply the less abundant chemical elements of our foods. **Vitamins**, on the other hand, are organic compounds, with well defined molecular structures. They are the organic compounds we need in small quantities in our foods, for life and good health. We don't use them directly for energy, and we don't use them directly for the materials of our bodies.

Vitamins are organic compounds that are essential in very small amounts for life and good health.

There's still another critical difference between them: their source and their origin. Plants pick up minerals directly from the soil, and animals get them from their food. If any particular mineral doesn't occur in the soil in which a plant grows, or in the food of an animal, there's no way in the world that it can be part of that plant or animal's makeup. Living beings simply can't generate minerals in their own bodies. All of our minerals became part of the earth at its birth and enter our bodies only from the earth, through the plants we eat or the animals that feed on them.

Vitamins, on the other hand, form biologically, through the life processes of the plants and animals we eat. Plants and animals synthesize them within their own bodies just as we synthesize protein and fat molecules within ours. Thus, the vitamins of plants come from the plants themselves, not from the soil or the air or any fertilizers. They're as much a part of the plant as a nose is part of your face. An orange contains vitamin C for the same reason it has a tough, orange-colored skin. Both the vitamin C and its orange skin develop as the fruit grows and matures. Otherwise, it wouldn't be an orange.

QUESTION

Would a chemical analysis of the soil of a vegetable garden reveal (a) what minerals we might find in the vegetables that come from the garden? (b) what vitamins we might find in the vegetables that come from the garden? Explain your answers.

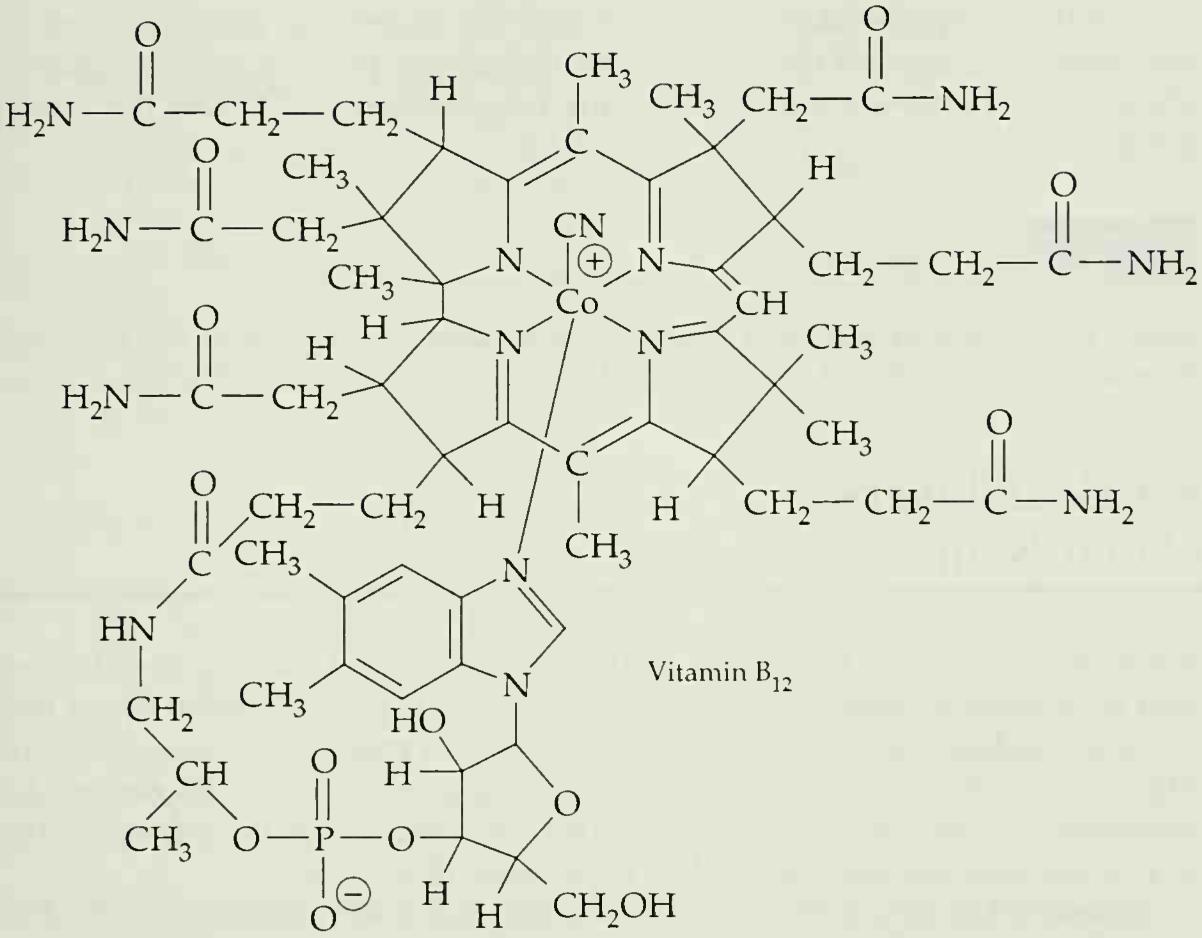
16.6 The Contribution of Casimir Funk

The word *vitamin*, came into our language in 1912, devised by the Polish biochemist (later, American citizen) Casimir Funk. He discovered these organic substances and believed that they were all amines (Section 15.2) that are vital to our health, or vital amines. Hence he gave them the name, *vitamines*, later shortened to our current *vitamins*. While we now know that vitamins are, indeed, vital to our health, we also know that some are amines and others are not.

Table 16.3 presents the best known vitamins and brief dietary descriptions. Figure 16.2 illustrates the range of complexity in their molecular structures, from the relatively simple vitamin C to the extraordinarily intricate B_{12}.

TABLE 16.3 The Vitamins

Chemical Name (and Letter Designation)	Dietary Source	Deficiency Symptoms or Disease
Water-Soluble Vitamins		
Ascorbic acid (Vitamin C)	Fruits, especially citrus; many vegetables	Scurvy; degeneration of tissues
Biotin	Various foods	Rare; nausea, loss of appetite
Cobalamin (Vitamin B_{12})	All foods of animal origin	Pernicious (fatal) anemia
Folic acid Folacin	Meat; green, leafy vegetables	Anemia
Niacin, or its equivalent in tryptophan (Vitamin B_4)	Meat; legumes; grains	Pellagra; skin, digestive, and nervous system disorders; depression
Pantothenic acid (Vitamin B_3)	Widely distributed; occurs in virtually all foods	Defects in metabolism
Pyridoxine Pyridoxal Pyridoxamine (Vitamin B_6)	Various foods; widely distributed	Deficiency is rare; results in defects in amino acid metabolism with various symptoms
Riboflavin (Vitamin B_2)	Meat, especially animal organs; milk and dairy products; green vegetables	Skin disorders
Thiamine (Vitamin B_1)	Pork; animal organs; whole grains; nuts; legumes	Beriberi; muscular weakness; paralysis
Fat-Soluble Vitamins		
Cholecalciferol (Vitamin D_3)	Liver and liver oils; fortified milk	Rickets; malformation of the bones; osteomalacia (adult counterpart of rickets)
Retinol (Vitamin A)	Liver and liver oils; carrots and other deeply colored vegetables	Night blindness; degenerative diseases of the eyes leading to total blindness
α-Tocopherol (Vitamin E)	Various foods, especially grain oils	Deficiency disease unknown in humans
Vitamin K	Plants and vegetables; produced by intestinal bacteria and absorbed through the intestinal wall	Deficiency disease unknown in adults; needed for blood clotting



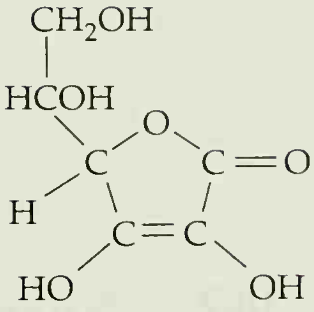


Figure 16.2

Vitamins B_{12} and C represent the range of complexity in the molecular structures of vitamins.

There's more to the story of vitamins, though, than appears in the data in Table 16.3. First, vitamins fall into two broad categories, those that are much more soluble in fats, hydrocarbons, and similar solvents than they are in water, the **fat-soluble vitamins**; and those with the opposite property, the **water-soluble vitamins**.

Vitamins A, D, E, and K constitute the fat-soluble class; the B complex of vitamins and C are water-soluble. (The B complex consists of several vitamins, including

- thiamin, B_1
- riboflavin, B_2
- pantothenic acid, B_3
- niacin, B_4
- pyridoxine, B_6
- cobalamin, B_{12}

All of these occur in minute quantities in a great variety of foods and are often considered as a group, the B complex. There is no single "vitamin B.")

This classification doesn't tell us much about what kinds of food contain any particular vitamin. Some fatty foods can be good sources of the water-soluble vitamins, and the moist, green, leafy vegetables often provide ample supplies of fat-soluble vitamins (Table 16.3). But it does explain some of the properties of the vitamins and their effects on our health.

The **fat-soluble** vitamins are much more soluble in fats, hydrocarbons, and similar solvents than in water. The **water-soluble** vitamins are much more soluble in water than in these other solvents.

A full description of the chemistry and the nutritional importance of all the vitamins is beyond the scope of this discussion. Instead, we'll emphasize three of the better-known vitamins: the fat-soluble A and D and the water-soluble C.

QUESTION

Name the disease or condition produced by a deficiency of each of the following vitamins: (a) B_1, (b) B_2, (c) B_{12}, (d) C, (e) D. ____________________

16.7 Vitamin A, Polar Bear Livers and Orange-Colored Skin

Vitamin A maintains the health of the eyes, skin, and mucous membranes and is particularly important for good vision in dim light. A deficiency of this vitamin produces an inability to see in dim light, a condition known as "night blindness." Other symptoms include dry, rough skin and, with severe deficiencies, a failure of the tear ducts. This, in turn, causes the surface of the eye to become dry and can lead to permanent blindness.

As one of the fat-soluble vitamins, vitamin A is readily stored in the body's fat cells, particularly in the liver. Accumulation of moderate excesses of vitamin A in our bodies does no harm whatever. We simply store it, largely in our livers, for use later, when it's in short supply. Large excesses, though, are another matter. They can overwhelm the body's storage capacity and produce toxic symptoms including headaches, dizziness, nausea, loss of appetite, sore muscles, blurred vision, loss of hair, and worse, including death.

Toxic doses of the vitamin can result from overzealous use of vitamin supplements, especially for small children, and from eating certain rare and bizarre foods that are particularly rich in vitamin A. Polar bear livers, for example, contain unusually large quantities of the substance, with a 3-oz portion providing about 200 times the RDA. There have been reports of extreme toxicity and death among early Arctic explorers who ate large quantities of the bear livers.

While animal livers can store very large concentrations of this vitamin, plants don't contain any. Carrots, which are supposed to be very good sources of the nutrient (and indeed *are*), have none whatever. This strange-sounding contradiction makes more sense when we examine the chemistry of the vitamin.

Here's why. Vitamin A, or *retinol*, has the structure shown in Figure 16.3. In addition to using retinol itself, our bodies can easily convert several chem-

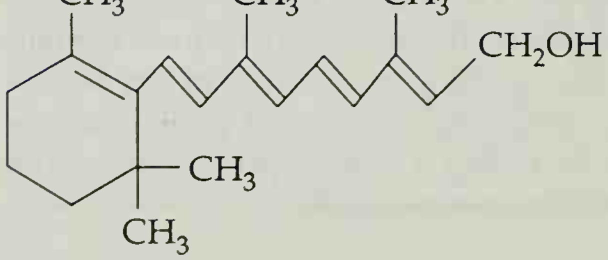


Figure 16.3
Vitamin A, retinol.

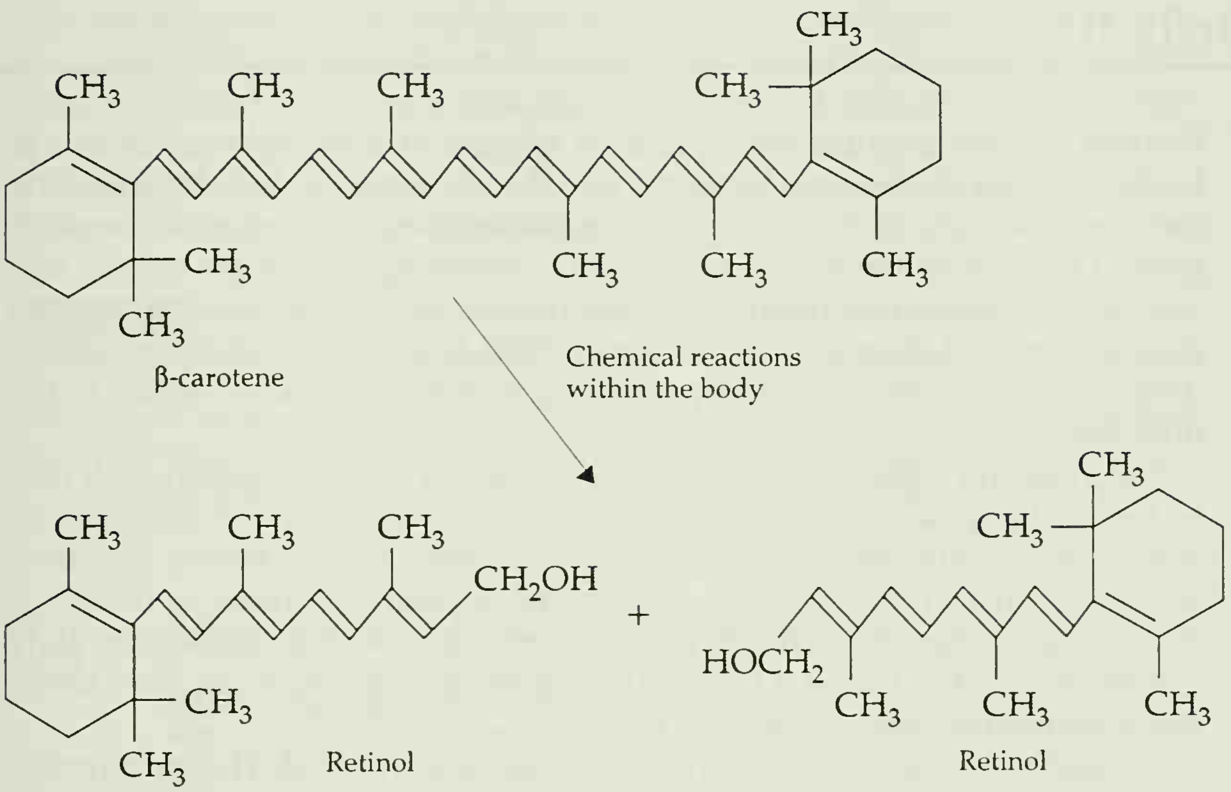


Figure 16.4
Human metabolism converts one molecule of β-carotene into two molecules of vitamin A.

ical structures closely related to retinol's into the vitamin, or use them directly as its equivalent. Several of retinol's esters (Sections 11.11 and 13.1), for example, are every bit as effective as retinol itself and are *physiological equivalents* of the vitamin. It's for this reason that vitamin levels in foods or supplements are sometimes stated as *Retinol Equivalents* of the vitamin, *REs*, or in *International Units, IUs*. REs and IUs represent not merely the quantity of the vitamin itself, but the total amount of the vitamin and all its physiological equivalents that can be converted into or used as the vitamin.

(One RE of vitamin A is equivalent to 1 μg—one *microgram* or 10^{-6} g—of retinol. One IU of vitamin A represents 0.3 μg of retinol. A little arithmetic shows that 3.33 IUs of retinol constitute one RE.)

Although carrots contain no retinol, they do provide large amounts of β-carotene, a deeply colored material that we easily convert to the vitamin itself (Fig. 16.4). With enough of the vitamin stored away in the liver, our bodies stop converting the β-carotene into retinol. As a result we can't very well poison ourselves by overeating carrots and other deeply colored red, orange, and yellow fruits and vegetables, all of which provide plenty of β-carotene in one form or another.

When we consume more β-carotene than we need, some of it reaches the surface tissues, where it's stored and begins imparting its own color to the skin and eyes. There are reports of people who turn yellow-orange from eating enormous quantities of carrots and tomato juice, which is also rich in carotenes, over a long period. It's a harmless and reversible condition that disappears when carrots and tomatoes are removed from the diet.

QUESTION

One average raw carrot provides us with 8000 IUs of vitamin A. Why is the amount of vitamin A given in terms of IUs rather than in a weight of retinol? ____________

16.8 Vitamin D, Or Is It?

Adding vitamin D to milk provides this micronutrient in a food that's naturally rich in calcium. Both are needed for the formation of healthy bones.

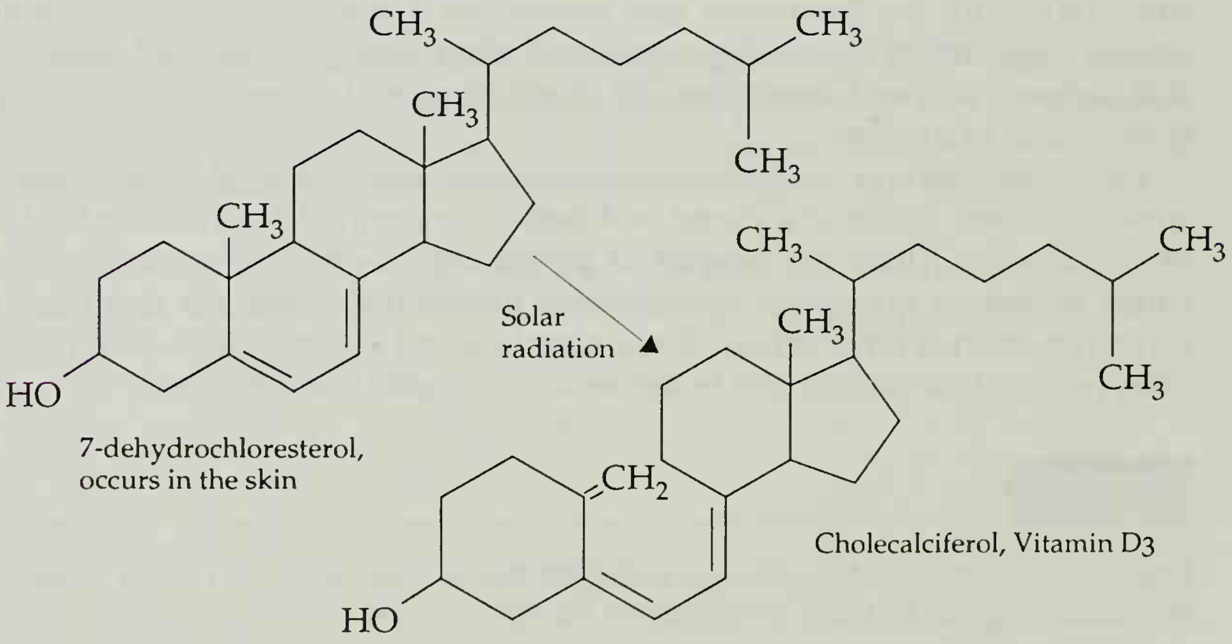
Vitamin D promotes the absorption of calcium and phosphorus from our foods, through the intestinal wall and into the bloodstream, thereby providing the raw materials for forming and maintaining healthy bones. Without vitamin D, children's bones develop poorly, resulting in severely bowed legs and other skeletal deformations of the disease known as *rickets*. Fortifying milk with added vitamin D makes sense. Milk is a major food of young children, it's rich in calcium, and the fat-soluble vitamin dissolves readily in the milk fats.

But vitamin D, like A, has its story. Both rickets and the vitamin itself may be largely the products of the way civilization has developed in the northern and southern latitudes. For some of us the chemical may not be a vitamin after all. Part of the reason for questioning whether it's really a vitamin is that, unlike other vitamins, D forms in our own bodies. Under the right conditions we don't need it in our foods; instead, it forms in our skin, under the action of the sun's ultraviolet rays.

Actually, vitamin D isn't even a single organic compound. The term applies to a set of very closely related molecular structures, differentiated from each other by subscripts. There are vitamins D_1, D_2, D_3, and so on, all with the same physiological function. As ultraviolet radiation strikes our skin, it converts a bodily substance named *7-dehydrocholesterol* into the form of the vitamin known as vitamin D_3 or, by its chemical name, *cholecalciferol* (Fig. 16.5). With plenty of sunshine, lots of exposed skin, and long hours in the outdoors, cholecalciferol would be in plentiful supply in all our bodies, rickets would be virtually unknown, and vitamin D wouldn't be a vitamin at all. But with the limited sunshine, copious clothing, and indoor living and working conditions of the more extreme northern and southern latitudes, the chemical becomes scarce. This could be especially tragic for children, whose bones are still growing. Under these conditions rickets would be common if it weren't for the addition of vitamin D to children's diets, usually in the form of fortified dairy products or, in their absence, cod liver oil or vitamin supplements.

It's probably impossible to produce dangerously high levels of vitamin D in the body through exposure to the sun, since the natural tanning of the

Figure 16.5
The formation of vitamin D.



skin blocks out the rays and stops the chemical conversion. Unfortunately the same can't be said about the excessive use of vitamin supplements. Overzealous use of vitamin D supplements has led to excessive absorption of calcium and phosphorus and the formation of calcium deposits in the soft body tissues, including the major organs such as the heart and the kidneys. Extreme cases have resulted in death.

QUESTION

Eskimos and other peoples living in the far northern latitudes receive little sunshine during the winter, wear a good deal of clothing for protection against the cold, and lack readily available vitamin supplements and fortified milk. Where does their vitamin D come from? ______________________________

16.9 Vitamin C, Bleeding Gums, and the Bulbul Bird

Water-soluble vitamin C, the best known of all the vitamins, is taken as a dietary supplement by more Americans than any other. As *ascorbic acid* (Fig. 16.2), its chemical name represents two properties of the substance, one chemical, the other biological. First, it's an acid, although it clearly doesn't belong to the class of carboxylic acids (Section 10.7). Moreover, the word *ascorbic* reflects its biological value in protecting against the disease *scurvy*. (The words *scurvy* and *ascorbic* come from the Latin word for the symptoms of the disease, *scorbutus*.)

Humans require vitamin C for formation of the connective tissue *collagen*. Tough fibers of this protein hold together the tissues of our skin, muscles, blood vessels, scar tissue, and other bodily structures. Since the gums are rich in blood vessels and are subject to wear and abrasion through eating and by brushing the teeth, the bleeding of gum tissue weakened by deterioration of its collagen becomes the first visible symptom of scurvy. As the disease progresses, the gums weaken and decay, the teeth fall out and the body bruises easily. Scurvy itself isn't fatal, but as it progresses it leads to a decline in the body's resistance to other, lethal diseases.

Until the last few hundred years, scurvy had been the scourge of sailors, explorers, and those on long military expeditions, people who had to survive for months or years on stored provisions. Although some, especially the sailors, were well stocked with meat preserved by salting and smoking, and with carbohydrate-rich grains, many of them lacked the fresh fruits and vegetables that could supply them with vitamin C. Descriptions of diseases affecting the Crusaders suggest that they suffered from scurvy. Vasco da Gama, the Portuguese navigator who, in 1497, was the first European to sail beyond the Cape of Good Hope at the southern tip of Africa, lost more than half his men to diseases probably brought on by the debilitation of scurvy.

Although some Dutch and English seamen of the 1500s knew of the value of fresh fruit and lemon juice in preserving sailors' health on long voyages, it wasn't until 1795 that the British navy officially made lemons part of the required stores of its fleet at sea. It took another 70 years for lemons to become an official part of the diet of the British merchant marine. Because lemons were known as "limes" in those days, British sailors, who were required to eat the "limes," became known as "limeys."

Curiously, humans are one of the few species of animals for which ascorbic acid is actually a vitamin. We're among the few that can't produce the acid within our own bodies but have to obtain it from our foods. The story seems to be connected to the trade-offs of evolution. Neither the newest of the animal species, we humans, nor the oldest, including the invertebrates and fishes, can produce it. The intermediate orders in the chronology of evolution, including amphibians, reptiles, and the more ancient birds, developed the ability to form ascorbic acid themselves. Then, as the thread of evolution lengthened, still higher orders lost the ability, perhaps in making way for more advantageous biochemical processes. The other primates, along with humans, also need to obtain ascorbic acid from food, as do the Indian fruit bat, the guinea pig, and a favorite songbird of the Orient, the bulbul bird.

QUESTION

In cooking fresh vegetables in water, it's advisable to cook them for a short period in the minimum amount of water required. Why does this make good nutritional and good chemical sense? ______________________________

16.10 Vitamin C: Myths, Realities, and Iodine

Although remarkable curative powers have been ascribed to various vitamins, some of them bordering on the bizarre, few have actually been demonstrated. The major medical use of the vitamins lies largely in curing the deficiency diseases, those caused by their absences from the diet. Vitamin A certainly alleviates the night blindness caused by a deficiency of vitamin A; vitamin D unquestionably prevents rickets; vitamin C dramatically cures scurvy.

But the other medical claims that have been made for the vitamins are spurious or unproven. Allegations that vitamin C cures the common cold or is effective in treating cancer have never been demonstrated clearly and unambiguously. Fortunately for anyone who takes massive doses of ascorbic acid as a dietary supplement, the vitamin is relatively nontoxic and is highly soluble in water, with 1 g dissolving in just 3 mL of water. Moreover, it isn't very soluble in fat and so it isn't stored in the body. When taken in amounts far in excess of daily requirement, ascorbic acid leaves through the urine almost as soon as it enters through the mouth. The consequences of taking large supplements of the vitamin over a long period aren't known with any certainty.

Another common belief, that cooking foods for a long time destroys vitamin C, is certainly true. You demonstrated the ease with which vitamin C reduces iodine in the opening demonstration. By looking at the same reaction from another chemical perspective, we can say that iodine easily oxidizes the vitamin. So does the oxygen of air. As you can demonstrate by using water of different temperatures, the oxidation of vitamin C takes place more rapidly at high temperatures than at low temperatures. Cooking food for extended periods can lower its content of the vitamin. Simply dissolving a powder gelatin dessert mix in boiling water before chilling it, for example, results in oxidation of a quarter to a third of its vitamin C. Even refrigerating it for long periods leads to a decrease through oxidation. As another illustration of the fragility of vitamin C, orange juice refrigerated in paper cartons reportedly loses half its vitamin C in three weeks.

But, as we've seen before, things are not as simple as they seem. In some ways these data aren't as serious as they may appear. The chemical products that vitamin C forms when it's oxidized can still retain some of the vitamin's biological activity. That chilled gelatin dessert continues to lose about 12% of its vitamin C each day, but only about 3% of its biological activity. On the other hand, low temperatures aren't a guarantee of safety. The vitamin seems to undergo oxidation faster in ice than in water. Even frozen orange concentrate reportedly loses a tenth of its vitamin C after a year.

The exceptional ease with which vitamin C is oxidized makes it a fine **antioxidant**. It's a compound that can protect other compounds from oxidation by sacrificing itself instead. We saw something of this sort in Sec. 6.18, with the use of galvanizing to protect iron. We'll see other examples of antioxidants in Chapter 17.

An **antioxidant** is a chemical so easily oxidized itself that it protects others from oxidation.

QUESTION

As we saw in the question at the end of Section 16.9, when cooking fresh vegetables in water, it's advisable to cook them for a short period in the minimum amount of water required. Give another reason, in addition to the reason you gave for that question, why this make good nutritional and good chemical sense. ____________

16.11 How Much Is Enough? The RDAs, Part II: Vitamins

As with the minerals, we can find recommended dietary allowances for the vitamins in the tables published by the National Academy of Sciences. A summary of their RDAs appears in Table 16.4. Note the range represented. At the high end we find the recommendation of an average daily intake of 60 mg (0.060 g) of vitamin C for most adult men and women (except those who smoke, and pregnant and lactating women, both of whom who need more). Compare that with the minuscule 2 μg (0.000002 g) of vitamin B_{12}, which we need to avoid a fatal form of anemia. For perspective, a teaspoon of table sugar weighs just about 5 g. Assuming that the vitamins have the same density as sugar, a teaspoon of vitamin C would supply a normal adult with enough ascorbic acid for almost 12 weeks, and a teaspoon of vitamin B_{12} would last for nearly 7000 years. Of course the water-soluble vitamins are not stored in the body; taking an entire teaspoonful of vitamin C in one swallow would supply the body's needs for perhaps only a day, with the excess lost in the urine.

More to the point, it takes only a daily half cup (4 oz) of orange juice, either fresh or frozen, to provide all the vitamin C most of us need. And since vitamin B_{12} occurs in every food of animal origin, including dairy products and eggs, only those vegetarians who eat plant foods exclusively, and rigorously exclude all animal products from their diets, need be concerned about a deficiency.

TABLE 16.4 Selected Recommended Daily Allowances (RDAs) for Vitamins[a]

		Weight		Height		Fat-Soluble Vitamins			Water-Soluble Vitamins						
Gender	Age	kg	lbs	cm	ft'in"	A (RE[b])	D (µg[c])	E (mg α-TE[d])	Folacin (µg[c])	Niacin (mg NE[e])	Riboflavin (mg)	Thiamine (mg)	B_6 (mg)	B_{12} (µg[c])	C (mg)
Both	0–0.5	6	13	60	2'	375	7.5	3	25	5	0.4	0.3	0.3	0.3	30
	0.5–1	9	20	71	2'4"	375	10	4	35	6	0.5	0.4	0.6	0.5	35
	1–3	13	29	90	2'11"	400	10	6	50	9	0.8	0.7	1.0	0.7	40
Men	15–18	66	145	176	5'9"	1000	10	10	200	20	1.8	1.5	2.0	2.0	60[f]
	19–24	72	160	177	5'10"	1000	10	10	200	19	1.7	1.5	2.0	2.0	60
	25–50	79	174	176	5'10"	1000	5	10	200	19	1.7	1.5	2.0	2.0	60
	51+	77	170	173	5'8"	1000	5	10	200	15	1.4	1.2	2.0	2.0	60
Women	15–18	55	120	163	5'4"	800	10	8	180	15	1.3	1.1	1.5	2.0	60
	19–24	58	128	164	5'5"	800	7.5	8	180	15	1.3	1.1	1.6	2.0	60
	25–50	63	138	163	5'4"	800	5	8	180	15	1.3	1.1	1.6	2.0	60
	51+	65	143	160	5'3"	800	5	8	180	13	1.2	1.0	1.6	2.0	60
—Pregnant						800	10	10	400	17	1.6	1.5	2.2	2.2	70
—Lactating															
(First 6 months)						1300	10	12	280	20	1.8	1.6	2.1	2.6	95
(Second 6 months)						1200	10	11	260	20	1.7	1.6	2.1	2.6	90

[a] Published in 1989.

[b] RE represents the number of retinol equivalents.

[c] 1 µg (one microgram) = 10^{-6} g = 10^{-3} mg (see Section 14.7).

[d] α-TE represents the number of α-tocopherol equivalents.

[e] NE represents the number of niacin equivalents.

[f] These represent recommended RDAs for nonsmokers. The RDAs of vitamin C for smokers are 67% greater than those for nonsmokers.

Although RDAs are tailored to our needs by gender, weight, height, and other factors, this precision can be their undoing. Food processors can't be expected to show each of us just how much of our RDA a serving of this cereal or that fruit juice provides. For a simpler approach to the question of micronutrient levels in our processed foods, the U.S. Department of Agriculture has adapted the RDAs into a set of numbers called the *U.S. Recommended Daily Allowances*, or *U.S. RDAs*. The U.S. RDA for any nutrient represents the *highest RDA* established for that nutrient by the National Academy of Sciences, sufficient for any healthy adult, male or female, regardless of age. As a result, consuming 100% of the U.S. RDA of each listed nutrient should provide enough of it to supply the maximum need for almost all of us, regardless of which category we're in. The U.S. RDA, then, represents enough of the nutrient for nearly all of us, and far more than enough for most of us.

U.S. RDAs appear on most processed food packages as percentages of the daily dietary requirement. For a one ounce serving of a typical package of cornflakes, excluding the nutrients that come along with the added milk, you'd get the percentages of the U.S. RDAs shown in Table 16.5. We're using the percentages of U.S. RDAs for a one ounce serving here because the manufacturer of the cornflakes estimates that's what you would take as an average serving. Be careful, though. Read all of the nutrition information on the label. Make certain that the stated U.S. RDA corresponds to the serving size and that both are reasonable. Some processors and manufacturers have been known to increase the number of servings in a box of processed food occa-

TABLE 16.5 U.S. RDAs in a 1-oz Serving of Cornflakes[a]

Mineral/Vitamin	Percentage of U.S. RDA
Folic acid	50
Niacin	50
Vitamin B_6 (pyridoxine)	50
Riboflavin	50
Thiamine	50
Vitamin A	25
Vitamin C	25
Vitamin D	10
Iron	10

[a] Adding milk introduces calcium and increases the percentage of the U.S. RDA for several nutrients.

sionally and raise the price along with them. It looks as if you're coming out even, maybe ahead, but that isn't the case at all. The processor simply keeps the net weight the same but decreases the estimate of the weight of the serving size. You get the same net weight, more servings, less per serving, and a greater cost overall.

QUESTION

Normally, we might expect that an adult, with a large body weight, would require considerably more of a vitamin each day than a child, whose body is much smaller. Yet according to the RDAs a 30 year old adult of normal weight (about 79 kg for a man, 63kg for a woman) needs only half the vitamin D as a year old infant who weighs just 9 kg. Why is this so? ______________________________

PERSPECTIVE: Natural Vs. Synthetic

In concluding, let's move from the question of quantity to the matter of quality. Given that we can get a satisfactory level of all the nutrients through our normal diets, does it matter where they come from? Is the calcium in a vitamin and mineral supplement the same kind of calcium that's in milk? Is the vitamin C that comes out of a chemist's laboratory as good as the vitamin C in a real, live orange? The answers to these questions depend on a bit of chemistry.

To the question "Are there different kinds of calcium?" the answer is *no* (except for insignificant differences among its isotopes). As we saw in Chapter 2, all atoms that contain exactly 20 protons in their nuclei are atoms of calcium. That holds true no matter what their source. A calcium atom, in short, is a calcium atom no matter where it comes from.

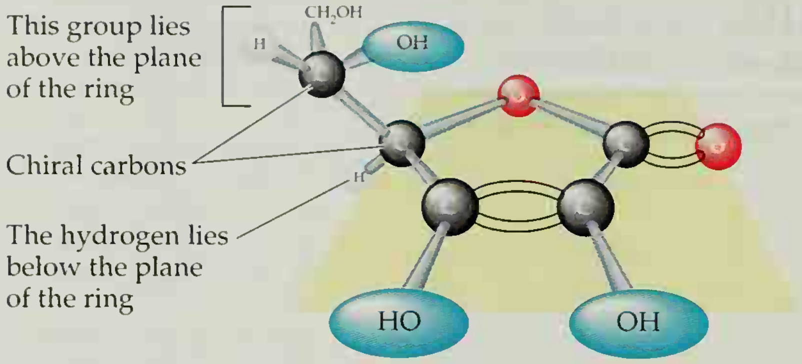


Figure 16.6 The stereochemistry of vitamin C. All molecules of vitamin C have this structure and stereochemistry, regardless of their source.

Pure ascorbic acid is all the same, regardless of its source. Whether it was extracted from food or prepared in a laboratory, the vitamin C of vitamin tablets is identical to the "natural" vitamin C of food.

But what comes along with it *could* matter. Recall that we need vitamin D to absorb calcium into our bloodstream, and phosphorus to add the calcium to our bones and teeth. So while all calcium atoms are identical in their chemical behavior, the calcium of food is much more likely to carry along with it any vitamin D that we might need, and phosphorus, than is the calcium of, say, an antacid tablet, or a piece of chalk, or a poorly formulated supplement.

Like all atoms of one isotope of any particular element, all molecules of any particular compound are mutually identical. For example, it takes exactly 20 protons, 20 electrons, and 20 neutrons, arranged so that all the protons and neutrons form the nucleus and all the electrons are organized into shells surrounding the nucleus, to make up the most common isotope of a calcium atom. Similarly, it takes exactly six carbon atoms, six oxygen atoms and eight hydrogen atoms to make up a molecule of vitamin C. Moreover, the atoms must all be organized into a precise arrangement, even to the exact arrangement of the atoms bonded to the chiral carbons (Section 14.5; Fig. 16.6).

With this specific molecular structure, including the chirality, we have vitamin C; without it we don't. Any molecule that *does* have the structure and chirality shown in Figure 16.6 *is* vitamin C; any other molecule *isn't*. It doesn't matter whether the molecule is formed inside an orange as it grows and ripens or whether it's formed in the apparatus of a chemical laboratory. It all depends on the molecular structure and *only* on the molecular structure. Any molecule that has this particular arrangement of atoms and chirality is indistinguishable from any other of exactly the same structure and chirality, regardless of its origin, and has all the chemical, physical, and biological properties of vitamin C (Fig. 16.7). *Pure* ascorbic acid obtained from living things is absolutely identical in every way, but one, with *pure* ascorbic acid (of the same chirality) synthesized in the laboratory. The *single* difference between the two is the (usually) higher cost of the "natural" vitamin.

(An exception to this mutual identity comes with the deliberate incorporation of isotopic atoms into a synthetic vitamin, which can produce exceedingly small differences between a synthetic vitamin and one obtained from plants or animals. Synthetic vitamins containing isotopic atoms are used for research, for detecting contamination or adulteration of foods and drugs, and in similar technical studies, rather than in human nutrition.)

Along with all this it's important to remember that while synthetic vitamins are absolutely identical to those occurring naturally in our foods, this doesn't mean that a vitamin and mineral pill is the nutritional equivalent of, let's say, an orange or a glass of milk. A balanced and varied diet provides a diversity of nutrients (including some, perhaps, not yet discovered) that no pills can match. Moreover, as with calcium, phosphorus, and vitamin D of milk, dis-

A molecule of vitamin C isolated from an orange, lemon, or lime

A molecule of vitamin C from a kilogram batch synthesized in large vats by a major pharmaceutical firm

A molecule of vitamin C of unknown origin, found in an ancient bottle, in an old attic

A molecule of a substance that may or may not have useful properties, but that is definitely *not* vitamin C

Figure 16.7
Vitamin C and molecular structure.

cussed earlier in this section, authentic foods often contain additional substances that enhance the absorption and utilization of their nutrients. The vitamin D present in milk aids in the absorption of the calcium.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

The _______ and minerals of our diet constitute our _______ . Except for carbon, hydrogen, nitrogen, and oxygen (and, by some definitions, sulfur), the elements of our foodstuffs make up the class of _______ . Of these, _______ is the major mineral of our body, located largely in our _______ . Sodium and _______ are the major cations of our bodily fluids, with _______ ions as the major anion. Among our vitamins (conveniently divided into the two categories of the _______ A, D, E, and K and the _______ B and C) are vitamin C, which is known chemically as _______ and which protects against _______ ; vitamin D, which protects against _______ ; and vitamin A, which protects against a vision defect known as _______ . Much of our vitamin A comes from the _______ of our yellow, orange, and green vegetables.

ascorbic acid
bones and teeth
calcium
β-carotenes
chloride
fat-soluble
minerals
micronutrients
night blindness
potassium
rickets
scurvy
vitamins
water-soluble

2. Explain, define or describe the significance of each of the following:

a. cholecalciferol
b. collagen
c. goiter
d. RDA
e. U.S. RDA
f. retinol
g. retinol equivalent
h. trace elements

3. What is the difference between a macronutrient and a micronutrient? Name two of each.

4. Describe the major function of (a) phosphorus in the bones, (b) sodium in the extracellular fluid, (c) fluoride in the teeth, (d) chloride in the gastric juices, and (e) cobalt in the body.

5. Name two trace elements in addition to those of Problem 4 and describe their functions.

6. Match the vitamin with the disease or condition associated with its deficiency.

_____ Folic acid	a. Rickets
_____ Niacin	b. Scurvy
_____ Thiamine	c. Anemia
_____ Vitamin A	d. Poor blood clotting
_____ Vitamin C	e. Night blindness
_____ Vitamin D	f. Pellagra
_____ Vitamin K	g. Beriberi

7. Name a vitamin that plays an important role in (a) protein synthesis, (b) the absorption of calcium.

8. Name two good sources of (a) vitamin A, (b) vitamin C, (c) vitamin D.

9. What is meant by the IU and the RE of vitamin A and what is the advantage of describing the RDAs of vitamin A in terms of its IUs and REs?

10. Why are bleeding gums one of the first symptoms of scurvy?

11. What nutritional characteristic do humans, guinea pigs, Indian fruit bats, and bulbul birds have in common?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

12. As shown in Table 16.5, 1 ounce of cornflakes provides 25% of the U.S. RDA of vitamin C. What weight of vitamin C does this represent? What is the weight-percent of vitamin C in cornflakes?

13. Using the information provided in Section 16.7, and assuming that an average carrot weighs 3 oz determine the weight-percent of retinol equivalent in an average carrot.

14. How many people aged 15 to 18 could receive a day's RDA from a single teaspoon of vitamin D? Assume that a teaspoon of the vitamin weighs 5 g.

THINK, SPECULATE, REFLECT AND PONDER

15. Explain the significance of this chapter's subtitle, "The Vital Accessories."

16. What is the difference between the RDA and the U.S. RDA for a micronutrient?

17. In what way is the RDA more useful than the U.S. RDA for a micronutrient? In what way is the U.S. RDA more useful than the RDA?

18. Could someone who is receiving the RDA for a micronutrient nonetheless be deficient in that nutrient? Explain.

19. Why is it advisable to cook fresh vegetables in the smallest volume of water that is practical?

20. Why is the vitamin A content of food better described in terms of International Units and Retinol Equivalents than in terms of actual weight?

21. Would you expect the vitamin C contained in an orange grown in soil of poor quality to be inferior to the vitamin C contained in an orange grown in high-quality soil? Explain.

22. In what chemical or physical way does the vitamin C produced by chemical reactions carried out in laboratory equipment differ from the vitamin C obtained from fruits and vegetables?

23. Vitamin B_3 is also known as "pantothenic acid," which comes from the Greek word *pantothen,* meaning "from all sides" or "from every side." Suggest a reason why "pantothenic" is an appropriate name for this acid.

24. To provide fresh meat on long voyages, sailors of past centuries took with them live cattle, which they slaughtered as they needed meat. With no supplies of fresh fruit and vegetables, the sailors often succumbed to scurvy. Why didn't the live cattle also develop scurvy?

25. Is the decolorization of tincture of iodine a reliable test for the presence of vitamin C in a food? Explain your reasoning.

17.1 The Mystery of Food

We have seen that we are indeed what we eat. We have seen that the macronutrients of food provide the materials of our bodies and the fuel to use them, while the micronutrients furnish necessary assistance in making use of the macronutrients. In short, we have looked at food as an extraordinarily complex mixture of chemicals whose atoms and molecules become the tissue and bones and fabric of our bodies, and whose chemical energy becomes our own energy.

Yet many of us view food as more than a blend of chemicals, however complex the combination may be. To many of us, foods exhibit spiritual or psychological components, especially evident in feasts and fasts, at traditional gatherings of families and friends, and even in ordinary social, business, and professional breakfasts and lunches. These components of food lie beyond the boundaries of the physical world. To the extent that we view food as more than a mixture of chemicals, we also believe that it harbors characteristics not easily defined and not readily explored by the scientific method. Eating certain foods at times makes some of us simply feel "better"; other foods don't seem to settle as well, leaving us feeling a bit "worse" for having eaten them. A good meal, whether it consists of a few raw vegetables (for some of us) or a rich feast of many courses (for others), can leave us with a sense of well-being that is not easily explained or described.

Recognizing this, some of us have come to believe that particular foods, because of the chemicals that make them up or for reasons that extend beyond their material substance, are inherently and mysteriously capable of bringing us health. Certain other foods, some believe, work against good health, not because of any known poison they may contain, but for more subtle and often obscure reasons. Some of us have come to believe in the powers of what we call *health foods* and *junk foods*.

Are there such foods? Let's see what sort of clarity the science of chemistry can bring to the topic. We'll begin by examining what we might mean when

A "health food" store, where we can find "organic foods," "natural foods," and foods "without chemicals."

we call one food a "health food" and another a "junk food." We'll look at what some of our processed and manufactured foods contain, as revealed by their ingredients labels, and how our conceptions of health food and junk food stand up against this information. Finally, we'll move beyond the macronutrients and micronutrients that are essential to our health and well-being, to the components of processed foods known as *food additives*. We'll learn what constitutes a food additive, what some of them are, and why they are used, and we'll ask whether they are desirable ingredients of our foods or whether they lower the quality of our food supply.

QUESTION

Are there occasions when (a) a meal you eat with friends is more satisfying than it would be if you were alone? (b) A meal you eat alone is more satisfying than it would be if you were with others? Explain. ______________________

17.2 Health Foods and Junk Foods

Our fundamental difficulty in discussing "health foods" and "junk foods" lies in the lack of a good general agreement on what these terms mean. One way of sorting one from the other is by balancing the number of calories in any particular food against its content of minerals and vitamins. Since we need energy, in moderate amounts, to maintain life and health and since *all* foods provide it, we can differentiate among our foods by focusing on the relative proportions of their calories and their micronutrients. (Since the micronutrients don't supply us directly with energy, we are dealing with two distinct categories here, with no overlap.) Using this approach and applying what we now know of the chemistry of food, we can describe at least one of the two classes of foods in chemical terms. A **junk food**, by one popular definition that also makes good chemical sense, is a food that supplies a large number of calories but few micronutrients.

By one definition, a **junk food** is a food that supplies a large number of calories but few micronutrients.

Sometimes the term *empty calories* enters into these discussions, often with reference to a food, such as highly refined sugar, that provides calories but few or no micronutrients to accompany them. Highly refined sugar is, as we know, purified sucrose, a carbohydrate. As such it's one of the three classes of macronutrients and furnishes us with energy at the rate of 4.0 Cal/g. We saw in Chapters 12 and 14 that sucrose and other carbohydrates provide the energy we need for our basal metabolism, physical activities, and specific dynamic action. Consumed in excessive amounts, sugar, or any of other macronutrients for that matter, also provides the energy we store as fat.

By one definition a **health food** is a food that supplies a large number of micronutrients compared with its calories. This definition does not take into consideration the food's content of saturated fats, cholesterol, or other factors that can affect our health.

Turning now to "**health foods**," we find that the label is used so loosely and with so little general agreement that it's nearly impossible to describe what we mean by it. Nonetheless, using the idea that the relative proportions of calories and micronutrients are important to good health we can conclude that, in general, the larger the ratio of micronutrients that a food provides and the fewer its calories, the more healthful it is. While this doesn't define or describe a "health food," and doesn't take into consideration cholesterol, saturated fats, fiber, and other factors that affect our state of health, it does give us a basis for examining various foods and assessing their nutritional value.

QUESTION

According to the U.S. Department of Agriculture, 1 oz of plain milk chocolate and 1 oz of pasteurized American cheese provide the following Calories and percentages of U.S. RDAs:

Nutrient	Milk Chocolate, 150 Cal (% U.S. RDA)	American Cheese, 110 Cal (% U.S. RDA)
Protein	4	15
Vitamin A	2	6
Vitamin C	<1	<1
Thiamine	2	<1
Riblflavin	6	8
Niacin	<1	<1
Calcium	6	20
Iron	2	2

a. Which of these two, plain milk chocolate or pasteurized American cheese, seems to provide the larger ratio of nutrients to calories?
b. Using the discussion in this section, which would you characterize as the more healthful food, plain milk chocolate or pasteurized American cheese? Explain your answer.

17.3 You Can't Tell a Book by Its Cover, but the Side of a Cereal Box Reveals a Lot about Its Contents

Try this the next time you're in a store where boxed cereals are sold. Find one in a box that shows a character who could have stepped out of a Saturday morning TV cartoon show. The box and its contents should obviously be aimed directly at the tastes of children and have all the emotional earmarks of a junk food (Fig. 17.2). Read the nutrition information provided on the side panel. Note the number of Calories provided by one ounce of the cereal and the U.S. RDA percentages of its minerals and vitamins.

Next pick out a box showing a rustic farmer, fields of grain, mounds of cereal spilling out of coarsely woven sacks, sunshine, and an unspoiled rural landscape, or similar, attractive scenery. Pick a box, in short, whose front suggests that the contents are clearly wholesome, straight from nature, and produced to be eaten by health-conscious adults (Fig 17.3). As before, read the nutrition information on the side panel.

In comparing the two you'll probably find a contrast similar to that in Figure 17.4, which compares the nutrition information actually appearing on a box of breakfast cereal very similar to what we've been calling the "children's

INGREDIENTS: ROLLED OATS, BROWN SUGAR, COCONUT OIL, RAISINS, HONEY, SESAME SEEDS, CINNAMON, SALT AND SOY LECITHIN (A NATURAL VEGETABLE INGREDIENT USED AS AN AID IN BLENDING).

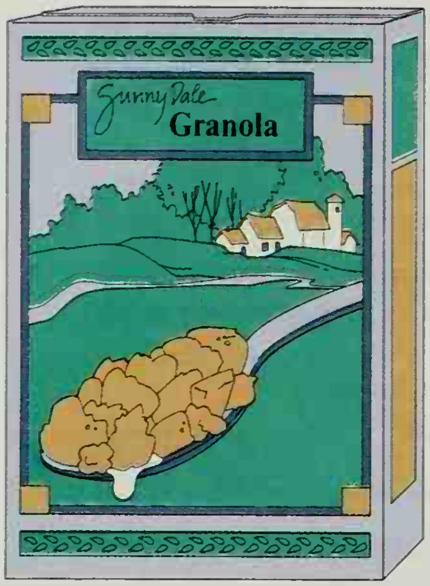


Figure 17.2
The cartoon-character cereal. Junk food or health food?

INGREDIENTS: SUGAR, OAT FLOUR, DEGERMED YELLOW CORNMEAL, CORN SYRUP, COCOA, CORN STARCH, WHEAT STARCH, DEXTROSE, SALT, GELATIN, CALCIUM CARBONATE, TRISODIUM PHOSPHATE, SODIUM ASCORBATE, ARTIFICIAL FLAVORS, NIACIN, IRON, VITAMIN A PALMITATE, PYRIDOXINE HYDROCHLORIDE, RIBOFLAVIN, THIAMINE MONONITRATE, VITAMIN B_{12}, AND VITAMIN D.

Figure 17.3
Granola. Health food or junk food?

breakfast,'' with similar information on a box of granola. Superficially, based on the images on the boxes, we might be inclined to call the cartoon-character cereal a ''junk food'' and the granola a ''health food,'' and perhaps by some rather vague definitions they are. But if we use the criterion of the relative amounts of calories and micronutrients, then we'll surely rank the cartoon-character cereal, with its lower calorie content and larger U.S. RDAs of micronutrients, as the more healthful food. The granola, with more calories and fewer micronutrients, must stand with the junk foods.

All of this, of course, says nothing about such factual and health-related details as sodium, fiber, and other nutritional factors we've already discussed, nor does it take into account our more subjective, personal preferences, the impact of advertising, or the actual tastes of the foods. It does suggest, though, that our judgments concerning ''health foods'' and ''junk foods'' are more soundly based when we rely on factual nutritional information than when we try to classify our foods through the images and mystiques associated with them.

Figure 17.4
A ''health food'' and a ''junk food.'' Which is which?

Nutritional information
per serving
Percentage of U.S. RDA's

PROTEIN	4
VITAMIN A	*
VITAMIN C	*
THIAMINE	6
RIBOFLAVIN	*
NIACIN	*
CALCIUM	*
IRON	6
PHOSPHORUS	8
MAGNESIUM	6
ZINC	4
COPPER	4

*Contains less than 2% of the U.S. RDA of these nutrients

Calories: 130 per ounce

Nutritional information
per serving
Percentage of U.S. RDA's

PROTEIN	2
VITAMIN A	25
VITAMIN C	25
THIAMINE	25
RIBOFLAVIN	25
NIACIN	25
CALCIUM	2
IRON	25
VITAMIN D	10
VITAMIN B_6	25
VITAMIN B_{12}	25
PHOSPHORUS	6
MAGNESIUM	6
ZINC	2
COPPER	4

Calories: 110 per ounce

that nature adds and the phosphates introduced by the processor. The only difference between them is that the law requires that they be listed explicitly on one label, but not on the other.

QUESTION

The list of ingredients in the cartoon-character cereal (which appears in Figure 17.2) also includes riboflavin and thiamine mononitrate. By what more common names are these chemical additives known? ________________________________

17.6 How the Search for Food Additives Led to Marco Polo's Adventures in the Orient and to Columbus's Discovery of America

Food additives of one sort or another have been with us for a long time. They've been in use since prehistoric cooks began salting and smoking meat. Our ancestors' deliberate addition of sodium chloride and of the chemicals of smoke were among the earliest methods used to preserve meat against decay. Food dyes to improve the appearance of food were introduced by the Egyptians as early as 3500 years ago. Adding herbs, spices, and sweeteners is also an ancient practice.

Another ancient practice, especially among the manufacturers and vendors of food, was the use of additives to make bad food more palatable. Covering the foul tastes and odors of spoiled food was the principal function of spices in the Middle Ages. Indirectly, the lack of good methods for preserving food in those times led to the opening of trade routes to the Orient and to the discovery of the Western Hemisphere. It was at least partly the search for foreign spices that led Marco Polo eastward to the Orient and Columbus westward to the New World.

As the centuries passed and as people throughout the world moved from the countryside to the cities in more modern times, the distance from the farm and the dairy herd to the dinner table lengthened and so did the time it took to transport food from where it was grown to where it was to be eaten. Because of a lack of effective methods for preserving foods—efficient and economical mechanical refrigeration is a product of the 20th century—food spoilage became widespread and so did the use of chemicals to preserve food and to mask the taste and odors of decay, just as in the Middle Ages.

With the development of chemical technology and food processing late in the 19th century, the use of chemical additives grew enormously. By 1886 the U.S. Patent Office had issued its first patent for a food additive, a combination of sodium chloride and calcium phosphate designed for use as a food seasoning. As the use of additives grew, the variety of the chemicals used as additives also increased and so did their hazards.

QUESTION

Describe briefly the result of the first recorded attempt to use refrigeration to preserve meat. (See Section 12.2.) ________________________________

17.7 Dr. Wiley's Poison Squad

In 1902, Dr. Harvey W. Wiley of the United States Department of Agriculture organized a Poison Squad of volunteers to begin the first tests of the effects of food additives on humans.

We now have effective governmental regulations to ensure the safety of the chemicals added to our foods. That wasn't always the case. In the United States of the late 1800s, the uninformed and indiscriminate use of chemicals as food additives led to frequent and sometimes fatal outbreaks of illness and, eventually, to detailed regulation by the federal government. The first step, taken in 1902, was the formation of a group within the U.S. Department of Agriculture to examine the usefulness and the dangers of food additives. Headed by Dr. Harvey W. Wiley, an American chemist who was at the time the chief of the Department's Bureau of Chemistry, the group became known as Dr. Wiley's Poison Squad. His group of a dozen healthy young volunteers taken from the Department actually ate the additives under investigation, along with their regular, carefully supervised meals, while Dr. Wiley watched for signs of illness.

His investigations and his vigorous public support of effective control of food additives, coupled with public indignation at the filth of slaughterhouses and meat products depicted in Upton Sinclair's novel *The Jungle*, stimulated Congress to pass both the Meat Inspection Act of 1906 and the Pure Food and Drug Act of 1906. Since 1906 the enforcement of the Pure Food and Drug Act and its subsequent revisions has been the responsibility of organizations bearing a variety of names and titles. In 1931 Congress created the Food and Drug Administration (FDA) to ensure the safety of the chemicals added to the food and drugs sold to the public. The FDA is now part of the U.S. Department of Health and Human Services.

QUESTION

In what department of the federal government did the first testing of food additives take place? ______________________________

17.8 The Law of Additives

Several amendments and other changes since 1906 have extended and strengthened the Pure Food and Drug Act. Currently, the law also covers cosmetics and is known as the Federal Food, Drug, and Cosmetic Act.

In effect, this law protects the public from unsafe food additives by declaring that *all* substances that might be added to food, in any way, are legally unsafe unless they are specifically exempted from the Act, or unless the Act itself describes ways in which they can be used safely. As we might expect, the effective operation of the law requires a definition of a food additive (and of the various exemptions) more attuned to the ears of lawyers, administrative officials, and judges than to the ears of the general public or scientists. The Act's definition of a food additive has thus been embellished into the legal jargon of the *single sentence* of Figure 17.5.

To paraphrase this elaborate, legal definition, a food additive, which, as we've noted, is legally unsafe unless declared otherwise, is any substance added to food, directly or indirectly, except for

The term "food additive" means any substance the intended use of which results or may reasonably be expected to result, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of any food (including any substance intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food; and including any source of radiation intended for any such use), if such substance is not generally recognized, among experts qualified by scientific training and experience to evaluate its safety, as having been adequately shown through scientific procedures (or, in the case of a substance used in food prior to January 1, 1958, through either scientific procedures or experience based on common use in food) to be safe under the conditions of its intended use; except that such term does not include—

1. a pesticide chemical in or on a raw agricultural commodity; or
2. a pesticide chemical to the extent that it is intended for use or is used in the production, storage, or transportation of any raw agricultural commodity; or
3. a color additive; or
4. any substance used in accordance with a sanction or approval granted prior to the enactment of this paragraph pursuant to this Act, the Poultry Products Inspection Act (21 U.S.C. 451 and the following) or the Meat Inspection Act of March 4, 1907 (34 Stat. 1260), as amended and extended (21 U.S.C. 71 and the following); or
5. any new animal drug.

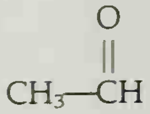
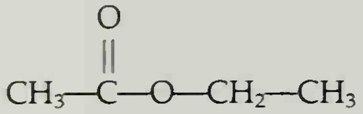
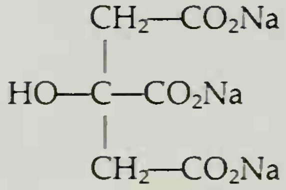
Figure 17.5
The legal definition of a food additive as it appears in the current version of the federal Food, Drug, and Cosmetic Act.

- those shown by scientific studies to be safe, at least under the conditions of their use in foods,
- those used as additives before January 1, 1958 (the date of passage of this part of the Act), and shown to be safe either by scientific studies or by our common experience,
- pesticides,
- color additives,
- substances approved by earlier acts of Congress, and
- new animal drugs.

To work backward, up this list of exemptions, the bottom four are defined and regulated either in other laws or in some other section of this Act and so they aren't actually considered to be food additives by this particular section of the law.

The second category results from a combination of expediency and common sense. By January 1, 1958, the date this particular section of the Act went into effect, so many substances had been used as food components regularly and for so long that testing all of them would have been entirely impractical. Instead, panels of scientists were set up to evaluate the safety of these materials that had been in common and long-term use. Those that were generally recognized by the panelists to be safe, on the basis of common experience

TABLE 17.1 Examples of GRAS Substances

Substance	Structure or Chemical Formula	Use or Classification
Acetaldehyde	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}H$	Spices, seasonings, and flavorings
Anise		
Cinnamon		
Ethyl acetate	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3$	
Aluminum calcium silicate	$CaAl_2(SiO_4)_2$ and $Ca_2Al_2SiO_7$	Anticaking agents
Sodium metabisulfite	$Na_2S_2O_5$	
Sorbic acid	$CH_3-CH=CH-CH=CH-CO_2H$	
Ascorbic acid	$C_6H_8O_6$	Dietary supplements and nutrients
Calcium phosphate	$Ca_3(PO_4)_2$	
Ferrous sulfate	$FeSO_4$	
Linoleic acid	$CH_3-(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-CO_2H$	
Zinc oxide	ZnO	
Dipotassium hydrogen phosphate	K_2HPO_4	Sequestrants (Section 17.13)
Sodium citrate	 $\begin{array}{l} \quad\;\; CH_2-CO_2Na \\ \quad\;\;\; \| \\ HO-C-CO_2Na \\ \quad\;\;\; \| \\ \quad\;\; CH_2-CO_2Na \end{array}$	

(but without laboratory testing), were compiled into a list of substances *G*enerally *R*ecognized *A*s *S*afe, the **GRAS list**.

In effect, this GRAS list constitutes the second category of exemptions. (Legally, GRAS substances aren't food additives either.) Both the calcium carbonate and the trisodium phosphate of the cartoon-character cereal are on the list, as are more familiar additives such as salt, pepper, sugar, vinegar, and baking powder. This GRAS list is by no means fixed and unchangeable, nor are all the substances on the list necessarily free of hazard. They are simply generally recognized as safe, and they are reviewed periodically to determine their continued suitability for GRAS status. Table 17.1 contains some additional examples of chemicals and other substances currently on the list, together with brief descriptions of their functions in food. We'll look at some of their uses in greater detail in the sections that follow.

The **GRAS list** is a list of food additives that are generally recognized as safe by a panel of experts, but that have not been subjected to laboratory testing.

The remaining exemption, the first one of the series, requires that newly developed chemicals, which are by no means GRAS, be shown by scientific studies to be safe before they can be used in foods. Of course once they are demonstrated to be safe and may legally be added to food, they're no longer legally defined as food additives. What we mean by "safe" and how chemicals are demonstrated to be safe for addition to our foods are topics we'll examine in Chapter 18, after we take a brief look at the more practical side of additives.

QUESTION

Legally, food dyes are not food additives. Explain why not. ____________

17.9 Tons of Food Add Up to a Small Fraction of an Ounce of Additives

By a practical definition, a **food additive** is anything intentionally added to a food to produce a specific, beneficial result.

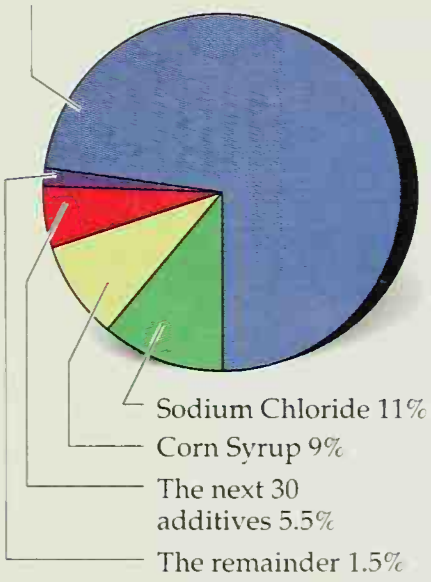
There are other good and workable (and certainly simpler) definitions of **food additives**, aside from the legal one of the Federal Food, Drug, and Cosmetic Act. A more practical definition holds that a food additive is simply *anything intentionally added to a food to produce a specific, beneficial result*, regardless of its legal status. Although the extended, legal definition of the Act has the force of U.S. federal law behind it and has the close attention of anyone who processes food for sale to the public, we'll use this simpler definition as we examine what chemical additives are doing in our food and why we use them at all.

A study published in 1973 by the President's Science Advisory Committee revealed that some 1900 food additives, as characterized by the simpler definition, were in current use in the United States. At that time the most heavily used of all these were the familiar substances sucrose (table sugar, eaten by the average person at the rate of 102 pounds per year), sodium chloride (table salt, at an annual 15 pounds per person), and corn syrup (a mixture of monosaccharides, primarily glucose and fructose, at an annual rate of 13 pounds per person). Use of all the remaining additives combined added up to an average of 9.3 pounds per year. A little arithmetic shows that the top three additives (table salt and the sweeteners table sugar and corn syrup) made up 93% of the total weight of all food additives consumed.

Beyond those first three, the next 30 additives made up 5.5% of all additives eaten, and consisted of such things as the chemicals of pepper, baking soda, mustard, yeast, food colorings extracted from vegetables, and similar familiar substances. The remainder of the 1900 accounted for 1.5% of the total weight of all additives consumed in the United States. The study showed that, omitting table salt and the sweeteners, on an overall average each person consumed just 0.08 oz (about 2.3 g) of each food additive per year. Naturally, some additives were consumed in far smaller amounts, some in far greater amounts. The trends since that study was completed show that the use of refined sugar is headed downward, with current consumption about two-thirds of what was reported in the Science Advisory Committee's 1973 report.

These statistics are summarized in Figure 17.6

Figure 17.6
U.S. consumption of food additives in 1973, by percentage.



Today the focus is on the dollar value of food additives. It's estimated that the total value of all the commercial additives used in processed food and drink sold in the United States in 1991 was about $5 billion. Of these, sweeteners made up the largest fraction, with about $1 billion, or 20% of the total. *Aspartame*, a synthetic, non-caloric sweetener sold under the trade name NutraSweet, has the distinction of being the food additive with the largest commercial value. In 1991 about $750 million worth of aspartame was consumed in the United States. We'll have more to say about aspartame in Chapter 18.

QUESTION

What element makes up the greatest weight of all the food additives we consume? You can arrive at your answer by starting with the molecular formula(s) of the most commonly used additives and a table of atomic weights. ____________________

17.10 Additives At Work

We use additives for a remarkably simple reason: to improve or maintain the quality of our foods. For many of us, adding some combination of salt, sweeteners such as sucrose or corn syrup, and seasonings like mustard, pepper, and other condiments improves the taste of an otherwise bland dish. Food colorings, another class of additives, enhance the appearance of our foods by converting a pallid frosting, for example, into the colorful decorations of a birthday cake.

Other additives function in less obvious ways. Adding vitamin D to milk doesn't add any appeal to the milk through taste, odor, or color, but it does improve the absorption of calcium into the body and so it helps protect against rickets, as we saw in Section 16.8. Similarly, the potassium iodide added to iodized table salt acts to prevent the formation of goiter (see Section 16.3). Ascorbic acid (vitamin C), on the other hand, not only improves the nutritional qualities of food but it also protects other food components from oxidation by contact with air. The ascorbic acid is itself so easily oxidized that it reacts preferentially with atmospheric oxygen. As a food additive, then, ascorbic acid acts both as a nutrient and as a preservative (specifically, an *antioxidant*; see Section 16.10).

Although additives serve a large variety of purposes in foods, we can place them into four major groups, according to their function. Generally, chemicals are introduced into foods in order to:

1. Make them more appealing.
2. Make them more nutritious.
3. Preserve their freshness and keep them unspoiled.
4. Make them easier to process and keep them stable during storage.

These categories aren't exclusive, and they even overlap a bit. We've just seen that, through its own preferential oxidation, ascorbic acid can act as a preservative as well as a nutrient. In this same sense, any one chemical additive can function in two or more of these categories. Nonetheless, we'll examine the categories individually in the following sections.

QUESTION

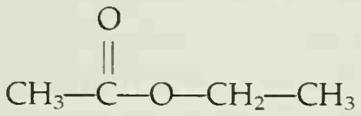
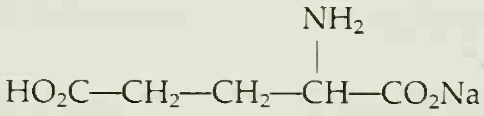
Into which of these groups does each of the following additives fall: (a) vitamin D, (b) potassium iodide, (c) pepper, (d) each of the three most widely used food additives?

17.11 Making Food More Appealing . . . With Nail Polish Remover!

Among the additives that make our foods more appealing to our sight, smell, and taste are the natural and synthetic sweeteners, colorings, flavor extracts, and flavor enhancers. Naturally occurring flavorings and fragrances include the essential oils and extracts of plants, such as oil of orange and vanilla extract, all of which contribute a bit of their own tastes and odors to foods. Some of the synthetic organic compounds used for these purposes also occur naturally in the plant essences. A particularly simple example is *ethyl acetate* (Table 17.2), a major commercial solvent and a naturally occurring ester (Section 11.11) widely distributed in the plant kingdom. Its fruity odor and pleasant taste (when it's considerably diluted) make it valuable in the formulation of synthetic fruit flavorings.

As with so many other chemicals, ethyl acetate has properties that serve very well in a variety of functions. In addition to its pleasant taste and odor,

TABLE 17.2 Representative Substances Used to Increase the Appeal of Foods

Substance	Structure or Chemical Formula	Function
β-Carotene	$C_{40}H_{56}$	Colorant
Ethyl acetate	 $CH_3-\overset{\overset{\displaystyle O}{\Vert}}{C}-O-CH_2-CH_3$	Flavoring and fragrance
Ferric oxide	Fe_2O_3	Colorant
Glucose	$C_6H_{12}O_6$	Sweetener
Monosodium glutamate, MSG	 $HO_2C-CH_2-CH_2-\overset{\overset{\displaystyle NH_2}{\vert}}{CH}-CO_2Na$	Flavor enhancer
Paprika		Flavoring and colorant
Sucrose	$C_{12}H_{22}O_{11}$	Sweetener
Titanium dioxide	TiO_2	Colorant

A menu from a Chinese restaurant advising that it does not use the flavor enhancer MSG.

its fine characteristics as a solvent and very low hazard to humans make it an excellent solvent for such consumer products as nail polishes and nail polish removers. Its ability to do either one of these jobs, to add its flavor to foods or to remove nail polish, doesn't detract in the least from its value in the other.

While these natural and synthetic flavorings and fragrances add their own flavors and aromas to our foods, the *flavor enhancers*, such as MSG, the *monosodium glutamate* of Table 17.2, sharpen some of the weaker flavors already present in the food without adding any significant taste of their own. MSG is used is preparing some processed canned and frozen foods, and it's often used in large amounts in Chinese foods. Some people develop symptoms including lightheadedness, headaches, an uncomfortable sense of warmth, and difficulty in breathing after eating a meal containing MSG. Because of the considerable quantities of MSG often used in meals served at Chinese restaurants, the condition has been named the *Chinese restaurant syndrome.* Many Chinese restaurants will omit MSG from a meal on request.

QUESTION

Monosodium glutamate is a salt of *glutamic acid.* To what class of compounds, described in Chapter 15, does glutamic acid belong? ______________________

17.12 Preserving and Protecting Food against Spoilage

The added minerals and vitamins that make our foods more nutritious constitute the next category of additives. Adding vitamin D to milk, for example, protects children against rickets. Canned fruit drinks often contain added vitamin C for nutritional quality. Some of the chemicals we add to food to increase its nutritional value are illustrated in Table 17.3.

Since we've already described the micronutrients in detail in Chapter 16, we'll move along to the next of the categories shown in Section 17.10, the preservatives. These keep foods fresh and slow down the process of spoilage and deterioration. Without these preservatives many of our foods would become unpalatable, completely inedible, or even hazardous to our health as they travel from the farm, the dairy, or the processor to our tables. As we saw earlier, chemicals were first added to food as preservatives with the smoking and salting of meat in prehistoric times. Even in those times a rudimentary form of food processing was needed to maintain the stability of the food supply.

Today mechanical refrigeration represents our primary nonchemical mode of preservation. To appreciate the important role of food preservation of every sort to our current way of living, imagine the chaos of a modern world without the food freezers and refrigerators of our stores and homes. Even though chemical preservatives are far less visible to us than these freezers and refrigerators, the abandonment of chemical preservatives could produce as great catastrophe as the disappearance of all forms of refrigeration.

TABLE 17.3 Representative Substances Used to Improve Nutrition

Substance	Chemical Formula	Function or Classification
Ascorbic acid	$C_6H_8O_6$	Vitamin C
β-carotene	$C_{40}H_{56}$	Provitamin A
Ferrous sulfate	$FeSO_4$	Mineral
Potassium iodide	KI	Prevents goiter
Riboflavin	$C_{17}H_{20}N_4O_6$	Vitamin B_2
Zinc sulfate	$ZnSO_4$	Mineral

The preservatives we rely on so heavily make up the group of compounds that protect against:

- Oxidation by air
- Spoilage by bacteria and other microorganisms.

We've already seen that ascorbic acid, by oxidizing preferentially, can slow the reaction between food chemicals and atmospheric oxygen (Section 17.10). In our opening demonstration it was the acidity of the citric acid of lemon, the acetic acid of vinegar, and the ascorbic acid of vitamin C tablets that inhibited the enzyme-catalyzed oxidation of slices of apple, banana, and potato. A pair of widely used antioxidants on the GRAS list are *BHA*, which is chemically a mixture of the two isomers (Section 7.6) of *b*utylated *h*ydroxy*a*nisole, known chemically as *2-tert-butyl-4-methoxyphenol* and *3-tert-butyl-4-methoxyphenol*; and *BHT*, also known as *b*utylated *h*ydroxy*t*oluene or *2,6-ditertbutyl-4-methylphenol* (Table 17.4).

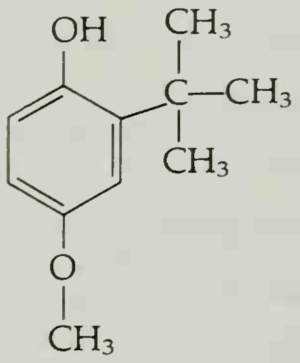
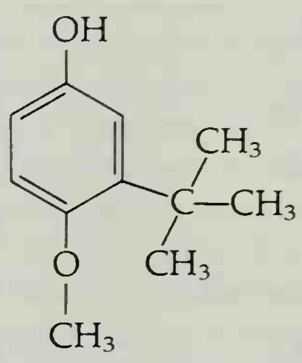
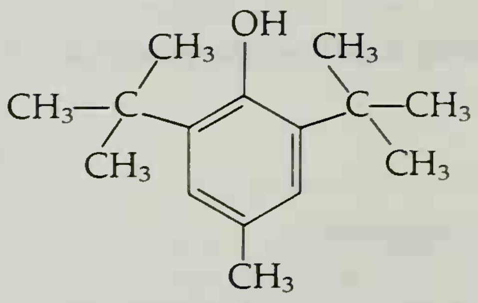
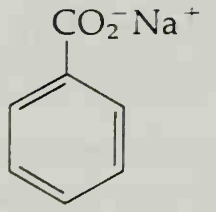
The additives that guard food against the growth of bacteria and other microorganisms not only preserve the taste and appearance of food, but they also protect us against microbiologically generated toxins. Labels on breads and other baked goods usually list *calcium propionate* (or, less often, *sodium propionate* or *propionic acid* itself) among their ingredients. Propionic acid occurs naturally in cheeses and other dairy products and both the acid and its salts effectively inhibit the growth of mold, a major cause of the spoilage of both dairy products and baked goods. Packaged acidic fruit drinks, especially those that don't have to be refrigerated before being opened, such as canned orange juice and grapefruit juice, usually contain added *sodium benzoate*. When present in amounts less than 0.1%, the sodium benzoate serves as an effective antimicrobial ingredient.

Table 17.4 shows some of these chemical preservatives.

QUESTION

Added vitamin C not only increases a food's nutritional value, but serves two additional functions as well. What are the additional functions? ____________________

TABLE 17.4 Representative Substances Used as Preservatives

Substance	Structure or Chemical Formula	Function
Ascorbic acid	$C_6H_8O_6$	Antioxidant and antimicrobial
Butylated hydroxyanisole, BHA	 	Antioxidant
Butylated hydroxytoluene, BHT		Antioxidant
Calcium propionate	$(CH_3{-}CH_2{-}CO_2)Ca(O_2C{-}CH_2{-}CH_3)$	Inhibits growth of molds and other microorganisms
EDTA (ethylenediaminetetraacetic acid)	(See Fig. 17.7) $C_{10}H_{16}N_2O_8$	Antioxidant
Sodium benzoate		Inhibits growth of microorganisms in acidic foods
Sodium nitrite	$NaNO_2$	Inhibits growth of microorganisms in meat
Sorbic acid and its salts	$CH_3{-}CH{=}CH{-}CH{=}CH{-}CO_2H$	Inhibits growth of molds and yeast, especially in cheese

17.13 Chemistry in a Crab's Claw

Some additives protect food against spoilage through complex and indirect, but nonetheless intriguing chemical actions. One of these, EDTA or *e*thylene*d*iamine*t*etraacetic *a*cid (sometimes called *edetic acid*), owes its prowess as an antioxidant to a peculiarity of its molecular structure and to a subtle aspect of oxidation chemistry. As shown in Figure 17.7, the intricacy of EDTA's molecular structure rivals the complexity of its name.

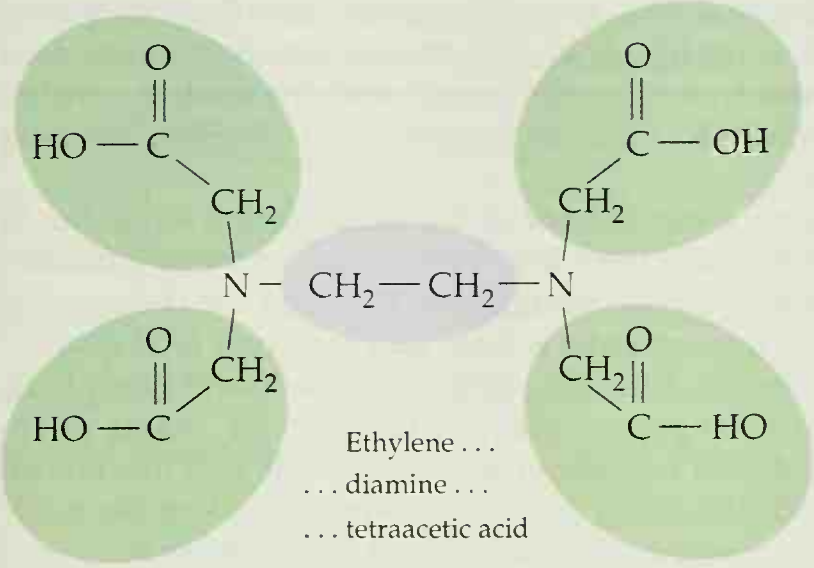


Figure 17.7
Ethylenediaminetetraacetic acid, or EDTA.

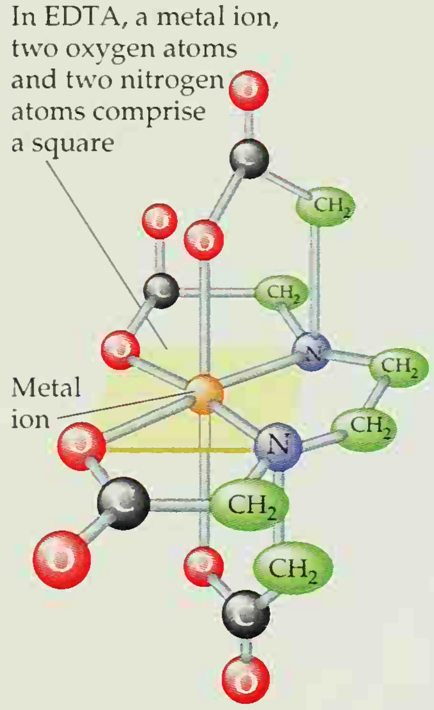
Behind EDTA's ability to protect foods against oxidation lies a bit of chemistry involving the catalytic effects of metal ions. Trace quantities of the ions of various metals—aluminum, iron, and zinc, for example—easily enter our processed foods as they go through their many stages of preparation in an assortment of ovens, vats, kettles, and other metal equipment. While these exceedingly small quantities of metal ions don't affect us or our foods directly, they can very effectively catalyze the air oxidation of many of the compounds that are present in food and thereby lead to spoilage. It's important to remove even the smallest traces of metal ions from some foods to protect against this catalytic oxidation, and that's where EDTA comes in.

A close look at Figure 17.7 shows that the molecule consists of an *ethylene* core (the —CH$_2$—CH$_2$— structural unit is the *ethylene* group, just as —CH$_2$— is the *methylene* group; Section 7.5) to which two *amine* nitrogens are attached. Each of these amine nitrogens is bonded to two groups derived from *acetic acid*, for a total of four acidic structural units. Putting all these groups together—one ethylene, two amine, and four acetic acid units—gives ethylenediaminetetraacetic acid, a long name but one that reflects very nicely the architecture of the molecule.

Note that six of the atoms of the EDTA molecule—the two amine nitrogens and four of the acetic acid oxygens—are relatively basic. The amine nitrogens have free, nonbonding electrons that they can use to form covalent bonds to acidic atoms (Section 15.2), and although the four basic oxygens of the acetic acid groups are already bonded to hydrogens, those four oxygens can also form similar bonds as each of their hydrogens is displaced by some other chemical species.

When EDTA or, more commonly, one of its sodium salts is added to a food, the molecule surrounds extraneous metal ions that may be present and bonds tightly to the metal through covalent bonds formed by the free electrons of its nitrogen and oxygen atoms. With this bond formation the EDTA wraps itself around the metal and holds it in a molecular grasp, much as a crab or a lobster holds a pebble in its claw (Fig. 17.8). This analogy gives these combinations of organic molecule and metal ion the name *chelates*, taken from the Greek *khēlē*, for a "crab's claw." What's more, with their firm hold on the metals, these chelates, in effect, remove them chemically from contact with the foods. As a result they prevent any traces of the metallic impurities from

Figure 17.8
The chemical claws of EDTH. The positions of the nitrogens and the oxygens within the molecule allow it to bond tightly to a metal through covalent bonds, thereby preventing the metal from catalyzing the oxidation of components of the food.



catalyzing a reaction of the food with air, as the metals might in the absence of the additive. As the chelating agents incorporate the metals into their own structures and remove them from chemical contact with the food, the chelating agents become **sequestrants**, from the English word *sequester*, meaning to remove or to set apart.

A **sequestrant** is an agent that is able to bond with a metal so firmly that it removes the metal from chemical contact with other substances.

To summarize, the chemical significance of this sequestering action lies in the ability of even trace amounts of free metal ions to catalyze the air oxidation of many of the compounds of foods. Isolating the ions into the chelate molecule effectively eliminates their catalytic activity and preserves food quality.

EDTA and other sequestrants, including salts of citric acid and phosphoric acid, are used as additives to protect the unsaturated side chains of triglycerides against the oxidation reactions that turn the fats and oils rancid. They're also added to foods to protect various vitamins, including the easily oxidized vitamin C, and to guard against air-induced discoloration of canned and processed corn, potatoes, and other vegetables, as well as fish, shellfish, dairy products, vinegar, meats, and many other kinds of foods.

QUESTION

Describe the chelation of EDTA with a metal ion in terms of the Lewis definition of acids and bases (Section 10.5). What is acting as the Lewis base? What is acting as the Lewis acid? ____________

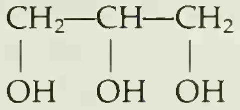
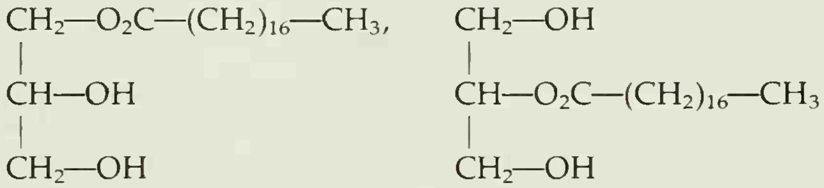
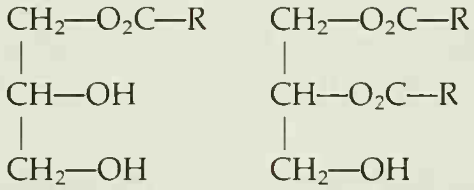
17.14 Stabilizers—Moist Coconut, Soft Marshmallows, And Creamy Peanut Butter

Finally there's the class of processing aids and stabilizers, which make it easier to prepare and to use processed foods and also help to prevent undesirable changes in the appearance or physical characteristics of foods while they're being stored. Among these are *humectants*, such as the *glycerine* that keeps shredded coconut moist and the *glyceryl monostearate* that softens marshmallows. *Anticaking agents*, such as *silicon dioxide* and the *calcium silicates*, keep table salt, baking powder, and other finely powdered food substances dry and free-flowing while they're being processed and as they stand on the store shelf or in the kitchen cabinet.

Glyceryl monostearate and other *mono-* and *diglycerides* also serve as *emulsifiers* that help whip peanut butter into a creamy smoothness and keep it that way until the jar is empty. *Xanthan gum* helps blend the oils and water that make up salad dressings and stabilizes the product as a smooth, homogeneous mixture. Chemically, emulsifiers are surfactants (Section 11.6) that make it possible to mix intimately two phases, oil and water for example, that don't ordinarily dissolve in each other. Acting very much like the laundry detergents of Chapter 11, the emulsifiers convert one of the phases into micelles, disperse them in the other phase, and stabilize the mixture by keeping the micelles from coming together. If it weren't for its emulsifiers, peanut butter would soon separate into a thick mass of peanut solids topped off by an unappetizing peanut oil.

Table 17.5 presents some typical processing aids and stabilizers.

TABLE 17.5 Representative Substances Used in Processing and to Maintain Stability

Substance	Structure or Chemical Formula	Function
Acetic acid	CH_3-CO_2H	Control of pH
Calcium silicates	$CaSiO_3$, Ca_2SiO_4, Ca_3SiO_5	Anticaking agents
Glycerine	 $\begin{array}{lll} CH_2- & CH- & CH_2 \\ \vert & \vert & \vert \\ OH & OH & OH \end{array}$	Humectant
Glyceryl monostearate	 $\begin{array}{l} CH_2-O_2C-(CH_2)_{16}-CH_3, \\ \vert \\ CH-OH \\ \vert \\ CH_2-OH \end{array}$ $\begin{array}{l} CH_2-OH \\ \vert \\ CH-O_2C-(CH_2)_{16}-CH_3 \\ \vert \\ CH_2-OH \end{array}$	Humectant
Gum arabic	(Gummy plant fluid)	Thickener, texturizer
Mono- and diglycerides	 $\begin{array}{l} CH_2-O_2C-R \\ \vert \\ CH-OH \\ \vert \\ CH_2-OH \end{array}$ $\begin{array}{l} CH_2-O_2C-R \\ \vert \\ CH-O_2C-R \\ \vert \\ CH_2-OH \end{array}$	Emulsifiers
Phosphoric acid and its salts	H_3PO_4, NaH_2PO_4, Na_2HPO_4, Na_3PO_4	Control of pH
Silicon dioxide	SiO_2	Anticaking agent
Xanthan gum	Complex polysaccharide from corn fermentation	Emulsifier, thickener

QUESTION

The glycerine and the mono- and diglycerides of Table 17.5 enter our bodies as food additives and also as the result of the metabolism of one of our macronutrients. Which macronutrient produces these chemicals as it is metabolized? ____________

PERSPECTIVE: Sodium Nitrite— Balancing Risks and Benefits

Another widely used additive, *sodium nitrite*, $NaNO_2$, presents us with a fine illustration of the need to balance risks against benefits in the use of chemicals as food additives. To sum it up, the risk in sodium nitrite is that it may cause cancer; the benefit is that it protects processed meats effectively against what may be the most deadly of all poisons, the microbial toxin *botulism*, which is responsible for a particularly lethal form of food poisoning. There's also an ironic twist to this story that complicates the issues involved in making any judgments about the value of sodium nitrite. We'll examine that twist after we've considered the risks and the benefits.

First, the risk. There's evidence that, under the chemical conditions that occur in the human stomach during the digestion of food, sodium nitrite can transform some of the digestive and metabolic products of proteins into a class of compounds known as *nitrosamines*. As a class of compounds these nitrosamines are among the most powerful **carcinogens** (cancer-causing agents) known. They've been found to produce cancer in every species of laboratory animal tested.

A **carcinogen** is a cancer-causing agent.

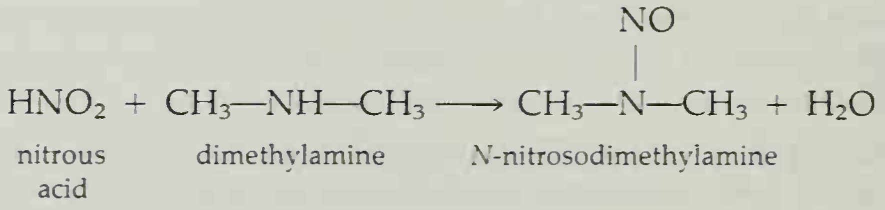
The conversion of sodium nitrite into a nitrosamine occurs as a part of a three-step process. It's known that when sodium nitrite and compounds like it dissolve in water they ionize to form a *nitrite anion*, NO_2^-.

$$\underset{\text{sodium nitrite}}{NaNO_2} \underset{\text{ionizes to}}{\longrightarrow} \underset{\text{sodium cation}}{Na^+} \underset{\text{and}}{+} \underset{\text{nitrite anion}}{NO_2^-}$$

It's also know that nitrite anion can react with hydrochloric acid (which occurs in our gastric juices) to form *nitrous acid*.

$$\underset{\text{nitrite anion}}{NO_2^-} + \underset{\text{hydrochloric acid}}{HCl} \longrightarrow \underset{\text{nitrous acid}}{HNO_2} + \underset{\text{chloride anion}}{Cl^-}$$

Finally, it's known that nitrous acid, the product of this reaction, can react with certain types of amines (similar to those formed during the digestion of proteins) to form nitrosamines. In reacting with *dimethylamine* in the laboratory, for example, nitrous acid generates *N-nitrosodimethylamine*. (The *N-* in the name of the compound tells us that the *nitroso* group, —NO, is bonded directly to the nitrogen and not to a carbon of the methyl groups).



$$\underset{\text{nitrous acid}}{HNO_2} + \underset{\text{dimethylamine}}{CH_3\text{—}NH\text{—}CH_3} \longrightarrow \underset{N\text{-nitrosodimethylamine}}{CH_3\text{—}\overset{\overset{NO}{|}}{N}\text{—}CH_3} + H_2O$$

Whether sodium nitrite, at the additive levels currently used, does actually generate nitrosamines in the human stomach and whether these nitrosamines (if they are, indeed, formed in our digestive system) do actually increase the risk of cancer in humans are uncertain at present.

We might think that this doubt and uncertainty is irrelevant. We might think that even the suspicion that sodium nitrite could generate a carcinogen would be enough to banish it as a food additive. In fact, though, the use of sodium nitrite as a food additive brings with it a very real and very important benefit. Sodium nitrite is very effective at preventing the growth of a microorganism known as *Clostridium botulinum*, which produces the botulinum toxin and is responsible for botulism food poisoning. (We'll have more to say about botulism poisoning in Chapter 18.) While removing sodium nitrite from meats might reduce the risk of cancer, removing this preservative would also certainly increase the risk of a particularly lethal form of food spoilage. As we'll see in Chapter 18, the use of *any* additive (or any other chemical, in any way) involves a balance of the benefits to be gained against the risks that it brings with it.

As for the ironic twist we mentioned earlier, we'd find that even a total ban on the use of sodium nitrite and other nitrite salts as food additives wouldn't remove the potential hazard. Only about a third of the nitrite salts in our bodies comes from the use of these additives. The remaining two-thirds results from the action of bacteria that live quite normally in our mouths and digestive systems. These bacteria convert sodium *nitrate* ($NaNO_3$) and other nitrate salts that occur naturally in the fresh vegetables of our diets into *nitrites*, as indicated by the following unbalanced equation.

$$\underset{\text{sodium nitrate}}{NaNO_3} \xrightarrow[\text{digestive system}]{\text{bacteria in the human}} \underset{\text{sodium nitrite}}{NaNO_2}$$

Thus nitrites would still be with us through the action of very natural processes even if they were never again used as food additives.

Instead of trying to assess the value of food additives by balancing the risks of their use against the benefits they provide, perhaps we can gain a clearer picture by balancing risks of one activity against risks of another. In the case of nitrites, we would balance the risk of generating a carcinogen within our own digestive systems (by using nitrites as additives) against a risk of the botulinum organism and its toxin contaminating our processed meats (by not using nitrites). Each is a risk of uncertain magnitude. Moreover, as we have seen, the entire matter is complicated by the natural occurrence of nitrates in our fresh vegetables and our conversion of these nitrates to nitrites within our own digestive systems.

Here, as in so many other cases in which we must perform a balancing act of this kind, chemistry can provide us with an understanding of our options and their potential consequences. In the matter of food additives, as we have already seen for the use of nuclear energy, petroleum products and gasoline, the internal combustion engine, and our own diets, and as we will see again in later chapters, we must ultimately apply our own judgment and sense of values to determine where the best balance lies.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

In its most general sense, a ______ is any substance deliberately added to a food to produce a ______ . Among the additives that make our foods ______ are ______ , which adds its flavor to foods; glucose and sucrose, which serve as ______ ; and ferric oxide and ______ , which add ______ . Increasing the ______ are additives such as ______ , which helps prevent goiter formation, and ______ . Several additives, including ascorbic acid and ______ help prevent the air oxidation of foods. ______ protects against oxidation by combining with traces of ______ and reducing their ability to ______ the process. ______ are surfactants that help ______ foods and keep them from separating during storage.

BHA and BHT
catalyze
color
desirable effect
EDTA
emulsify
ethyl acetate
ferrous sulfate
food additive
metal ions
mono- and diglycerides
more appealing to the senses
nutritional value
potassium iodide
sweeteners
titanium dioxide

2. Define, explain, or identify each of the following:

a. the GRAS list
b. The Federal Food, Drug, and Cosmetic Act
c. Harvey W. Wiley
d. calcium propionate
e. MSG
f. sodium benzoate
g. humectant

3. What is the chemical in lemon juice that prevents the enzymes in apples, bananas, and potatoes from catalyzing a reaction that turns these substances brown?

4. What are four major benefits a chemical can provide when it is added to a food?

5. What does the term *empty calories* imply and how can it be used to distinguish between a "junk food" and one that provides substantial nourishment?

6. Describe at least one function each of the following chemicals provides when it is used as a food additive: (a) potassium iodide, (b) iron salts, (c) calcium propionate, (d) calcium carbonate, (e) mono- and diglycerides, (f) acetic acid.

7. What is the function of a *humectant*? Name a chemical used as a humectant and name a food to which it is added.

8. What *two* functions does ascorbic acid serve when it is used as a food additive? (You may wish to review Chapter 16 in answering this question.)

9. What function does sodium nitrite ($NaNO_2$) serve when it is used as an additive in processed meats?

10. What is the hazard to using sodium nitrite as a food additive?

11. Name a chemical that is used as a food additive and also has an important use that is completely unrelated to food. Name or describe that unrelated use.

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

12. The following information appears in the nutrition panels of three different brands of cholesterol-free egg substitute. All the data represent the same serving size.

	Brand A	Brand B	Brand C
	Percentage U.S. RDAs of Micronutrients		
Vitamin A	6	15	8
Thiamine	4	4	8
Riboflavin	10	15	20
Calcium	2	4	4
Iron	6	6	6
Vitamin D	4	6	6
Vitamin B_6	4	6	4
Zinc	4	4	4
Pantothenic acid (see Problem 23, Chapter 16)	8	10	10

Based on this information alone, do you see any difference in the nutritional quality of these three brands? If you do, rank them in order of nutritional quality. If you don't, explain why you don't.

THINK, SPECULATE, REFLECT, AND PONDER

13. Name a food that you would put into the category of: (a) junk food, (b) health food.

14. Why were spices one of the most widely used food additives of the Middle Ages?

15. One definition regards a food additive as "anything intentionally added to a food in order to produce a specific, beneficial result," regardless of its legal status. In what way is this definition (a) more useful than the legal definition? (b) Less useful than the legal definition?

16. Another possible definition of a "junk food," in addition to the one proposed in this chapter, is: "A junk food is any food that is so enjoyable that people tend to eat too much of it." Do you think this is an acceptable definition? Explain.

17. According to law, in what sequence must ingredients appear on a label of a processed food?

18. A newly developed, dry breakfast cereal is being marketed by a major food processor. The first 25 entries of its ingredients label are cornmeal, wheat bran with other parts of wheat, whole grain barley, sugar, whole-grain rolled oats, rice, crisp rice, brown sugar, almond pieces, raisins, walnut pieces, dried prunes, tricalcium phosphate, salt,

cranberries, fructose, glycerine, corn syrup, dried apples, wheat starch, honey, malt extract, partially hydrogenated soybean oil, calcium carbonate, and brown sugar syrup. More ingredients are listed, but we'll stop here.

By law, these ingredients are listed in decreasing order by weight. Where in this sequence (first, second, third, or some other position) do you find the first ingredient that is present primarily to furnish sweetness to the cereal? Of all the ingredients listed, no matter where they appear in the sequence, how many would you say were added only to furnish sweetness? Suppose all the ingredients that are present primarily to furnish sweetness were combined into a single category that we might call "sugars and other sweeteners." Based only on the information provided here, speculate on where this combination ingredient might appear in the sequence of ingredients.

19. How would it be possible for a combination of sugars of various kinds [sucrose, glucose, fructose, and the invert sugar of honey (Section 14.9)] to be the major ingredient of a label on a box of breakfast cereal, yet not be listed first on the list of ingredients?

20. What is the function of the glycerine in the cereal in Problem 19?

21. *EDTA* and *edetic acid* are short names for the chemical *ethylenediaminetetraacetic acid*. Suggest an origin for each of these two shorter names.

22. Many chemicals used as food additives have never been subjected to scientific laboratory tests for safety, and yet their use is perfectly legal. What do all these legal, yet untested, additives have in common?

23. Suppose you were making a fruit salad to serve at a holiday dinner for your family and friends. To preserve the fresh color of the apples and the bananas in the fruit salad, to keep them from turning brown before the guest arrive and the food is served, you add some lemon juice to them. Would you consider the lemon juice to be a food additive? Explain.

24. Suppose that someone proposed a law that would require that *all* foods sold in stores have ingredients labels that would list all the chemicals known to occur in them. This law would apply to fresh, unprocessed foods, such as eggs, potatoes, carrots, raw meat, and the like, as well as to processed and manufactured foods. Would you be in favor of such a law or opposed to it? Describe your reasoning.

25. Assuming that it's desirable to test chemicals that are added to our foods to determine their effects on us, do you believe it is better to test them on laboratory animals or on human volunteers, such a those of Dr. Wiley's Poison Squad (Section 17.7) Under what conditions, if any, would you voluntee to participate in such a test?

Poisons, Toxins, Hazards, and Risks

18

WHAT'S SAFE AND WHAT ISN'T

Skydiving: safe or unsafe?

Figure 18.1

When we spray an insecticide into the air, we release a toxin into our environment in order to eliminate insects that may carry diseases. As we use an insecticide, we balance the risk of one hazard against the risk of another.

Spreading Poison All Around

For the opening demonstration of this chapter, you deliberately release a toxic chemical into your own environment, subjecting yourself, your friends, and others to its effects. Whether you actually follow the directions or pass this one by is, of course, up to you. But it's something many of us have already done many times. Maybe you have, too. The toxic chemical is the active ingredient of a commercial insecticide; the directions are whatever instructions the manufacturer has printed on the label. Whenever you spray an insecticide in a room or outdoors you are, indeed, releasing a potent poison into your environment (Figure 18.1).

To put this into a bit of perspective, we can use the same sort of risk–benefit analysis we discussed in the concluding section of Chapter 17. There we considered both the risks and the benefits of using nitrites to preserve processed meats. Applying the same sort of reasoning here, we can see that using an insecticide in our homes and gardens provides a clear benefit. It rids us of annoying, possibly destructive, disease-bearing insects and similar pests. There's also a risk involved: the possible hazard that the active ingredient in the insecticide, the chemical that does the killing, may put humans at risk of injury, poisoning, or illness.

In this chapter we'll examine some of the factors affecting the hazards that poisons of various kinds present to us. Before we begin, though, let's take a closer look at the risk of poisoning presented by the insecticide. We'll find, as we progress through this chapter, that the toxic risk depends on two factors, one qualitative, the other quantitative. With the insecticide, the qualitative aspect hinges on what kind of poison is present as the active ingredient. As we'd expect, an effective insecticide is particularly lethal to insects. Naturally, the more potent it is toward insects, the less we need to use and the less of it we, ourselves, are exposed to.

For the quantitative facet, let's compare the concentration of the poison in the insect's body with that in a human body. To simplify the comparison, we will assume we're dealing with a flying insect weighing about 0.7 g and a person who weighs about 70 kg. With this ratio of weights, our typical person weighs about 10^5 (100,000) times as much as the insect. If the person doing the spraying, or someone nearby, absorbs the same weight of the active ingredient as the insect does, the weight-percent of the poison in the human's body (Chapter 9), would be about 10^{-5} (1/100,000th) as great as it is in the insect's body. Even if our assumptions are a little off, it's not hard to see that the insecticide can be lethal at its very high concentration in the insect's body, yet produce no noticeable effect at its very low concentration in a human.

(Naturally, some of the poisons used in commercial insecticides are particularly hazardous and can harm humans and pets if enough of the poison is absorbed. This is particularly true of some chemicals used in lawn care. Some of these can pass through the skin on contact and enter the bloodstream directly. Anything designed to kill insects or other pests has to be considered as a poison and must be used with caution. Always follow the manufacturer's directions).

18.1 Chemical Poisons, Biological Toxins

In this chapter we'll examine poisons and toxins of various kinds. We'll learn how some of them work and how we can assign quantitative values to their lethal effects. We'll explore some of the risks and hazards they present to us. One of our most important topics will be safety itself. We'll examine what we mean when we say something is "safe" or "unsafe" and we'll look at a definition of safety that's especially useful in dealing with the ordinary things of our everyday lives. Of particular interest will be the chemicals of our foods.

Considering the number of hazards already present in our foods—the sugars that can decay our teeth, the saturated fats and cholesterol that can harden our arteries, the sodium that can aggravate high blood pressure, the minerals and the fat soluble vitamins that can make us ill if consumed in excess—it's surely worth wondering about the value of all the chemical additives introduced into our foods. Are they hazardous? Do their benefits outweigh the increased risks they bring along with them? We'll focus our concerns about chemicals in our foods on two crucial questions:

- Are there actually poisons in our foods?
- Is our food supply safe?

Answering these questions requires, first, good definitions of the key words *poison* and *safe*. We begin with "poison" and its close relative, "toxin."

Generally, when we speak of a **poison** we're referring to a chemical substance that can cause illness or death when it enters our bodies in one way or another, but usually through eating or drinking. The word **toxin** usually refers to a poison of biological origin, specifically a protein molecule produced by a plant or animal, with origins ranging from the secretions of microbes to the venoms of poisonous snakes. Toxins can reach us by way of spoiled foods, infectious diseases, or, more violently, through bee stings, snake bites, or other wounds.

A **poison** is a substance that can cause illness or death when it enters our bodies, usually as a component of our food or drink. A **toxin** is a harmful substance that has a biological origin.

The ways we use the words reflect something of their origins. *Poison* comes to us from a Middle English word that was spelled either *poysoun* or *puison* and that referred to a potion or a poisonous drink. The word originated in the Latin *potare,* "to drink," and still carries the implication of something hazardous entering our bodies through food and drink. Toxin was carried into English via the Latin *toxicum,* a poison, especially a poison smeared on arrowheads used in warfare. The ancient Romans got their *toxicum* from words for arrow poisons that trace back to *toxon,* an ancient Greek term for bows and arrows, poisoned or not. Our own sense of the word usually emphasizes the biological origin of the poison, especially when we speak of such substances as botulism, diphtheria, and tetanus toxins or the toxins of poisonous plants and animals.

Even with this distinction between a poison and a toxin, these words and others closely related to them are often used interchangeably. Despite the industrial origins of chemicals that pollute our environment, for example, we often speak of them as "toxic wastes." And despite the biological origin of snake toxins, we call the snakes that produce them "poisonous." With this in mind, we'll consider the words *poison* and *toxin* virtually interchangeable in this discussion.

QUESTION

Using the definitions in this section, name a substance you would consider to be (a) a poison; (b) a toxin. ______________________________

18.2 Degrees of Danger and Powers of Poisons

Sodium cyanide, aspirin (acetylsalicylic acid), table salt (sodium chloride), and water. In large enough quantities, each can be lethal.

The world, as we're well aware, is filled with dangers. But we're also aware that the dangers are unequal. Some hazards are more severe than others, with dangers coming in various degrees and poisons in different shadings of potency. Hydrogen cyanide and sodium cyanide, for example, are both powerfully lethal. It takes only a very little of either to kill. Ethyl alcohol is also a poison, but much less potent than the cyanides. Aspirin, the most widely used nonprescription drug in the world, can also kill. Although the drug seems harmless enough in ordinary use, partly because it's such a familiar medicine, it led all other chemicals, years ago, as the leading cause of the accidental poisoning of young children in the United States. Its victims mistook it for candy and swallowed the tablets, often in lethal doses. To protect children from accidental poisoning of this sort, through misuse of ordinary household products, Congress in 1970 enacted the Poison Prevention Packaging Act. Among other things, it requires that hazardous household substances, including aspirin, be packaged in containers that are especially difficult for children to open.

Before August 1972, the date this act went into effect for aspirin, children under five years of age were dying at the average rate of about 46 per year from accidental aspirin poisoning. After 1972, with increased protection, the rate dropped abruptly to about 25 per year.

Ordinary table salt, the sodium chloride of chemists, is another common but very weak poison. Eating enormous amounts, far more than the average person would consider palatable, upsets the balance of the ions of the body and can cause illness and death. A few years ago, for example, a six-year old boy with a history of an insatiable taste for table salt reportedly died from what was called the "grossly excessive" amount of salt he had added to his meal.

Even water, the compound that makes up more than half of our weight, the substance without which there can be no life at all, is harmful and even deadly in excess. Very much like eating huge quantities of sodium chloride, drinking enormous volumes of water leads to intolerable and potentially fatal imbalances in the composition of the body's electrolytes and fluids. The result can be mental confusion, lethargy, stupor, coma, and ultimately death. Medical reports tell of endurance runners who, after drinking huge quantities of water during races, exhibit a set of symptoms called "water intoxication" and then lose consciousness. These runners were hospitalized with seizures resembling those of epilepsy. In another case, recorded a few years ago, a woman died tragically from drinking as much as 4 gallons of water a day in an effort to rid herself of poisons she believed were accumulating in her body. It was the excessive water rather than her imaginary poisons that killed her.

The key word in all this is *excessive*. Anything consumed in large enough quantities, including household staples such as aspirin, table salt, and even water, can act as a poison. ("The poison," it's been said, "is in the dosage.") Since *anything* can be harmful to us in large enough quantities, ingested immoderately, we're forced to regard literally *everything* as poison. The question, then, isn't whether any particular substance—a macronutrient, a micronutrient, a food additive, a medicine, a household staple, even water itself—can be lethal. The question is, How much does it take? How do we determine the lethal quantity of a chemical?

QUESTION

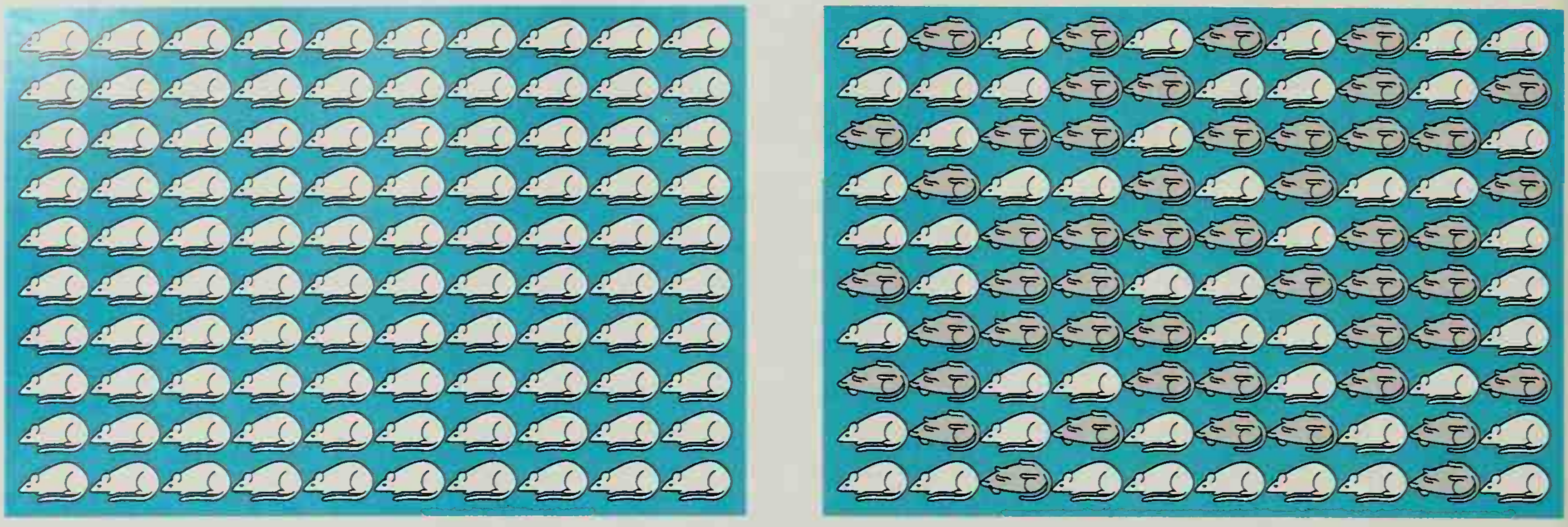
Arrange the following in order of their ability to cause illness or death (placing the most hazardous or lethal first in your list, the least hazardous last): aspirin, sodium chloride, sodium cyanide, water. ______________________________

18.3 LD_{50}'s

The most sensible way to measure the virulence of a poison or a toxin is to go directly to the heart of the matter and determine the amount needed to do the ultimate harm to a living thing, the amount needed to kill, or the **lethal dose**. There are some problems with this approach, though, even aside from any ethical issues involved in deliberatly killing an animal to measure a chemical's lethal strength. As a practical matter, simply feeding the substance in question to a laboratory animal, perhaps a mouse or a rat, and determining the amount needed to kill the creature don't give a satisfactory measure of the lethal dose.

The **lethal dose** of a substance is the quantity that causes death.

Individual animals of the same species, even of the same litter, can show different responses to identical stresses and to identical poisons. Some unusually sturdy individuals, for example, can survive relatively large amounts of any particular toxin while others, more susceptible, succumb to traces. To



Feeding aspirin to a large group of mice at the level of 1.5 g of aspirin per kg of mouse . . .

. . . kills half of them.

Figure 18.2
The LD_{50} for aspirin.

The **LD_{50}** of a chemical is the amount that kills exactly half of a large population of animals.

nullify the effects of these relatively rare individuals, it's customary to apply the test substance to large groups of animals, with each group containing a large, statistically realistic spectrum of individual susceptibilities. One useful measure that comes from studies of this sort is the amount of a chemical that kills exactly half of a large population of animals, usually within a week. It's the *L*ethal *D*ose for *50%* of the group, or the **LD_{50}**.

Since a chemical's capacity to cause harm depends partly on its concentration in the animal's body, it's common practice to report the LD_{50} of a substance in terms of the weight of the poison per unit weight of the test animal. Moreover, because the method used for administering the substance often affects the results, that too is usually included. For example, the LD_{50} for aspirin fed orally to mice and rats is 1.5 g/kg. This means that feeding aspirin orally to a large group of mice or rats, at the level of 1.5 g of aspirin per kilogram of animal, kills half of the population (Fig. 18.2). From still another viewpoint, we could say there's a 50% chance that 1.5 g of aspirin per kilogram of body weight will kill any particular mouse or rat that eats it.

In contrast, the LD_{50} of sodium cyanide is only 15 mg/kg, fed orally to rats. Since LD_{50}'s serve as a good guide to the potency of poisons, we can conclude that sodium cyanide is about 100 times as lethal as aspirin to rodents, orally, at any rate. Notice that the smaller the value of the LD_{50}, the less it takes to kill and the more toxic the substance. Table 18.1 lists the LD_{50}'s of some more familiar chemicals.

While these LD_{50}'s serve as a useful guide to a poison's lethal power, they have to be interpreted with a bit of caution. Different animal species often respond differently to a particular chemical and, as we noted earlier, the method of introducing the substance into the animal influences the results. Even for the same species different methods of administration—orally, by injection under the skin (*subcutaneously*), directly into the abdominal cavity (*intraperitoneally*), or directly into the bloodstream (*intravenously*)—can produce different values for the LD_{50}. The LD_{50} for nicotine administered to mice is 230 mg/kg orally, 9.5 mg/kg intraperitoneally, and only 0.3 mg/kg intravenously.

Considering that *anything* can cause harm if it's used in excess (a word whose meaning varies with the material we're talking about), it's clear that

TABLE 18.1 LD_{50}'s of Some Familiar Substances

Substance	Animal[a]	LD_{50}
Acetaminophen (an analgesic in medications such as Excedrin and Tylenol)	Mice	0.34 g/kg
Acetic acid (major organic component of vinegar)	Rats	3.53 g/kg
Arsenic trioxide (poison of mystery stories)	Rats	0.015 g/kg
Aspirin	Mice, rats	1.5 g/kg
BHA (antioxidant food additive)	Mice	2 g/kg
BHT (antioxidant food additive)	Mice	1 g/kg
Caffeine	Mice	0.13 g/kg
Citric acid	Rats (abdominal injection)	0.98 g/kg
Ethyl alcohol	Rats	13 mL/kg
Glucose	Rabbits (intravenous)	35 g/kg
Niacin (vitamin B_4)	Rats (injection under skin)	5 g/kg
Nicotine	Mice	0.23 g/kg
Sodium chloride	Rats	3.75 g/kg
Thiamine hydrochloride (vitamin B_1)	Mice	8.2 g/kg
Trisodium phosphate (pH-adjusting food additive)	Rats	7.4 g/kg

[a] The substance is administered orally unless noted otherwise.

to be realistic we've got to put *everything* around us into the same category. This includes chemicals ranging from cyanide and the most lethal biological toxins to caffeine and nicotine, to glucose and sodium chloride. It even includes water and our food's macronutrients, micronutrients, and chemical additives. Each one of these is a potential poison.

Understanding this, we're now in a position to answer one of the questions that began this chapter: "Are there actual poisons in our foods?" The answer must be, "Yes, there are." But since everything presents a potential hazard, both the question and its answer have lost most of their meaning.

The significant question now is whether our foods, with all their chemicals, are actually *safe*. The answer to this one isn't quite as clear-cut. Before taking up the matter of safety we'll examine, in the next few sections, some of the most powerful chemical poisons known.

QUESTION

What are the three most powerful poisons in Table 18.1, administered orally to mice or rats? What are the three least powerful poisons administered in the same way?

18.4 The Most Deadly Molecules

It's sometimes useful to discuss the hazards of chemicals in terms of the categories of their use. The chemicals that affect our everyday world can be described, for example, in terms of pesticides, food additives, industrial toxins, environmental pollutants, household hazards, and so on. While useful, categories such as these can also be misleading. Take ethyl acetate, for example. Consumers encounter this ester as a solvent in both nail polish removers and paint strippers (Section 11.11) and as a food flavoring (Section 17.11). It's also used as an industrial solvent in the manufacture of various consumer products. With all these functions, it's not particularly useful to categorize ethyl acetate as a cosmetic ingredient, a food additive, a household chemical, or an industrial solvent. It belongs in each of these categories. Chlorine furnishes another illustration. This element is a disinfectant for swimming pools and drinking water, a household bleach, and an industrial chemical in the manufacture of products ranging from plastics to pharmaceuticals. Chlorine was also used as a war gas in World War I. Nicotine, another example, is the major toxin of tobacco and a useful agricultural insecticide. Instead of looking at individual chemicals in terms of their use, we'll look at them in terms of their hazard, regardless of use.

We might expect that with all the ingenuity at a chemist's disposal and with all the power of molecular design, the most lethal of all the poisons around us would be those synthesized by chemists in the chemical apparatus of a chemical laboratory. That simply isn't so. By far, the most powerful poisons and toxins are created by nature, as shown clearly in Table 18.2. This table presents the LD_{50}'s of the most deadly of all chemicals. The LD_{50}'s in the table generally represent the most lethal method of administering the substance to mice or rats, whether orally or through injection.

Microphotograph of *Clostridium botulinum*. These microorganisms produce the deadly botulinum toxin, the most deadly poison known. It's the cause of the botulinum poisoning that results from eating spoiled food.

Leading the list as the deadliest poison of all is a work of nature known as *botulinum toxin*, especially a strain called *botulinum toxin A*. It's a polypeptide, much like those described in Chapter 15, produced by a common microorganism of the soil called *Clostridium botulinum*. This microbe thrives in many foods, especially improperly canned fruits and vegetables and poorly preserved meats. Fortunately, the microbe doesn't survive inside the human body, although the toxin it produces does. The microbe is easily killed by the high temperatures used in approved methods of canning. Moreover, formation of the toxin doesn't occur in acidic foods with a pH below 4.6. Whatever botulinum toxin may be present in contaminated foods is destroyed by cooking at high temperatures. Nonetheless, the toxin that the microorganism does produce is particularly lethal and dangerous.

Both "botulism" (the term for the illness) and "botulinum" (which applies to both the microorganism and the toxin it produces) owe their ultimate origin to the language of the ancient Romans. The first well-recorded outbreak of the disease occurred in 19th century Germany with more than 200 cases of poisoning. The origin of the epidemic was finally traced to contaminated sausages, which eventually gave a variation of their Latin name, *botulus*, to the disease itself. Later, with the isolation and identification of the organism that produces the toxin, the sausage connection was transferred to it as well.

Since the beginning of this century, the overwhelming majority of the cases

TABLE 18.2 Approximate LD_{50}'s of the Most Lethal Poisons

Substance	LD_{50} (mg/kg)
Botulinum toxin A	3×10^{-8}
Tetanus toxin A	5×10^{-6}
Diphtheria toxin	3×10^{-4}
Dioxin[a]	3×10^{-2}
Muscarine	2×10^{-1}
Bufotoxin[b]	4×10^{-1}
Sarin[a] (also known as isopropoxymethylphosphoryl fluoride)	4×10^{-1}
Strychnine	5×10^{-1}
Soman[a] (also known as pinacoloxymethylphosphoryl fluoride)	6×10^{-1}
Tabun[a] (also known as dimethylamidoethoxyphosphoryl cyanide)	6×10^{-1}
Tubocurarine chloride	7×10^{-1}
Rotenone	3
Isoflurophate[a] (also known as diisopropyl fluorophosphonate)	4
Parathion[a]	4 (female rats) 13 (male rats)
Aflatoxin B_1	10
Sodium cyanide[a]	15
Solanine	42

[a] Manufactured; others occur in nature.

[b] Toxicity to cats; all others refer to mice or rats.

of botulism poisoning in the United States, roughly 90%, have been caused by foods prepared and preserved in the home rather than by commercially canned foods. The chief offenders have been home-preserved foods that aren't heated to high enough temperatures or for long enough periods to kill the microorganism.

Using an LD_{50} of 3×10^{-8} mg/kg for botulinum toxin A (Table 18.2) and a body weight of 70 kg for the average adult (and assuming that humans respond to the toxin exactly as mice do), we can calculate that 5 g of the toxin, about a teaspoonful, would kill half of a group of 2,400,000,000 adults. Looking at the same statistics from a different angle, one teaspoon of botulinum toxin A could be enough to kill a quarter of the world's entire current population, one of every four persons alive today.

Another calculation shows that a teaspoon of tetanus toxin, the second deadliest toxin in the table and another one of nature's wonders, would be enough to kill half a population of 14,300,000 people, or roughly half of the total population of Texas. Tetanus toxin is a secretion of the *Clostridium tetani* bacillus and enters the body through dirty cuts and punctures.

The secretion of the microorganism that produces diphtheria comes in third in the roster, with 1/10,000th the lethal power of botulinum.

QUESTION

Applying LD_{50}'s obtained with mice and other laboratory animals directly and quantitatively to humans requires the doubtful assumption that humans respond to poisons in exactly the same way as mice. For a more realistic illustration of the potency of botulinum toxin, calculate the total population of a large group of mice, half of which would be killed by a single teaspoon of botulinum toxin. Assume that the average mouse weighs 20 g. ______________________________

18.5 Now Comes the Chemist, Here and There

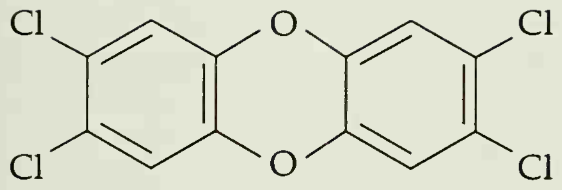
Only now, fourth on the list, comes a chemical produced by chemists, using chemical equipment in a chemical laboratory, rather than by one of nature's own creatures. With an LD_{50} of about 0.03 mg/kg, this synthetic chemical bearing the formal name *2,3,7,8-tetrachlorodibenzo-p-dioxin* (Fig. 18.3) is only about a hundredth as lethal to a mouse as is nature's bronze medal winner, tetanus toxin. The name of the compound is sometimes abbreviated to *TCDD*.

Since the chemical name of this compound is quite a mouthful, it's been shortened in general, nonscientific use to its last few syllables, "dioxin." This is a particularly unfortunate contraction since the term "dioxin" also represents an entire class of organic compounds of related structures, and, in addition, it's been used for a long time as the common name of still another, unrelated compound. This other "dioxin," which is also known as *dimethoxane*, is an innocuous compound that has been used in cosmetics and paints for many years without any significant hazard.

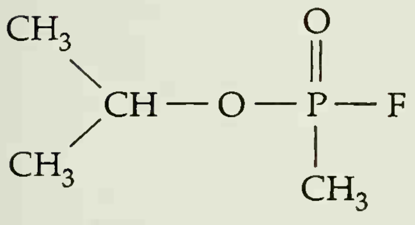
Yet, because of the widespread publicity given to the more lethal "dioxin"—partly through extensive, worldwide reporting of an industrial explosion in Seveso, Italy, in 1976, which released many pounds of the material into the atmosphere resulting in illnesses among nearby inhabitants and many deaths of domestic animals—the more convenient *dioxin* has become firmly bound to this very hazardous substance. Because of this unfortunate but well-fixed association, we'll use the more popular and recognizable term *dioxin* in this discussion.

To describe the potency of dioxin in the same sort of terms we used for botulism and tetanus, terms based on studies with laboratory animals, a teaspoon of this substance should be lethal to about half of a population of 2500 people. As an unwanted contaminant generated in certain industrial preparations of herbicides, dioxin represents the most lethal of the known laboratory-produced chemicals.

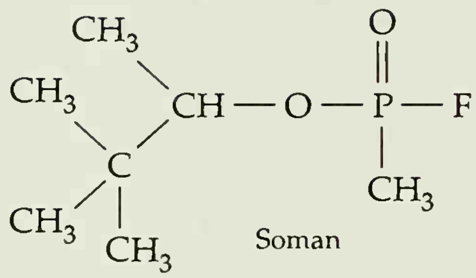
Following dioxin we find a set of toxic chemicals ranging from *muscarine* (LD_{50}, 0.2 mg/kg) to *solanine* (LD_{50}, 42 mg/kg). Interspersed among these are some highly specialized, closely related, phosphorus-containing synthetic chemicals that are highly effective in keeping nerve cells from transmitting



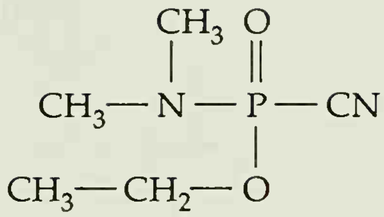
2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin
(Dioxin)



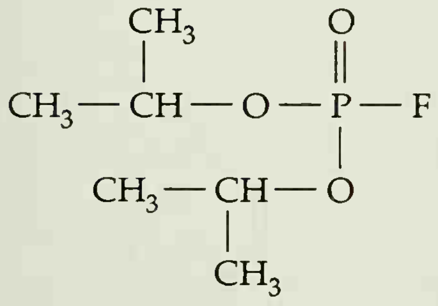
Sarin



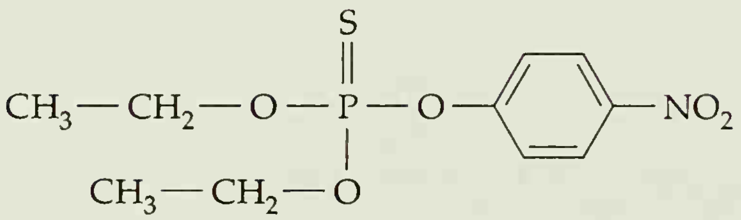
Soman



Tabun



Isoflurophate



Parathion

NaCN

Sodium cyanide

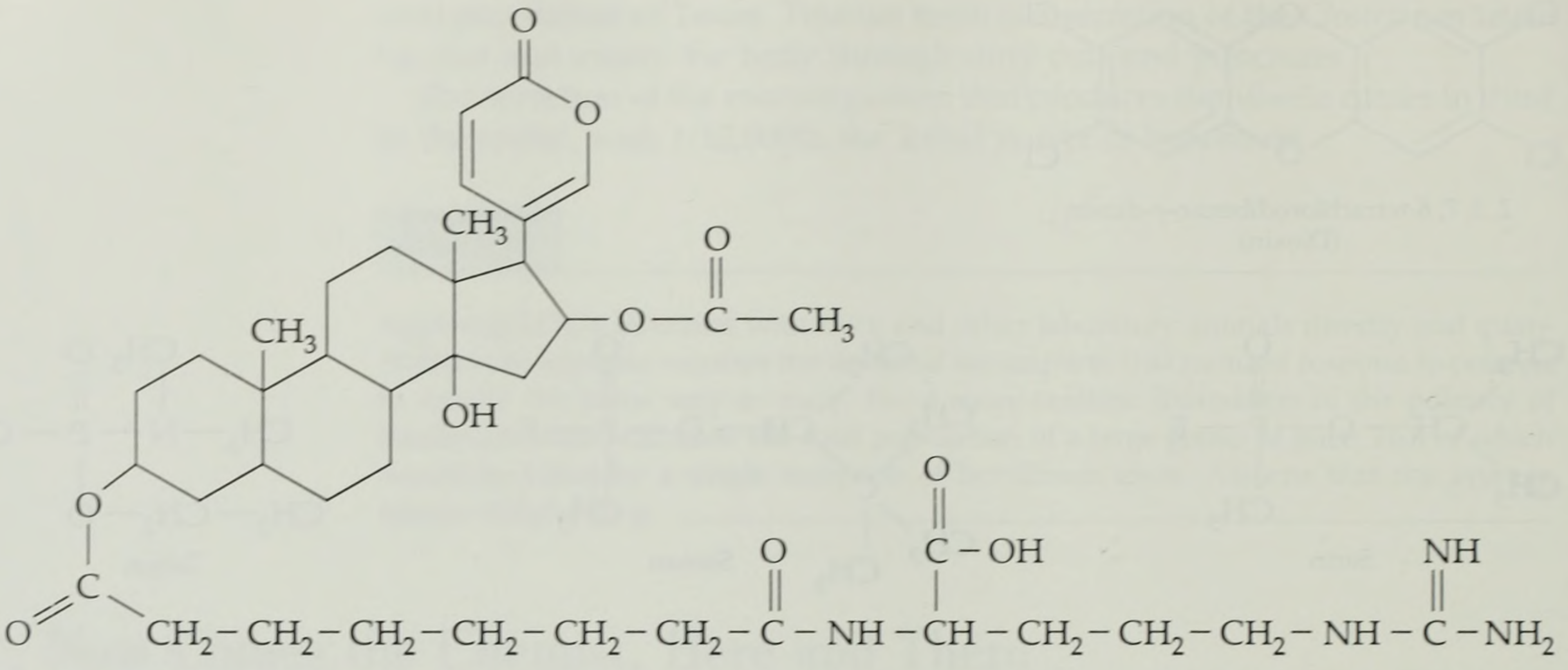
Figure 18.3
Manufactured poisons.

signals to each other. Among these are *sarin*, *soman*, and *tabun*, which arouse interest because of their potential as nerve gases in chemical warfare. With human LD_{50}'s estimated to be as low as 0.01 mg/kg, these seem to be particularly lethal to people. Other compounds with molecular structures similar to the nerve gases have uses a bit closer to our everyday experiences. *Isoflurophate* is effective in contracting the pupil of the eye in veterinary medicine, and *parathion* serves as a particularly toxic agricultural insecticide. *Sodium cyanide*, the last of the synthetic chemicals on this list, has various important commercial and industrial applications, ranging from the extraction of gold from ores and the electroplating of metals, to fumigation and pest control. The structures of these synthetic chemicals appear in Figure 18.3.

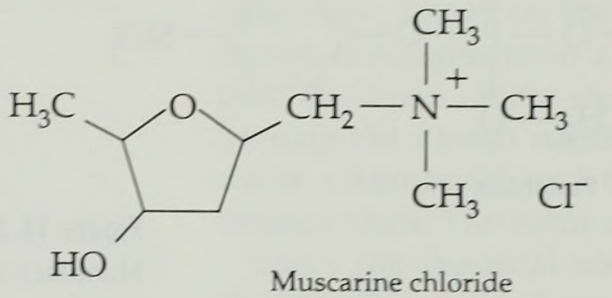
The remaining natural toxins in Table 18.2 include, in order of decreasing toxicity, the following:

- *Muscarine*, the lethal ingredient of deadly mushrooms such as the fly agaric or fly fungus.
- *Bufotoxin*, the active component of the venom of the common toad, *Bufo vulgaris*.
- *Strychnine*, which occurs in the seeds of trees native to Australia, India, and countries of the southern Orient, and which has been used as a natural rat poison for centuries.
- *Tubocurarine*, the toxin of curare, a plant extract used by South American Indians as an arrow poison.

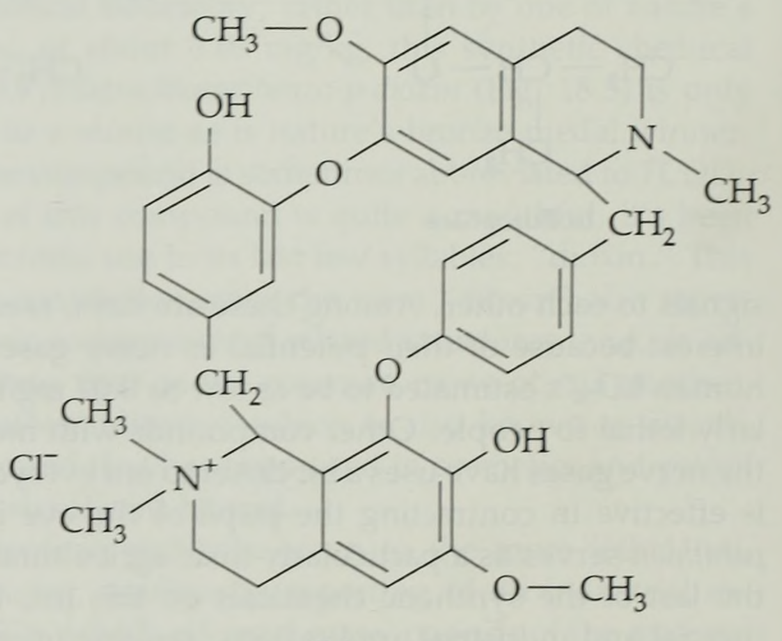
Soldiers wearing masks and protective clothing as a defense against nerve gases such as sarin, soman, and tabun.



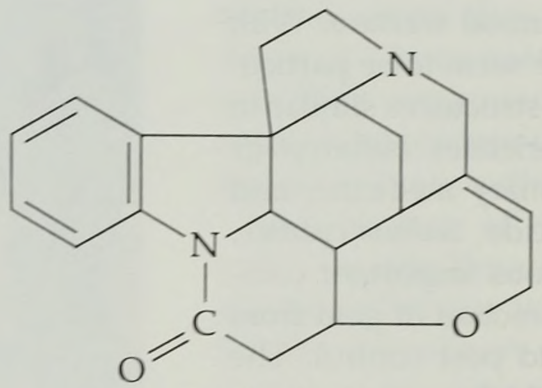
Bufotoxin



Muscarine chloride



Tubocurarine chloride



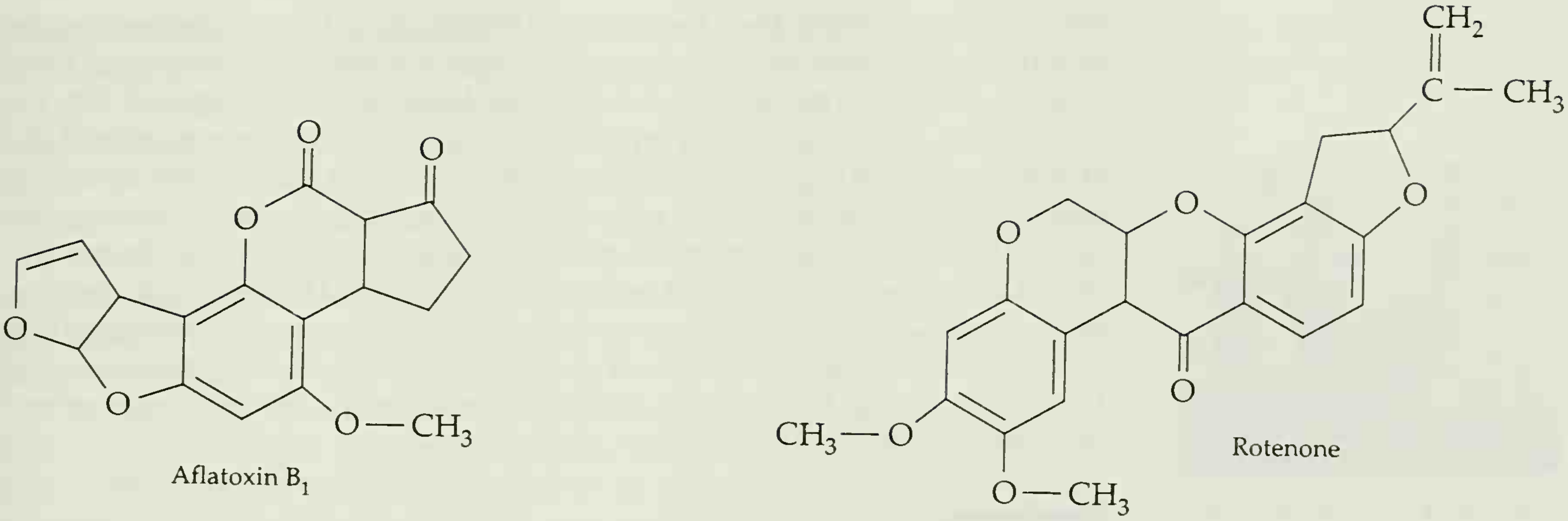
Strychnine

- *Rotenone,* a naturally occurring insecticide found in the roots of derris vines.
- *Aflatoxin* and *solanine,* both of which affect our foods, as we'll see in the next section.

Figure 18.4 presents the molecular structures of these natural toxins.

QUESTION

Which of the natural toxins described in this section (a) Contains a segment resembling cholesterol (Fig 13.1)? (b) Contains a glucose ring? ____________________


Aflatoxin B_1

Rotenone

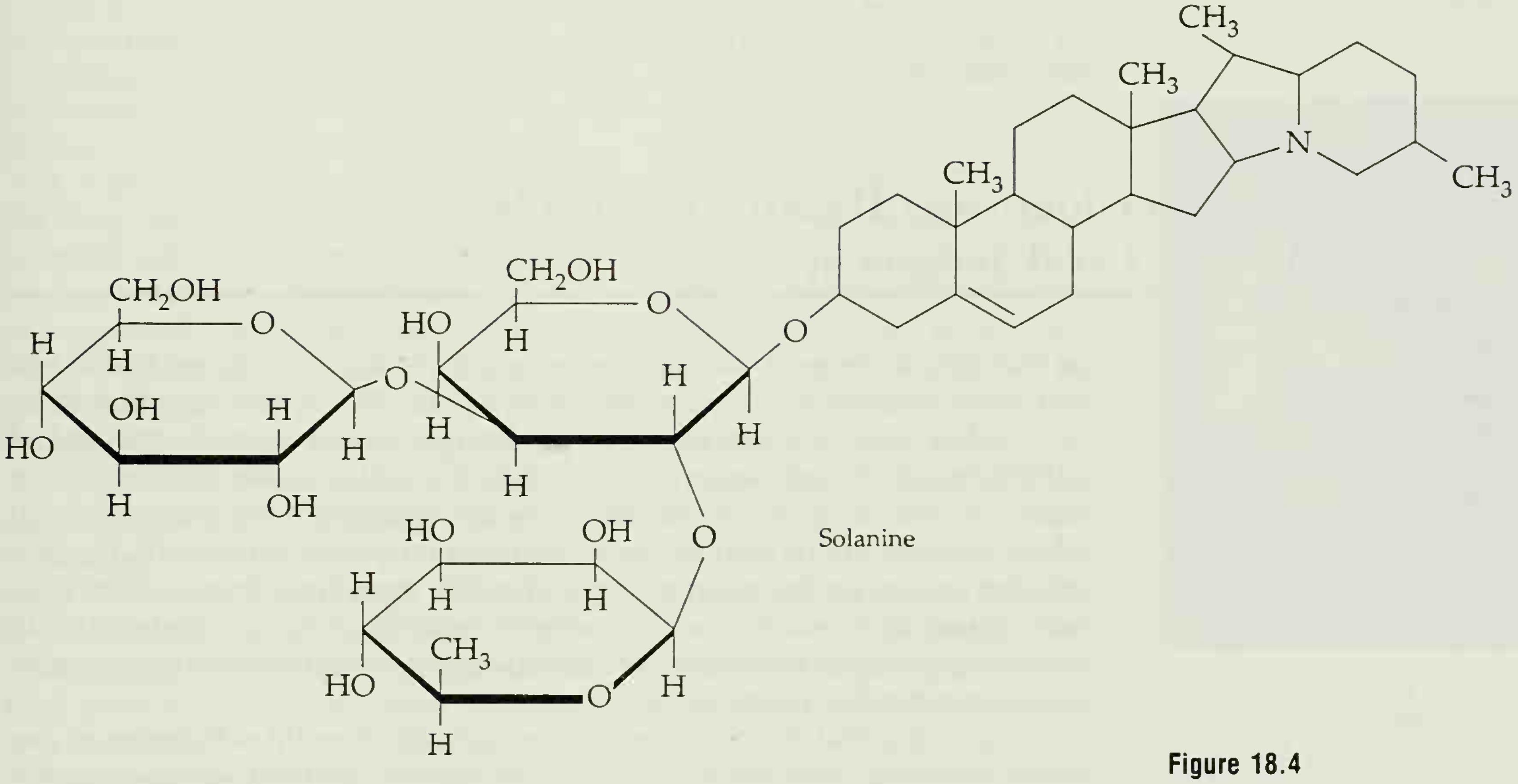

Solanine

Figure 18.4
Nature's toxins.

18.6 Back to Food

The last two on the list, nature's *aflatoxin* and *solanine*, bring us back to our questions about the safety of the food supply. Aflatoxins are a group of toxins produced by a mold that flourishes on various grains and legumes, including peanuts, wheat, and corn. Not only are the aflatoxins this mold releases highly toxic, they are among the most potent liver carcinogens known.

Differences in the effects of aflatoxin B_1 on newly born mice and on day-old ducklings illustrate very nicely the enormous variations in LD_{50}'s that occur with different species of animals and different methods of administration. For the mice, the LD_{50} is about 10 mg/kg for aflatoxin injected directly into their abdominal cavity; for the ducklings, oral feeding produces an LD_{50} of 18×10^{-3} mg/kg. The two values differ by more than a factor of 500.

Solanine, which occurs in potatoes, especially in or near green areas of the skin and near fresh sprouts projecting from the potato, inhibits the transmission of nerve impulses. In this respect it resembles the synthetic phosphorus-containing compounds described earlier. Solanine's potency, like that of the aflatoxins, depends on how it enters the body. Its LD_{50} by direct injection into mice is 42 mg/kg, while oral feeding of 1000 mg/kg produces no ill effects at all. (Direct ingestion can produce ill effects and death in many other species, though, including humans. It's best to cut green areas and fresh sprouts out of potatoes before using them.)

QUESTION

Give two different illustrations of how the hazard presented by a substance can depend on the species (and age) of the animal and the method by which it is introduced into the animal's body. ______________________________________

18.7 Safety—Freedom from Hazards or Simply a Matter of Good Judgment?

To sum up, we've seen that any chemical can be hazardous to our health and that lethal potencies can be measured as LD_{50}'s. We've also seen that these LD_{50}'s vary with the species of test animal used and with the method of administering the substance. Nonetheless, it's still possible to estimate the relative toxicities of various chemicals by ranking them with respect to each other. Although both botulism toxin and ordinary table salt can kill, the protein that makes up the toxin is unquestionably more toxic than sodium chloride. Taken as a whole, nature's poisons outrank, both in number and in virulence, synthetic chemicals, which include the manufactured dioxin, nerve gases, insecticides, cyanides, and so on.

Recognizing that there are, indeed, potentially harmful substances in our foods—poisons—we can now turn to the second question we asked at the beginning of this chapter: Are our foods safe? A reasonable answer requires a reasonable definition. Often, when we say that something is "safe" we imply that it is free of danger, hazard, or harm. But no substance is inherently and totally free of danger, hazard, or harm. We know that the harm any substance can do to *us*, each one of us, depends on

- its chemical characteristics
- how much of it we use
- how we use it
- how susceptible to its hazards we are as humans, and
- how susceptible we are as individuals.

For a more realistic test of safety, we can ask whether, knowing the risks involved in using a chemical (or in anything else for that matter), we are willing to accept those risks. In this sense **safety**, as it's defined by William Lowrance, a contemporary American organic chemist, is *the acceptability of risk*. It's a realistic and practical definition of a subtle and sometimes ambiguous term and it provides us with a convenient way to examine the safety of our food supply and of chemicals in general. With this definition in mind we can look to our own (informed) judgment in deciding matters of safety.

By one useful definition, **safety** is the acceptability of risk.

In short, everything in life involves a risk of one sort or another. Those risks we find acceptable are the ones we, ourselves, define as safe. Those we find unacceptable we define as unsafe. All of us, collectively, make similar judgments about the risks we are willing to take as a society.

Viewing safety as a matter of acceptable risk shines a somewhat clearer light on any attempts to prove that something is indeed safe. It is simply impossible to prove that anything is safe in the sense that it presents no hazard whatever, to anyone, at any time, in any possible circumstances. We might think that if we tried to demonstrate in 10,000 different ways that a certain chemical, for example, is harmful to mice and failed each time, we might have shown it to be safe. Yet all this is negative evidence, which proves nothing at all. There's always the possibility that one ingeniously designed additional test, a 10,001st experiment, might show that the chemical does, indeed, do harm to the mice.

The traffic signal is a device that makes acceptable the risks involved in crossing a busy street or driving into an intersection.

A tragic illustration of this occurred in the late 1950s and early 1960s with the drug *thalidomide* (Fig. 18.5). The drug, which had been developed as a sleeping pill, passed several routine toxicity tests with no evidence that it might be harmful. With the belief that this negative evidence was a demonstration of safety, physicians in England and other countries began prescribing it as a sleeping pill for pregnant women. In Germany it was sold as an over-the-counter drug, with no prescription required. (Doubts about the results of the animal testing kept it off the market in the United States.)

A welder using safety equipment that makes acceptable the risks of a hazardous job.

Within a few years, some 4000 babies in Germany, 1000 in Great Britain, and 20 in the United States (to women who had obtained the drug on trips to Europe) had been born with severe birth defects, including severely shortened or absent arms and legs. These defects were traced eventually to thalidomide that the women had taken within the first 12 weeks of pregnancy. Thalidomide is an example of a **teratogen**, a substance that produces severe birth defects. The word comes from the Greek *teras*, meaning a "monster" or a "marvel."

A **teratogen** is a substance that produces severe birth defects.

More extensive studies of the drug, spurred by the birth defects, showed that while it posed no apparent hazards to rats, dogs, cats, chickens, and other species, it did act as a teratogen in monkeys and rabbits, neither of which had been used in the original studies. Rats, in fact, are immune to thalidomide's teratogenic effects at as high a level as 4 g/kg per per day, while

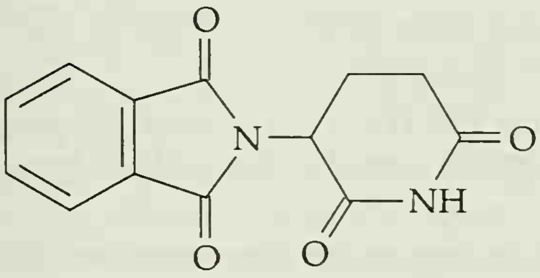


Figure 18.5

Thalidomide. Prescribed as a sleeping pill for pregnant women before its dangers were known, thalidomide acted as a teratogen in women who took it within their first 12 weeks of pregnancy.

women who took a single dose of 0.5 mg/kg, per at just the right time during their pregnancy, produced a deformed child. It was all clearly a case of a 10,001st experiment that, tragically, had not been performed.

QUESTION

Which of the following does our society (as represented by its laws) consider to be safe? We have discussed several of the following in the sections noted (a) the use of trisodium phosphate as a food additive (Section 17.8); (b) the use of ethylenediaminetetraacetic acid as a food additive (Section 17.13); (c) the use of gasoline containing tetraethyllead in cars that are *not* equipped with a catalytic converter (Section 8.10); (d) cigarette smoking in private by adults; (e) easy access to aspirin by children under age five (Section 18.2).

18.8 The Laws of Safety

With the definition of safety as the acceptability of risk, then, the question of which risks are acceptable and which are not falls on us as individuals and also as members of a larger society, one represented by our elected government and its laws. As individuals, for example, we're free to choose whether or not to use aspirin as a drug to relieve headaches and other minor pains, inflammations, and fevers. The choice is ours, individually, and the judgment of safety rests with each of us as individuals.

In 1970, though, with the passage of the Poison Prevention Packaging Act, our representatives in the Congress placed a larger, societal judgment on free access to aspirin. Aspirin, they said in effect, is safe enough to be handled freely by anyone who can open a simple but obstinate twist-and-snap cap, but it is unsafe for those very young children who can't. That judgment has become society's assessment of the safety of aspirin.

It also serves as a model for our decisions about the safety of chemicals in our foods. While each of us makes daily decisions about what to eat, our representatives at the centers of government decide what chemicals are safe enough to be used as additives in commercial foods and in what quantities these additives may be used. The executive branch of the government operates through the Food and Drug Administration (the FDA), and many other agencies as well, to implement legislative judgments of the safety of various chemicals. In addition to the FDA, these other agencies include the following:

- Environmental Protection Agency (EPA), which regulates chemical pesticides, among other matters affecting the environment.
- Occupational Safety and Health Administration (OSHA), which is concerned with exposure to chemicals in the workplace.
- Bureau of Alcohol, Tobacco and Firearms (BATF), a division of the Department of the Treasury that has jurisdiction over the chemicals of beer, wine, liquor, and tobacco.
- U.S. Public Health Service (USPHS), which, among its other activities, investigates outbreaks of illness due to food spoilage.

QUESTION

Give the titles of two acts passed by Congress that contain expressions of its judgment about the safety of chemicals used by consumers. (You may wish to review Section 17.8.) ______

18.9 A Factor Of 100

Through its rules and regulations the FDA exercises a societal judgment over the safety of the chemicals that concern us most in this survey, those that are added to our foods. In practice the agency must first determine that any proposed additive does, indeed, produce a desired, beneficial effect, which is one of the necessary characteristics of any food additive. The FDA then determines the acceptable level of an additive's use in foods through examination of

- The LD_{50} of the proposed additive in at least two (and often more) species of animals
- The chemical's maximum "no-effect" level, and
- Its long-term hazards, if there are any.

Values of LD_{50} represent the acute or immediate hazard in using a chemical. Naturally, a substance must produce a beneficial effect in foods at a level well below its acute toxicity if it's to be used as an additive. How much below, though, is a matter of judgment.

In making judgments of this kind the FDA requires that the substance be fed to at least two different species of animals for several months, and that the animals be examined thoroughly throughout and at the end of this study period for any changes the chemical may have produced. By feeding tests of this sort it's possible to determine the *maximum* daily amount of the chemical that produces no observable effect on the animals. This is the *no-effect level*, measured as milligrams of the additive per kilogram of the animal's body weight.

With a safety factor of 100, the FDA permits no more than 1/100th or 1% of this no-effect level in commercially prepared foods, based on estimates of the average person's daily consumption. This represents the additive's **acceptable daily intake**, or **ADI**. Any evidence that humans are even more sensitive to the additive than the test animals are, or that the additive can do its job at less than the 1% level, can result in even lower ADIs. Then again, if there's evidence of harm detected through much longer feedings tests, sometimes lasting several years, the substance may be prohibited entirely.

The **acceptable daily intake**, or **ADI**, of a food additive is 1% of the maximum daily amount of additive that produces no observable effect on laboratory animals.

These long-term feeding tests reveal the chronic effects of proposed additives, including some of the more dreaded hazards we sometimes associate with synthetic chemicals. Long-term studies uncover the ability of a chemical to affect an animal's ability to reproduce (fertility effects) and to affect offspring either through the development of severe birth defects (teratogenic effects) or through lesser genetic changes (mutagenic effects). Such studies also reveal a chemical's ability to produce cancer, to act as a carcinogen.

It's this last hazard, the possibility of chemically induced cancer, that arouses some of our strongest feelings about the chemicals of our foods and our environment. We'll turn now to the question of carcinogens in our foods and to an examination of our search for safety in its strictest form, absolute safety.

QUESTION

In what circumstances would an ADI be lower than 1/100th of the no-effect level of a chemical? ____

18.10 The Legacy of James J. Delaney

Through the original Food and Drug Act of 1906 and its many revisions, Congress has generally given federal agencies substantial leeway in setting the standards of safety for chemicals in our food, drugs, and cosmetics and in public areas such as the workplace and municipal drinking water. The matter of safety is, as we have seen, a matter of judgment; our lawmakers have been content, by and large, to delegate the finer, more technical matters of judgment to agency officials and their technical experts.

Yet with respect to one particularly fearsome hazard, the risk of cancer from food additives, federal law sets a *zero tolerance* level. That is, with the notable exception of saccharin, which we'll examine in detail in the next section, our society judges that there is *no* acceptable level of risk of cancer from a food additive. We'll now see what this zero tolerance implies, how it came about, and why an exception has been made for saccharin.

In 1958 Congressman James J. Delaney of New York introduced an amendment into a revision of the Food, Drug and Cosmetic Act which provided that:

> . . . no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal . . .

In effect this portion of the Act, now known as the *Delaney Amendment* or the *Delaney Clause,* prohibits the use of any chemical as a food additive, at any level, if the chemical is found to produce cancer in any way, in any test, at any concentration, in any animal. Although the FDA has established acceptable daily intake levels for various chemical additives of known acute toxicity, including some of those listed in Table 18.1, the Delaney Amendment sets a zero tolerance for the deliberate addition to food of any chemical known to cause cancer in humans or in laboratory animals.

While this legislative legacy has served as an effective bar against the addition of known carcinogens to our processed foods, it also brings into focus a larger need for balancing the potential hazards of any particular food additive against the very real and very desirable benefits that additive may provide. An illustration of this balance occurred a few years ago with the nonnutritive sweetener *saccharin.* (A nonnutritive sweetener is one that sweetens a food while introducing few or no calories per serving.)

QUESTION

As described in Section 18.9, a safety factor of 100 is applied to the results of feeding studies to determine the ADI for a newly proposed food additive. What safety factor is applied if the proposed additive is discovered to be a carcinogen? ____________

18.11 The Story of Saccharin

In 1879 Ira Remsen, Professor of Chemistry at the newly founded Johns Hopkins University, and Constantine Fahlberg, a student of Remsen's, were studying some of the more esoteric aspects of the reactions of organic compounds. Remsen was later to become president of the University and one of the major influences on the teaching and practice of chemistry in the United States.

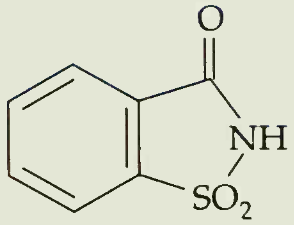


Figure 18.6
Saccharin. A nonnutritive sweetener about 500 times as sweet as sucrose, saccharin has been shown to be a weak carcinogen. It is still used as a food additive because of public demand.

One evening at dinner, after having finished his laboratory work and cleaned up, Fahlberg noticed a peculiar sweetness in the bread he was eating. He traced the source of the exceptional taste to his hands and arms. Recognizing that it must have come from residues of chemicals he had been in contact with that day, he returned to his laboratory to find its origin. By using the sensitive but very risky technique of tasting remnants of his work here and there in the laboratory, he traced the unusual sweetness to his chemical apparatus and to the compounds on which he had been working. He and Remsen immediately published their discovery of the source of the sweetness, the newly prepared chemical *saccharin*. The name of the sweet compound comes from the Latin and Greek words for sugar itself.

Saccharin (Fig. 18.6) provides neither energy nor the materials from which we produce our body tissues, and so it has no food value. Yet its intense sweetness, about 500 times that of table sugar, lasts even to incredible dilutions. Dissolve one teaspoon of pure saccharin, about 5 g, in 145,000 L of water—enough water to fill a cube just over 52.5 m on a side, or enough to cover a football field about an inch and a quarter deep—and the sensation of sweetness is still present.

Soon after Remsen and Fahlberg's discovery, saccharin was in use as a food preservative and as an antiseptic, and then as a replacement for sugar. Around 1907 commercial food canners discovered its popularity with people who had diabetes, and it's been with us ever since as a nonnutritive, noncaloric sweetener. With the passage of the 1958 Food, Drug and Cosmetic Act, saccharin, which had been in general use for about half a century, joined the GRAS list of approved food additives (Section 17.8).

Saccharin has been used as a non-nutritive sweetener since around the beginning of the 20th century. Although it has been shown to cause cancer in mice, saccharin continues to be used as a food additive because of public demand. All products containing saccharin must carry a warning label.

Although sugar-free foods for those with diabetes formed the original market for the sweetener, the demand for diet soft drinks that sprang up in the early 1960s brought saccharin into much wider use. By 1977 between 50 and 70 million Americans were regular users of saccharin, consuming about six million pounds each year, about three-quarters of it in soft drinks.

With this widespread public consumption, doubts arose about saccharin's safety. A few years earlier, in 1972, the FDA had removed it from the GRAS list and placed temporary restrictions on its further use pending the outcome of laboratory tests. Laboratory studies soon indicated that saccharin produces

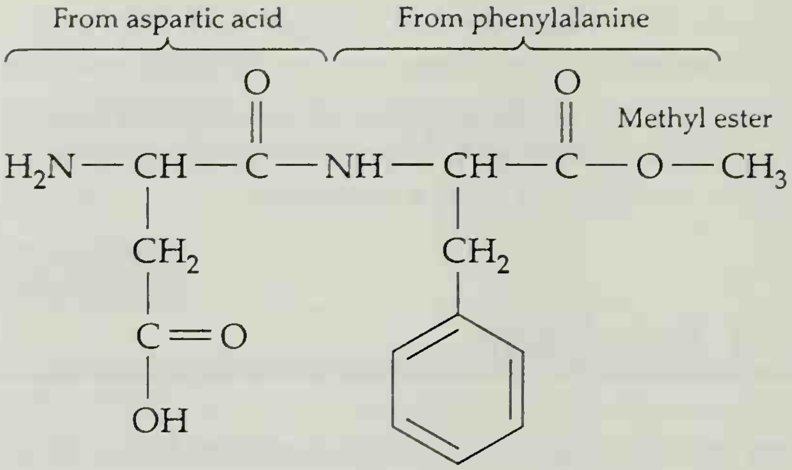


Figure 18.7
Aspartame, a dipeptide about 160 times as sweet as sucrose.

bladder cancer in mice. Even though the sweetener proved to be an extremely weak carcinogen, posing (according to the experts who examined it) a trivial and perhaps undetectable threat of cancer to the general population, the Delaney Amendment came into operation through its zero-tolerance provision and forced the FDA, early in 1977, to announce its intention to ban saccharin as a food additive.

Before the FDA's order could take effect, a public outcry against the proposed prohibition overwhelmed Congress. Saccharin was, at the time, the only sweetener available to those who wanted sweetness without calories, taste without the accompanying prospect of weight gain. One physicist published scholarly calculations suggesting that for a person 10% overweight the health risk from the saccharin in one diet soft drink was less than the health risk from the calories of the sugar it replaced.

Spurred on by public pressure, Congress acted. Through the Saccharin Study and Labeling Act of 1977 it ordered additional studies of saccharin and temporarily prohibited the FDA from banning it as a food additive. Congress also required that a label appear on all commercial foods containing the additive, warning that it causes cancer in laboratory animals and that "use of this product may be hazardous to your health." The moratorium against FDA action has been extended every few years and continues even now.

The public had decided, through its elected representatives, that the benefits accompanying continued use of saccharin outweighed the risk of cancer. The risk was judged to be acceptable and as a result saccharin was to be considered safe. Today, though, saccharin stands in the shadow of still another synthetic sweetener, *aspartame*.

Aspartame itself is a synthetic dipeptide (Section 15.8) of aspartic acid and the methyl ester of phenylalanine (Fig. 18.7). As a dipeptide, it provides the same 4.0 Cal/g as do proteins, yet its intense sweetness, about 160 times that of sucrose, allows it to provide the equivalent sweetness of table sugar with about 1/160th as many calories.

QUESTION

Assuming that an average of 60 million Americans were regular users of saccharin in 1977, what was their average daily consumption, in grams? ____________

18.12 An Ingredients Label for the Mango

We might speculate briefly on what our attitude would be toward the chemicals of our foods and toward the hazards they present if *all* foods, both processed and unprocessed, bore ingredients labels. Imagine what we might find if an orange growing on a tree or a potato freshly dug up from the ground carried a stamp showing all the chemicals it contained. Certainly one major difference between processed foods and those prepared by nature is that packages of processed foods must carry lists of their ingredients, while foods taken directly from the ground don't. To learn what's in unprocessed foods like oranges freshly off the trees or potatoes freshly out of the ground, or in apples, steaks, tomatoes, and the like, we're forced to turn to the chemists who analyze them and study their components.

Without exception, the lists of chemicals isolated from foods grown on the farm and in the orchard and sold with little or no processing far exceed those appearing on the ingredients panels of processed foods. The oil of an orange, for example, contains more than 40 different chemicals, grouped by organic chemists into categories such as alcohols, aldehydes, esters, hydrocarbons, and ketones. A potato yields some 150 different compounds, each of which can be synthesized in a chemical laboratory or poured from a bottle on the chemist's shelf. Each is a chemical put there by nature, synthesized by the plant itself as it grows.

The mango, a particularly tasty tropical fruit, offers an excellent example of what an ingredients label on a piece of a natural, unprocessed fruit might look like. Mangoes are prized delicacies throughout much of the world, especially in India and the Far East. In terms of total tonnage consumed, the mango is the most popular of all fruits. Figure 18.8 presents a partial list of the chemicals responsible for the flavor of a typical mango. It represents only a small fragment of all the chemicals that make up the fruit. Within the figure the chemicals appear in decreasing order by their relative abundance in the essential oil, just as they would on an ingredients label. Very few of them have been examined sufficiently for use as food additives.

Is the mango safe to eat? By any reasonable standard, and based on the masses of people throughout the world who eat mangoes daily without ill effects, the answer must be *yes*. (Of course, the answer could be *no* for those individuals who may be allergic to mangoes, for those with diabetes who may have to avoid the mango's sugars, and for others who may be sensitive to individual chemicals within the fruit.) Yet since its chemicals have not been tested for safety and have not been approved for use in foods, an identical mango that might somehow be manufactured in a food processing plant could not be sold legally as a food.

QUESTION

At least one of the major flavor ingredients of the mango (Fig. 18.8) has been approved for use in foods. Which one has this approval? (See Section 17.11 for help.)

Figure 18.8

A Partial Ingredients List for a Typical Mango.

α-Terpinolene, Ethyl butanoate, 3-Carene, Ethyl acetate, Ethyl 2-butenoate, α-Terpinene, α-Thujene, Dimethyl sulfide, Limonene, β-Phellandrene, Myrcene, *p*-Cymen-8-ol, β-Caryophyllene, *cis*-3-Hexene-1-ol, Hexadecyl acetate, 5-Butyldihydro-3H-2-furanone, *trans*-2-Hexenal, Ethyl tetradecanoate, α-Humulene, Sabinene, 2-Carene, Camphene, Ethyl octanoate, 4-Isopropenyl-1-methylbenzene, 1-Hexanol, γ-Terpinene, Hexanal, Ethyl hexadecanoate, α-Copaene, Hexadecanal, Ethanol, Ethyl propionate, Dihydro-5-hexyl-3H-2-furanone, Carveol, Geranial, Ethyl decanoate, Furfural, Butyl acetate, Methyl butanoate, Dihydro-5-octyl-3H-2-furanone, *p*-Cymene, Octadecanal, 6-Pentyltetrahydro-2H-2-pyranone, 2,3-Pentanedione, 1,1-Diethoxyethane, Pentadecanal, Butyl formate, 1-Butanol, 5-Methylfurfural, Ethyl dodecanoate, 2-Acetylfuran, 2-Methyl-1-butanol, 4-Methylacetophenone, Acetaldehyde, Cyclohexane

18.13 The Questionable Joys of Natural Foods

The example of mangoes can be repeated with all of our other foods, many times over and sometimes with sinister implications. Many of the compounds that form in plants and that become part of our food supply are very effective insect poisons, rivaling commercial insecticides in toxicity (certainly to insects and probably to humans) and overwhelming them in number. For every *gram* of synthetic pesticide that we eat as an unwanted residue of a commercial, agricultural spray, an estimated *10 kg* of natural pesticides enter, our bodies as natural poisons of natural foods. More poisons enter our bodies each day as the natural chemicals of our natural foods than from all other sources combined.

With some reflection, this shouldn't surprise us. With eons of evolution behind them, it's entirely reasonable that plants should develop powerful toxins as part of their chemical armory against insects and other predators. Unlike animals, plants can't run from their enemies; they can only poison them.

The armaments of some plants include chemicals that are not only toxic in the more common sense of the word, but are carcinogenic as well. *Safrole,* for example, makes up about 85% of oil of sassafras, which comes from the bark around the root of the sassafras tree and is also a minor component of cocoa, black pepper, and spices and herbs such as mace, nutmeg, and Japanese wild ginger. It produces the taste of sassafras tea and was at one time used as the principal flavoring ingredient in the manufacture of root beer.

Both the oil of sassafras and safrole itself have been banned from use as food additives. Safrole produces liver cancer in mice and has been listed as a carcinogen by the Environmental Protection Agency. The FDA judges both safrole and the oil to be too dangerous for use in foods and considers any food containing either one of them to be adulterated.

Figure 18.9 shows safrole and several additional plant substances that produce tumors in mice:

- *Allyl isothiocyanate,* a pungent, irritating oil, that occurs in brown mustard as well as horseradish and garlic and is also known as mustard oil.
- *Estragole,* a major component of oil of tarragon and occurring also in the herbs basil and fennel.
- *Symphytine,* a component of the comfrey plant and one of its natural defenses. (The comfrey plant is used for brewing herbal teas.)

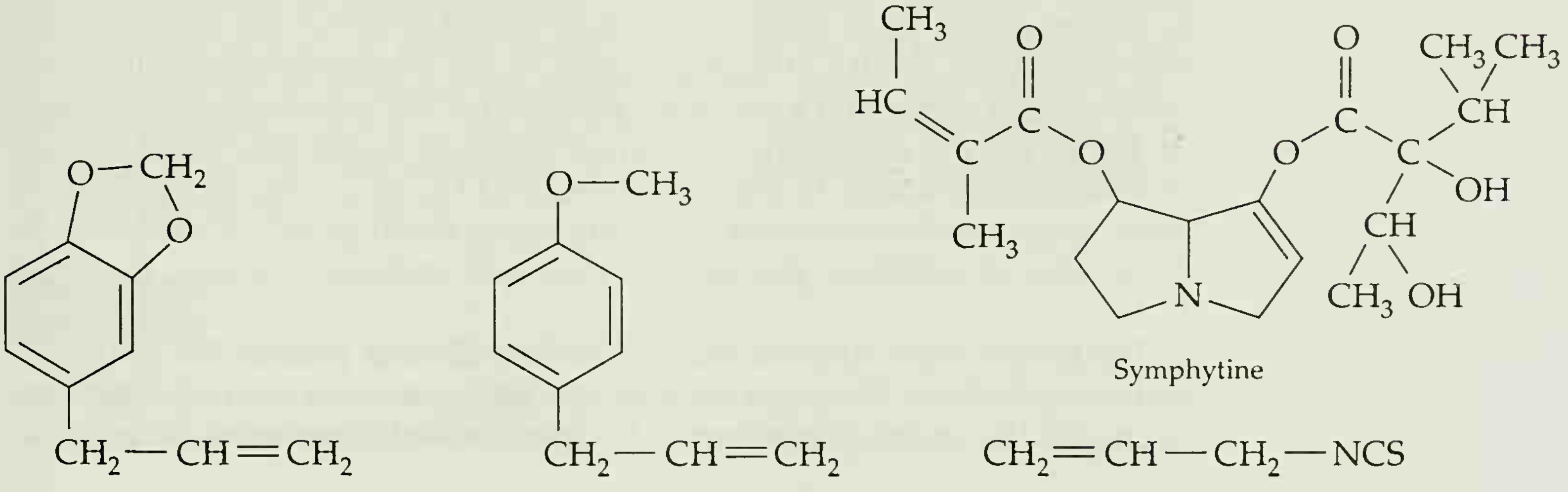
Examples of foods containing hazardous chemicals. Nutmeg contains myristicin, a chemical that can produce liver damage and hallucinations when taken in very large amounts. Large amounts of the glycyrrhizic acid of licorice can damage the cardiovascular system. The allyl isothiocyanate of horseradish, the symphytine of comfrey, and the estragole of basil can produce tumors.

The roster of toxic, carcinogenic, or otherwise hazardous chemicals in our natural food supply continues, seemingly without end (Table 18.3). Yet we do accept the hazards of our natural food supply, those that exist through the action of nature even in the absence of any processing or chemical additives. Despite the presence of an enormous variety of naturally occurring chemicals that may cause harm to us, we ordinarily consider the fruits, vegetables, grains, legumes, dairy products, eggs, meats, poultry, fish, and other foods that we eat in our daily meals to be safe, especially when we eat each in some measure of moderation.

This word *moderation* holds the key to our own defenses against food toxins. For most of our ordinary foods, normal levels of consumption lie far below anything that might produce an acute illness. Although the *myristicin* of nutmeg (Table 18.3), eaten in very large quantities at one sitting, can produce hallucinations and liver damage, the amount of nutmeg ordinarily used in

Figure 18.9

Plant substances that produce tumors.



Safrole

Estragole

Symphytine

Allyl isothiocyanate

TABLE 18.3 Toxic or Carcinogenic Chemicals Occurring Naturally in Foods or Produced through Cooking

Food Substance	Source	Potential Hazard
Allyl isothiocyanate	Brown mustard, horseradish, garlic	Tumors
Benzo(*a*)pyrene	Smoked and broiled meat	Gastrointestinal cancer
Cyanides	Oil of bitter almond, cashew nuts, lima beans	General toxicity
Dimethylnitrosamine	Cooked bacon	Cancer
Estragole	Basil, fennel, oil of tarragon	Tumors
Glycyrrhizic acid	Licorice	Hypertension and cardiovascular damage
Hydrazines	Raw mushrooms	Cancer
Lactose	Milk	Gastrointestinal distress (see Sec. 14.13)
Myristicin	Black pepper, carrots, celery, dill, mace, nutmeg, parsley	Hallucinations
Oxalic acid	Rhubarb, spinach	Kidney damage
Saxitoxin	Shellfish	Paralysis
Symphatine	Comfrey plant	Tumors
Tannic acid and related tannins	Black teas, coffee, cocoa	Cancer of the mouth and throat
Tetrodotoxin	Pufferfish	Paralysis

even the most heavily spiced meal runs about 1 or 2% of the quantity needed to produce anything more notable than flavorful food.

To suffer cardiovascular damage from the *glycyrrhizic acid* of licorice seems to require eating up to 100 g of the candy each day for several days. *Caffeine*, with its LD_{50} of about 130 mg/kg in mice, is the major physiologically active compound of coffee and a powerful stimulant of the central nervous system. At 100 to 150 mg of caffeine to a cup of coffee, it would take about 70 cups of coffee at one sitting to reach the mouse's LD_{50} in a 70-kg human. Surely other, urgent problems would arise long before the approach of a lethal dose. (Structures of caffeine, glycyrrhizic acid, and myristicin appear in Figure 18.10.)

The body's most effective shield against molecular poisons lies in the operation of the liver. This organ can call up a great variety of metabolic reactions to change the chemical structures of poisons, usually rendering them harm-

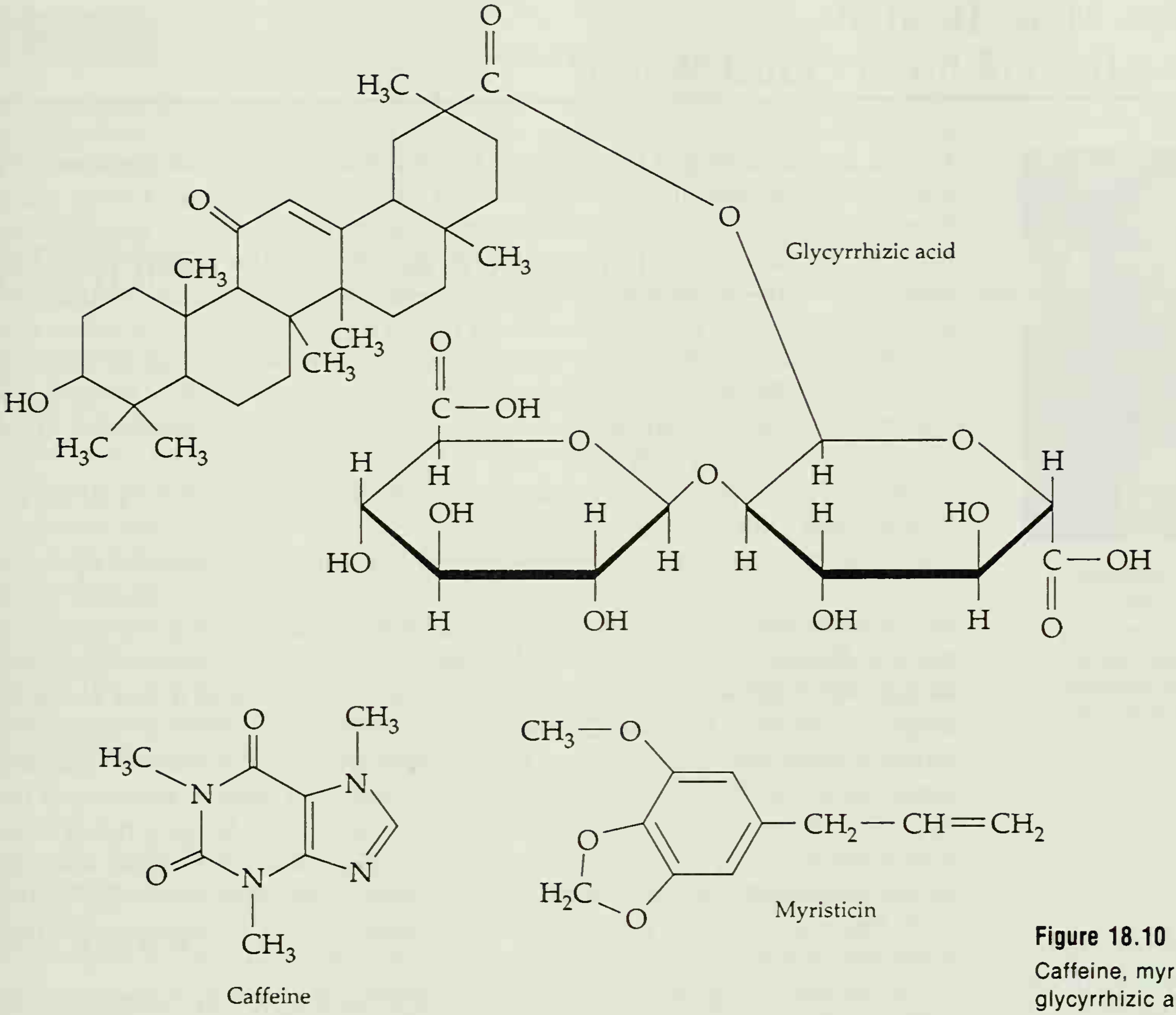


Figure 18.10
Caffeine, myristicin, and glycyrrhizic acid.

less. As long as a healthy liver isn't overpowered by a massive dose of any one toxin, it can employ its strategies effectively to protect the rest of the body. By using a variety of metabolic defenses, the liver far more easily disposes of, say, a tenth of a gram of each of 10 different toxins than the same total weight, one gram, of a single toxin. While small amounts of the 10 poisons might be metabolized effectively by 10 different enzymatic reactions, a large dose of a single poison could overwhelm the only biochemical path available for its removal. In this sense a varied diet, which implies eating foods containing a variety of natural toxins, each present in exceedingly small amounts, is far less hazardous than a diet that concentrates on large quantities of only one or two foods.

QUESTION

What are natural sources of each of the following chemicals: (a) oxalic acid, (b) caffeine, (c) tetrodotoxin, (d) symphytine, (e) safrole? ____________________

18.14 How Many Dead Mice Is a Bowl of Fresh Cereal Worth?

Bruce N. Ames, developer of the Ames test to determine whether chemicals produce mutations in certain bacteria. A positive Ames test suggests that the chemical may also cause cancer.

Back at the beginning of this century, Dr. Wiley's Poison Squad (Section 17.7) enlisted human volunteers to test the food additives then in use. Today, using humans on the scale needed for modern, scientifically reliable toxicity tests for food additives would run counter to the ethics of our society. Now laboratory animals, usually mice, replace the human Poison Squad volunteers. Even now, though, the combination of both a heightened sense of ethics and the costs of large-scale animal testing are behind moves toward developing other, faster, less expensive, and more humane tests: laboratory studies of a type that would provide accurate information without the sacrifice of large numbers of laboratory animals.

New laboratory procedures such as the *Ames test*, developed by Bruce N. Ames of the University of California, Berkeley, may point the way to better, less expensive, and surer methods of toxicity testing. The Ames test operates on the assumptions that both cancer and mutations begin with genetic damage of some sort, and that a chemical mutagen stands a very good chance of being a chemical carcinogen as well. The test uses a strain of bacteria known as *Salmonella typhimurium* that is modified biologically to make it very sensitive to genetic damage by chemical means, and therefore sensitive to chemically induced mutation. What's more, the bacteria are altered further so that the amino acid *histidine*, which is normally a *nonessential* dietary amino acid for the bacteria, becomes an *essential* amino acid (Section 15.4). As a result of its newly acquired dependence on histidine as an essential amino acid, a colony of the biologically altered bacteria won't grow in the absence of this amino acid. But exposing it to a mutagen that switches it back to its more common form allows it to synthesize its own histidine and to flourish.

In practice the investigator places the altered bacteria in a medium that contains all the needed nutrients for growth, except histidine, as well as an extract taken from rat livers. Using the liver extract helps identify chemicals that may not be mutagens themselves but that are converted into other, mutagenic substances as the liver enzymes detoxify them. Adding the chemical under examination starts the test. Rapid growth of the bacterial colony, at a rate comparable to that of unaltered bacteria under the same conditions, indicates that the added chemical (or whatever it's being metabolized to) is a mutagen and causes the bacteria to switch back to the form for which histidine is a nonessential amino acid.

Because of a very good overlap between the list of chemicals known to produce mutations and those known to cause cancer—about 90% of the chemicals on each list appear on the other—the Ames test and similar techniques can serve as useful, rapid, and inexpensive screening tools for identifying chemical carcinogens. Yet laboratory animals, which stand far closer to humans in their genetic makeup than bacteria do, still offer the best and most reliable estimate of chemical dangers to humans. In this respect, questions of ethical and economical values in animal testing must be balanced against the reliability of the animal experiments in protecting humans against chemical harm.

QUESTION

What conclusions, if any, could you draw from a positive Ames test (with bacterial growth) in an examination that did *not* contain added liver extract? What if this same examination produced a negative result? ______

PERSPECTIVE: The Search for Safety

In concluding, we return to the questions about safety that began this chapter. We've seen that chemicals—all chemicals—present hazards. We've seen that there are, indeed, poisons and carcinogens in our foods, and that they are to be found in processed foods and in natural, unprocessed foods as well.

We've seen that various governmental agencies have the power to protect us from excessive, known chemical risks, but that it is our own judgment of the acceptability of risks, both as individuals and as members of society, that ultimately determines the issue of safety.

We've seen, finally, that the idea of *absolute* safety is a phantasm. To the extent that we are well informed and that our judgments are sound, we can weigh the very real benefits that chemicals provide and balance them against the very real risks of their use. In this way, and only in this way, can we ensure that our world, while never free of hazards, is indeed safe.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used only once.

Since anything can be harmful if we consume it in excessive amounts or use it carelessly or improperly, everything we come in contact with presents some risk of ______ . Because of this we find it useful to define safety as the ______ of ______ . One measure of lethal risk in the chemicals we consume is the ______ , which is the weight of the substance (per unit of ______) that is ______ to ______ of a large population of laboratory animals. According to this measure, the deadliest chemical known is ______ , produced by a common microorganism. Second and third on the list of deadly chemicals, respectively, are ______ and ______ . The fourth most lethal chemical is one produced by laboratory reactions carried out by humans, ______ , which is also known by the simpler but ambiguous term ______ (made popular by accounts of its hazards). Other risks, not immediately lethal, include the risk of severe birth defects, produced by ______ , the lesser genetic changes induced by ______ , and the risk of cancer, generated by ______ . Among the carcinogens are natural products such as ______ , which is a component of ______, and the synthetic sweetener ______ . Both of these chemicals are banned from use as food additives by provisions of the ______ , but the sweetener is in continued use because of the enormous public demand for it. The regulation of food additives is the responsibility of the ______ , an agency of the federal government.

2,3,7,8-tetrachlorodibenzo-*p*-dioxin
acceptability
body weight
botulinum toxin A
carcinogens
Delaney Amendment
dioxin
diphtheria toxin
Food and Drug Administration,
  or FDA
half

injury
LD_{50}
lethal
mutagens
oil of
  sassafras
risk
saccharin
safrole
teratogens
tetanus toxin

2. Describe, define, or identify the following:

a. aflatoxin	c. isoflurophate	e. parathion
b. comfrey	d. OSHA	f. solanine

3. What contribution did each of the following make to the subject matter of this chapter: (a) William Lowrance, (b) James J. Delaney, (c) Bruce N. Ames, (d) Ira Remsen and Constantine Fahlberg, (e) Harvey W. Wiley?

4. Name a chemical affected by each of the following acts of Congress and describe how the law affects our use of the chemical: (a) the Poison Prevention Packaging Act of 1970, (b) the Saccharin Study and Labeling Act of 1977.

5. In what food does each of the following chemicals occur: (a) lactose, (b) glycyrrhizic acid, (c) myristicin, (d) oxalic acid, (e) benzo(a)pyrene, (f) tetrodotoxin?

6. What governmental agency is responsible for (a) investigating outbreaks of illness caused by food spoilage; (b) the chemicals of beer, wine, liquor, and tobacco; (c) chemical pesticides; (d) exposure to chemicals in the workplace; (e) chemicals used as food additives?

7. What was thalidomide used for before it was found to produce birth defects?

8. What is the difference between (a) a *teratogen* and a *mutagen*? (b) A *mutagen* and a *carcinogen*?

9. On what factors does the harm that any particular substance can do to us depend?

10. What characteristic or property of a chemical does the Ames test reveal?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

11. Which is more toxic to rodents when administered orally: (a) arsenic trioxide or sodium chloride? (b) aspirin or trisodium phosphate? (c) caffeine or nicotine? (d) acetaminophen or BHA?

12. Commercial aspirin contains 325 mg of aspirin (acetylsalicylic acid) per tablet. Assuming that the LD_{50} for aspirin in mice and rats applies equally well to humans, how many aspirin tablets, taken all at once, would produce a 50% chance of a lethal dose of aspirin in a 70-kg person?

13. Canned fruit drinks often contain 0.1% of sodium benzoate as a preservative. Studies provide a value of 4 g/kg for the LD_{50} of sodium benzoate, orally in rats. Assuming that humans respond to this chemical as rats do, and assuming that the density of a commercially canned fruit drink is 1.0 g/mL, how many liters of canned fruit punch would a 70-kg person have to drink, all at the same time, to produce a 50% chance of a lethal dose of sodium benzoate?

14. Solanine has the highest LD_{50} of the poisons in Table 18.2. What amount of solanine would a 70-kg person have to consume at one time to produce a 50% chance that it would be lethal?

15. Why is the quantity of a chemical that is lethal to 50% of a population a better measure of its hazard than the quantity that is lethal to 100% of a population?

16. What is the ADI of a chemical that produces no detectable effect on laboratory animals when they are fed it at a level of 1 mg/kg per day, but produces bladder cancer at a level of 2 mg/kg per day? Explain.

THINK, SPECULATE, REFLECT, AND PONDER

17. Give two definitions of safety described in this chapter. Is it possible to achieve absolute safety under either definition? If so, under which? Is it possible to prove that something is safe under either definition? If so, under which?

18. What do the molecular structures of the nerve gases sarin, soman, and taubin have in common with the molecular structure of the insecticide parathion?

19. What hazard is associated with each of the chemicals of Exercise 5?

20. With "safety" defined as the acceptability of risk, name three activities you would consider to be unsafe.

21. Suppose that laboratory tests on a newly discovered chemical showed that it produced absolutely no effects on any animal tested, no matter how or at what level it was administered. Would you consider this new chemical to be "safe"? Explain.

22. A statement sometimes used about the hazards of medicines is: "The poison is in the dosage." Explain what this means.

23. Describe your own thoughts about the safety of each of the following: (a) sodium chloride, (b) aspirin, (c) ethyl alcohol, (d) caffeine, (e) nicotine.

24. If we can say that *anything* is hazardous if it is used in excess, can we also say that *everything* is safe if used in very small amounts? Explain.

Gases

19

THE THIRD STATE

The air above us.

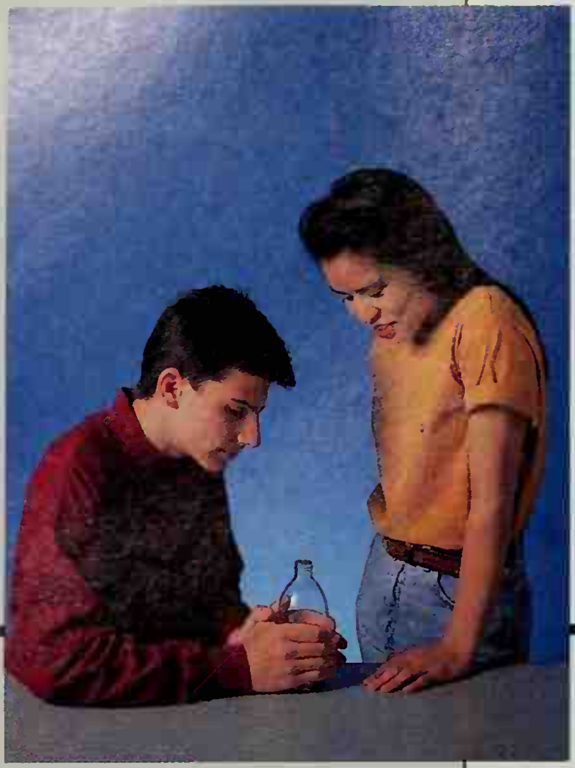


Figure 19.1

"Squeezing" air out of a bottle. Warming the air in a cold bottle causes the air to expand and escape, making a coin pop (as shown in top photo) and producing bubbles (as shown in bottom photo).

Squeezing Air Out of a Bottle

Here's another parlor stunt that illustrates an important scientific principle. Announce that you are going to squeeze air out of a glass bottle with your bare hands. Before making this announcement, put an empty glass soda bottle in a freezer for about half an hour. (You can leave the paper label on the bottle, but for best results remove any insulation that might be wrapped around the glass.) Remove the bottle from the freezer—you may want to do this out of viewing range so that no one else knows you are using a well-chilled bottle—invert it, wrap your warm hands around it, and place its mouth well below the surface of a saucer or glass of water. Act as if you are squeezing the bottle, *but don't actually put any force on it*. Squeezing a glass bottle could be hazardous. If the bottle is flawed it could break in your hands, producing a nasty cut. As the air inside the bottle warms up, bubbles start coming out of the mouth, as though you were, indeed, squeezing air out of it.

In a variation of this stunt, you can set the cold bottle upright on a table, wet the rim, and place a coin, such as a quarter, over the bottle's mouth. (Wetting the rim produces a weak but effective seal between the coin and the glass.) Wrap your hands around the bottle, as before. Soon, as the air inside the bottle warms, the coin starts making a pinging noise as the air in the bottle expands and forces its way out, lifting the coin periodically.

The secret is in the science. At constant pressure, any given quantity of air, such as the air inside the cold bottle, takes up more room when it's warm than when it's cold. As the heat of your hands warms the air inside the bottle, the gas lightly trapped inside expands and leaves the bottle either as bubbles, in the first form of this stunt, or in short bursts that lift the coin, in the second form (Fig. 19.1).

In this chapter we'll learn more about gases, the third state of matter (in addition to the solid and liquid states we examined in Chapter 11), and a few of the more important chemicals that normally exist as gases. In another variation of our theme that any particular chemical can benefit us or harm us, depending on where it is and how we use it, we'll learn of a chemical, ozone, that can pollute the air we breathe and, at the same time, protect us from a dangerous form of the sun's radiation. We'll see that how it affects us depends on what part of the atmosphere it occupies. We'll also see that what was once believed to be a set of the safest and most useful of all commercial gases, the chlorofluorocarbons, or CFCs, threaten to destroy the protective shield of the ozone layer. We'll start by examining the atmosphere itself, the gas we live in.

19.1 The Gas We Live In

It isn't a nutrient, yet we can't live without it. It's invisible, and yet the most ordinary of all substances. It's with us always, yet we sense it only as it moves or as it carries odors and haze. People breathe it, birds soar on it, jets fly through it, fish succumb to it, clouds form within it, and the most brilliant of the early chemists studied it. It's the air, earth's atmosphere. It's a gas.

We can survive without food for weeks, without water for days, but without air we can't last more than a few minutes. This gas that sustains our lives, moment by moment, enters our lungs as a complex mixture of simple substances. Nitrogen makes up 78.1% of dry air, measured by volume and at sea level; oxygen, 20.9%; argon, 0.9%; and carbon dioxide, 0.03%. The infinitesimal remainder, in order of decreasing proportions, consists of a combination of neon, helium, methane, krypton, hydrogen, oxides of nitrogen, and xenon (Fig. 19.2). Humid or wet air also contains water vapor, which lowers the percentages of the other gases in the total combination; polluted air carries with it noxious fumes or colloidal suspensions of solids or liquids in the form of smoke or haze (Section 11.7).

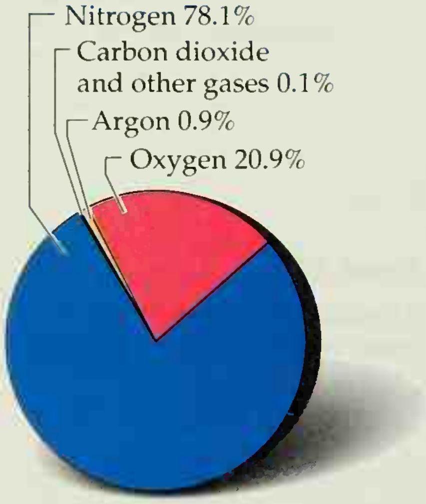


Figure 19.2
Composition of dry air.

As we travel upward through the atmosphere we find that its composition and physical characteristics change with altitude, creating the regions of Figure 19.3. Immediately above the surface of the earth lies the region known as the **troposphere**, which gives us our clouds, wind, rain, and snow. The temperature of the air drops steadily as we ascend, until we reach the **stratosphere**. There the air is dry, clear, and cold, with a relatively uniform temperature of about −55°C at the earth's middle latitudes. The stratosphere, as we see in Figure 19.3, is the home of the *ozone layer*, which we'll examine in more detail at the close of this chapter. Above the stratosphere the temperature now rises with increasing altitude, then drops, and then rises again as we enter the **ionosphere**, a region in which the gases that make up the air are ionized by the sun's radiation. This layer of ionized gases reflects radio waves effectively and makes possible shortwave radio transmissions.

The troposphere is the region of the Earth's atmosphere that rises from the earth's surface and that produces the phenomena of our weather. The **stratosphere** lies above troposphere and holds the ozone layer. The **ionosphere** is a higher region of the atmosphere that is filled with ionized gases and serves to reflect shortwave radio transmissions.

The combined weight of all the gases above any particular point, either on the earth's surface or anywhere in the atmosphere itself, generates the **atmospheric pressure** at that spot. At sea level the total mass of the entire atmosphere, estimated at about 5×10^{18} kg (about 5.5×10^{15} tons), produces the same pressure, on average, as a column of mercury (chemical symbol, Hg) 760 mm high. Average sea-level pressure, then, is 760 mm-Hg, which is equivalent to about 14.7 lb/in^2 (Fig. 19.4). Each of these values represents a pressure of *one atmosphere*.

The **atmospheric pressure** at any point on the earth's surface or above it is the pressure generated by the combined weight of all the atmospheric gases above that point.

Figure 19.3
The regions of the atmosphere.

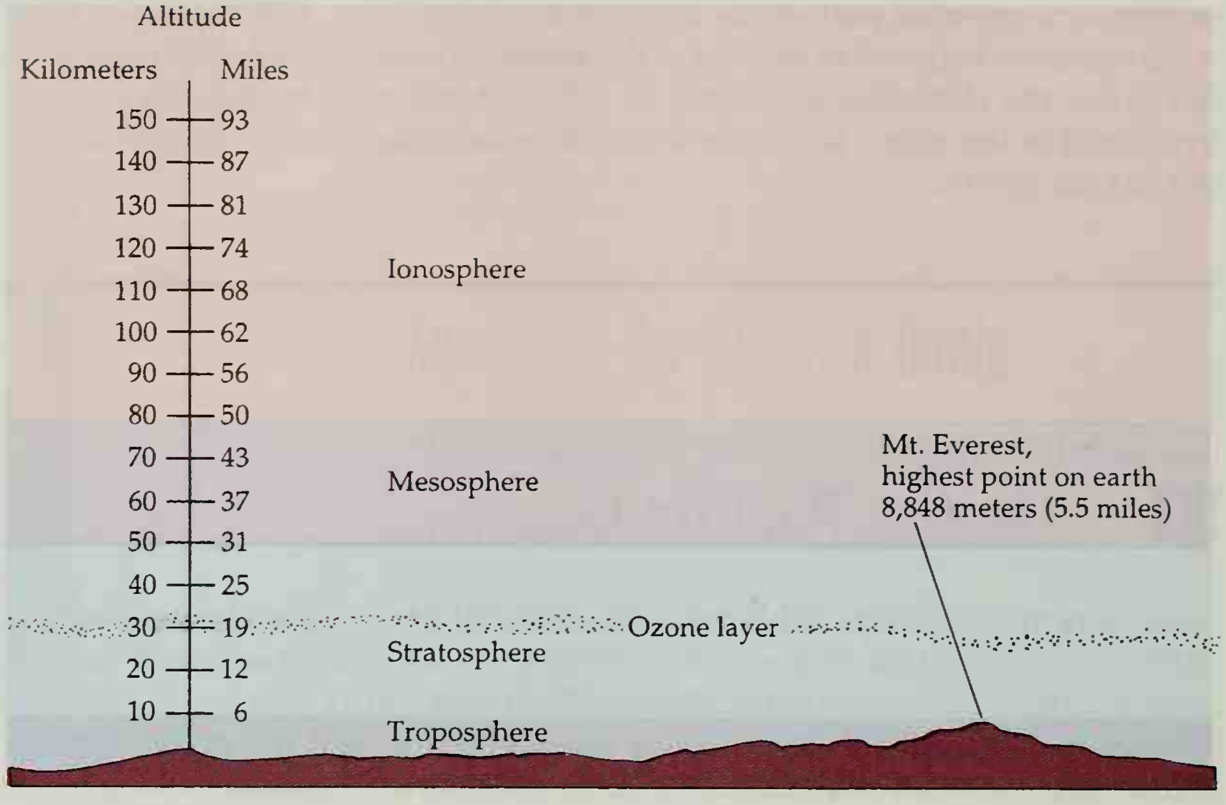
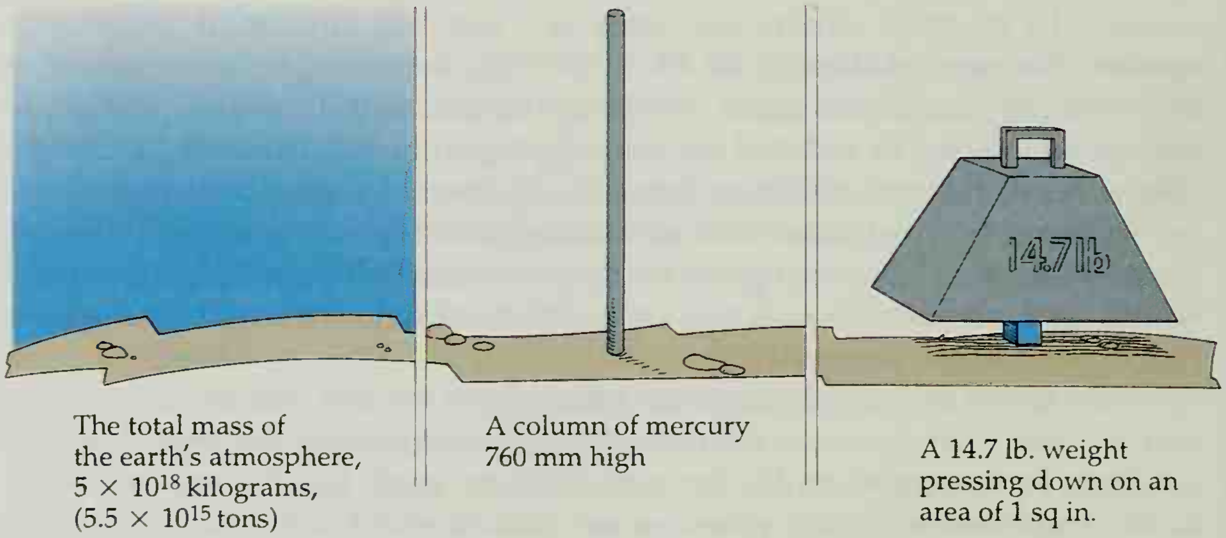


Figure 19.4
Atmospheric pressure at sea level, 760 mm-Hg or 14.7 lb/in^2.



We'll use the hyphenated *mm-Hg* as a unit of *pressure*, distinct from the unhyphenated *mm Hg*, which would represent the actual metric height of a physical column of mercury. An alternative unit for the *mm-Hg* is the *torr*, named for the Italian physicist and mathematician Evangelista Torricelli, 1608–1647. Torricelli, who served as Galileo's secretary during the last few months of that great physicist's life, was the first to suggest that the atmosphere has mass and that it exerts a pressure on everything within it, just as the water of the sea presses on everything submerged. In 1643, the year following Galileo's death, Torricelli confirmed his ideas with his invention of the *barometer*, an instrument for measuring atmospheric pressure (Fig. 19.5). *Barometer* itself is a combination of two Greek words, *baros* for "weight" or "pressure," and *metros*, meaning "measure."

Atmospheric pressure drops rapidly with altitude, decreasing to about 90% of its sea-level reading at a height of just under 900 m (a little under 3000 ft) and to half the sea-level value at about 5500 m (18,000 ft). Changes in the density of the atmospheric gases above the earth's surface produce regions of high atmospheric pressure and low atmospheric pressure, the "highs" and "lows" of our weather forecasts. A rising atmospheric pressure usually forecasts a change to bright, sunny skies, while the reverse indicates cloudy, rainy weather ahead.

This air of ours is only the most immediate example of a gas, a state of matter that we discussed briefly along with solids and liquids in Section 11.2. *Solids*, you'll recall, are substances with distinct volumes and shapes. They're held together, often as very orderly and well-shaped crystals, by the relatively large cohesive forces of their ionic, interatomic, or intermolecular attractions. As we add energy to a solid in the form of heat, its temperature rises and the translational energies of its chemical particles grow, finally overcoming the forces that hold them in their lattices. The ions, atoms, and molecules then begin to flow freely about one another and, as they do, the substance liquefies. A *liquid* possesses a volume that's independent of its container, but it always takes the shape that the container imposes.

With increased internal disorder at still higher temperatures the substance loses even its own volume and becomes a *gas*. Here, in the ideal case, its chemical particles move about freely, completely independent of each other. All attractive forces vanish, at least in comparison to the kinetic energies of the particles. In this gaseous, third state of matter the substance loses all identity of both volume and shape, taking those of whatever container encloses it (Fig. 19.6).

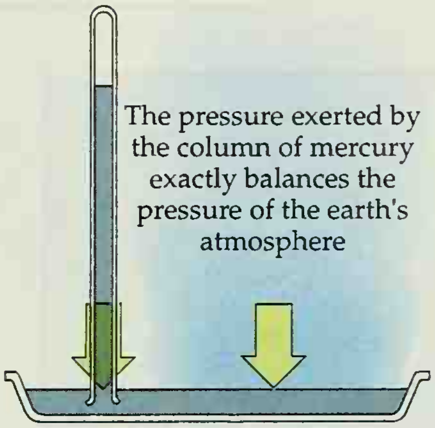


Figure 19.5
The Torricelli barometer.

QUESTION

As we inflate a bicycle tire, what shape and volume does the air take as it enters the tire? When a bicycle tire goes flat and the air that was inside it escapes into the open, what shape and volume does the air take as it leaves the tire? ____________

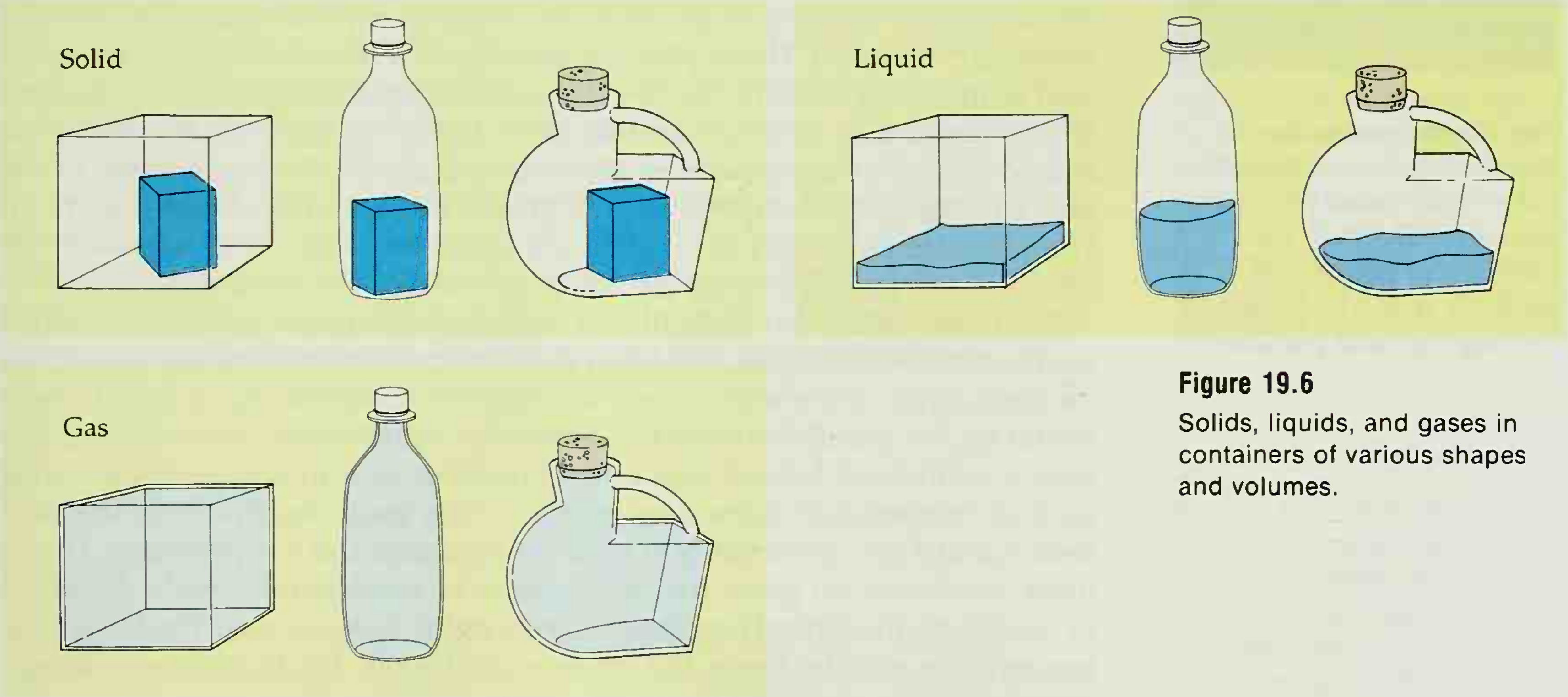


Figure 19.6
Solids, liquids, and gases in containers of various shapes and volumes.

19.2 The Kinetic-Molecular Theory: From Ricocheting Billiard Balls to Ideal Gases

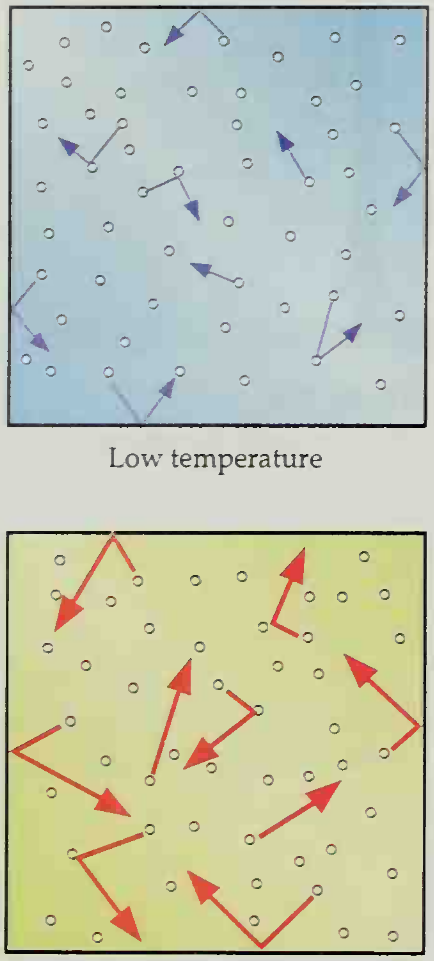


Figure 19.7
Molecular motion in an ideal gas. The higher the temperature, the greater the energy of molecular motions.

The **kinetic-molecular theory of gases** explains the behavior of gases by assuming that they are made up of point-sized, perfectly resilient, constantly moving chemical particles.

If you've ever used a hand pump to inflate a tire, you know that the pumping gets harder as the tire becomes fully inflated. Maybe you've checked a tire's pressure cold, before starting on a trip, and then again after it has warmed up from some travel. If you have, you know that the pressure rises as the tire and the air inside it heat up. Perhaps you've watched a hot air balloon being prepared for flight. As a flame warms the air inside, the heat makes the air less dense than the surrounding atmosphere, giving the balloon buoyancy, and finally lifting it upward. If you've emptied an aerosol can, down to the last bit of its contents, you've noticed a considerable drop in the pressure as the very last bit of propellent leaves the nearly empty canister. Maybe you've also read the label warning of a possible explosion if you toss the empty can into an incinerator.

Each of these gaseous phenomena we observe in today's world parallels in some way the observations made by a handful of 17th- and 18th-century scientists who were the first to study gases in a systematic way. Today we sum up the knowledge they gathered about the behavior of gases and the theories they formulated to explain that behavior into what we now call the **kinetic-molecular theory of gases**. According to this model, gases act—ideally, at least—as though their individual, component molecules or atoms were perfectly resilient, infinitesimal billiard balls, taking up no space whatever. They behave like completely elastic spheres that have no diameters, no circumferences, no volumes, and that move about continuously, bouncing merrily off each other and off the walls of their containers, losing no energy in the process and exerting absolutely no attraction for one another. Any gas made up of chemical particles that behave in exactly this way is an *ideal gas*.

According to this view the physical properties of any gas—or at least any gas that behaves as if it were an ideal gas—depend *only* on the *kinetic* energy (the energy of motion) of its *molecules*. (That's why it's called the "kinetic-molecular" theory.) These physical properties remain completely independent of the space actually filled by the molecules and completely independent of any real forces of attraction that draw them together. What's more, the kinetic energy of the molecules depends entirely on the temperature of the gas. The higher the temperature, the greater its molecular energy (Fig. 19.7). The pressure of the gas in an enclosed container results from repeated collisions of the particles of the gas with the walls of the container.

Of course atoms and molecules of real gases do occupy an extremely small but finite amount of space, and they do exert small but measurable attractions for each other. Otherwise no gas would ever condense into a liquid; there would be, for example, no such substance as liquid water. Nevertheless, this idea of point-sized billiard balls careening about with an energy that depends on their temperature alone does give us a very good description of the ideal behavior of a gas, particularly at high temperatures and low pressures. Under these conditions all gases follow a pattern of relationships easily described by simple mathematical equations known as the *ideal gas laws*. The higher the temperature and the lower the pressure of the gas, the more nearly the gas approaches the ideal and the more closely it follows these laws.

The gas laws come to us from the observations and the insights of the early scientists who studied the ways gases respond to changes in pressure, temperature, and volume, and who formulated the mathematical equations that describe their behavior. In the next few sections we'll examine the properties of gases through the eyes of the most important of these scientists:

Robert Boyle (Irish-English, 1627–1691)
Jacques Alexandre César Charles (French, 1746–1823)
Joseph Louis Gay-Lussac (French, 1778–1850)
William Thomson, Lord Kelvin (British, 1824–1907)
Amedeo Avogadro (Italian, 1776–1856)
John Dalton (English, 1766–1844)
William Henry (English, 1775–1836)

QUESTION

Describe two ways in which the chemical particles that make up a real gas differ from those of an ideal gas. ______________________________

19.3 Robert Boyle: Pressure and Volume

Robert Boyle, 14th child of the first Earl of Cork, Ireland, became the first of the great gas law investigators shortly after the middle of the 17th century. In 1657 he read of a newly devised air pump. With some ingenuity he improved its original design, built a model, and began studying the effects of pressure on the volume occupied by a quantity of air. Soon he described what we now know as **Boyle's Law**: *With the temperature and the number of moles of a quantity of gas held constant, the volume of the gas varies inversely with its pressure.* That is, with a fixed temperature and a fixed number of moles, as the pressure rises, the volume of the gas shrinks; as the pressure drops, the volume grows.

Robert Boyle discovered that, for a fixed quantity of gas at a constant temperature, the volume of a gas varies inversely with the pressure. As the pressure rises, the volume shrinks; as the pressure drops, the volume expands.

Take a specific, fixed weight (a fixed number of moles) of a gas and keep it at a constant temperature. As you increase the pressure on the gas you squeeze it into a smaller volume. Lower the pressure and the gas expands into a larger volume. More quantitatively, double the pressure and the volume of the gas drops to half (Fig. 19.8). Decrease the pressure to half, and the volume doubles. To whatever extent the pressure changes, the volume change is exactly the inverse. We can express this mathematically as

$$\text{pressure} \times \text{volume} = \text{a constant}$$

or

$$P \times V = k.$$

This equation tells us that with the temperature and the total number of molecules held constant, the product of the pressure and the volume of any fixed weight of a gas is always constant. Plotting an infinite number of pres-

Boyle's Law states that with the temperature and the number of moles of a quantity of gas held constant, the volume of the gas varies inversely with its pressure.

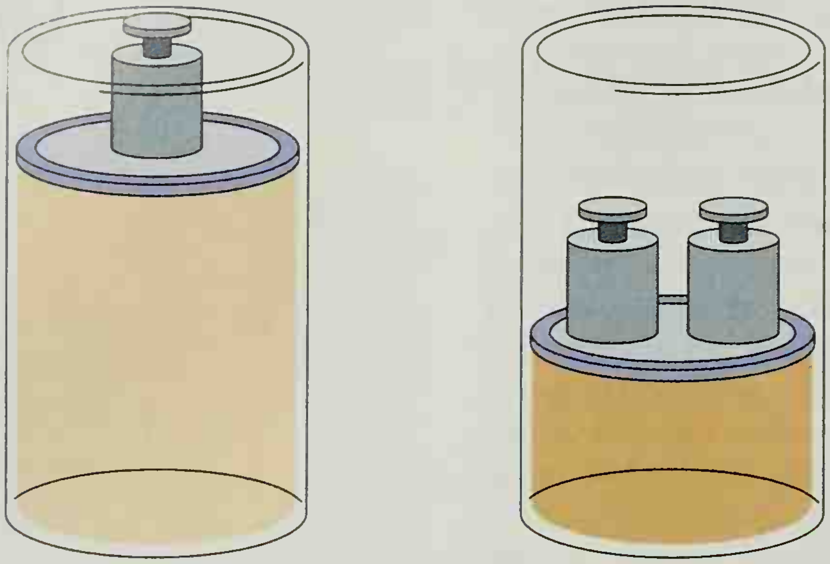


Figure 19.8

The effect of pressure on a gas. Double the pressure on the gas, at constant temperature, and its volume decreases to half.

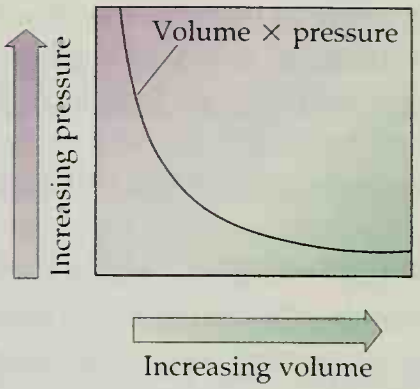


Figure 19.9

Boyle's Law: the pressure–volume relationship for a fixed quantity of gas maintained at constant temperature.

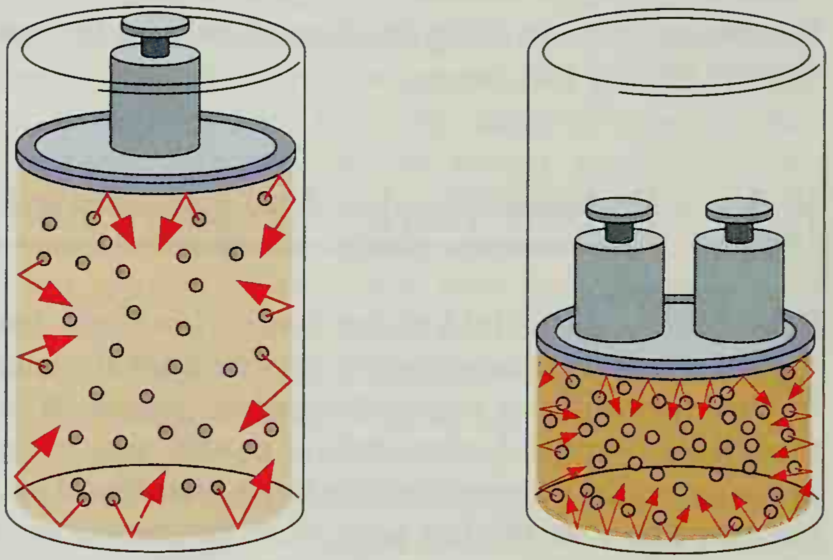


Figure 19.10

Boyle's Law and the kinetic- molecular theory of gases.

sures and the infinite number of corresponding volumes gives the curve in Figure 19.9.

The kinetic-molecular theory of ideal gas behavior explains Boyle's Law nicely. The pressure the gas exerts on the walls of its container results from the force of its molecular collisions with the walls. The greater the number of collisions at any instant, the greater the pressure on the container. Squeeze the gas into half its original volume and the rate at which the molecules bounce off the walls doubles and so does the pressure. Double the volume of the gas and the rate of collisions drops to half. So does the pressure. (This works both ways. Double the pressure exerted *on* the gas and the pressure exerted *by* the gas doubles in response. The only way this can occur, with the temperature and the total number of molecules kept constant, is for the gas's volume to decrease to half.) Figure 19.10 illustrates the connection between the kinetic molecular theory and Boyle's Law.

EXAMPLE A LITTLE LESS PRESSURE

Suppose that at sea level you fill a balloon, made of a perfectly elastic substance, to a volume of exactly 1 L. Now, keeping its temperature constant, you carry it up the side of a mountain to an altitude of some 900 meters, where the atmospheric pressure is exactly 90% of its value at sea level (Section 19.1). What would the new volume of the balloon be?

Although in solving this problem we use the equation for Boyle's Law, $P \times V = k$, we certainly don't have to know the actual numerical values of all the measurements involved, nor do we have to calculate the value of k. Since we're working with two different pressures (which we can call P_1 and P_2 to represent the first and second pressures, respectively) and also with two different volumes (V_1 and V_2, the first and second volumes), we can set up a ratio that eliminates k entirely. Since

$$P_1 \times V_1 = k$$

and

$$P_2 \times V_2 = k$$

and since the two k's are identical, then

$$P_1 \times V_1 = P_2 \times V_2$$

and

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

Since P_2 is 90% of P_1, we can set P_1 at 100 and P_2 at 90 without being concerned about the units, which cancel out in the fraction anyway. With just a little rearrangement this gives

$$\frac{V_2}{1.0 \text{ L}} = \frac{100}{90}$$

or

$$V_2 = 1.0 \text{ L} \times 100/90 = 1.1 \text{ L}$$

The volume of the balloon at the 900-m level is 1.1 L.

We'll use this sort of approach whenever possible as we consider the effects of conditions on the characteristics of a gas.

QUESTION

The volume of a quantity of a gas held at constant temperature and 760 mm-Hg pressure is 10 mL. What pressure does it take to reduce the volume to 8 mL? ________

19.4 Can a Gas Shrink to Nothing at All?

William Thomson, Lord Kelvin, devised the Kelvin temperature scale, in which temperature measurement begins at absolute zero and moves upward in Celsius degrees.

Charles' Law states that with the pressure and the number of moles of a quantity of gas held constant, the volume of the gas varies directly with its temperature.

Absolute zero is the lowest possible temperature. It is 0 K or −273°C.

Born 89 years after Boyle first read of the newly devised air pump, J. A. C. Charles turned to science from a career in the French Ministry of Finance. In 1787, four years after he became the first person to inflate a balloon with hydrogen gas (which is less dense than air) and to use it to ascend some 3 km into the atmosphere, Charles discovered that a quantity of gas kept at a constant pressure expands as it warms and contracts as it cools.

In 1802 Joseph Louis Gay-Lussac, lecture demonstrator at the French Ecole Polytechnique (and soon to become professor of physics at the Sorbonne), independently discovered what Charles had learned earlier about the effect of temperature on gases. Gay-Lussac went beyond Charles' works, though, as he discovered that for every one-degree (Celsius) change in temperature, this change in volume amounts to 1/273th of the volume the gas occupies at 0°C. Gay-Lussac exceeded Charles also in balloon ascensions, reaching a height of over 7 km, or well over 4 miles, and in gathering data on atmospheric temperature, humidity and chemical composition, and the strength of the Earth's magnetic field.

The combination of Charles' and Gay-Lussac's studies gives us the gas law now known generally as **Charles' Law**, in recognition of his earlier description of the principle: *With the pressure and the number of moles of a quantity of gas held constant, the volume of the gas varies directly with its temperature.* Mathematically, this amounts to

$$V = k \times T$$

with T representing the temperature. Charles' Law explains our opening demonstration nicely. As the heat of your hands increases the temperature of the gas inside the chilled bottle, the volume of the gas also increases, forcing it out as bubbles or as the short bursts that pop the coin.

TABLE 19.1 Boiling Points of Representative Gases

Gas	Formula	Approximate Boiling Point (°C, 1 atm)
Water	H_2O	+100
Chlorine	Cl_2	−35
Hydrogen chloride	HCl	−85
Methane	CH_4	−164
Oxygen	O_2	−183
Fluorine	F_2	−188
Nitrogen	N_2	−196
Hydrogen	H_2	−259
Helium	He	−269

The numerical value of the temperature used in this equation comes from a scale designed by the British physicist William Thomson, who was given the title of Lord Kelvin by Queen Victoria partly in recognition of his contributions to the design, manufacture, and placement of the first trans-Atlantic telegraph cable. The *Kelvin* or *absolute* temperature scale begins 273 degrees below the Celsius zero (−273°C), at **absolute zero**, and moves upward with degrees the same size as those of the Celsius scale. The zero of the Celsius thermometer becomes +273 on the Kelvin or absolute scale (Fig. 19.11). (The degree symbol, °, is not used in expressing temperatures on the Kelvin scale.) As the term *absolute* suggests, Lord Kelvin's zero represents the lowest possible temperature. Nothing can become colder than absolute zero, 0 K or −273°C. To convert from a Celsius temperature to Kelvin, add 273 to the Celsius reading; from Kelvin to Celsius, subtract 273 from the Kelvin value.

The physical relationship that Charles and Gay-Lussac independently discovered implies that an ideal gas, with its volumeless chemical particles, would vanish completely at absolute zero. Mathematically,

$$V = k \times T$$

If $T = 0$, then

$$V = k \times 0 = 0$$

But all gases show ideal behavior only at *high* temperatures (and low pressures), not at temperatures anywhere near absolute zero. The real volumes of gas particles and the real attractive forces they exert on each other cause all real gases to liquefy as temperatures drop and pressures rise. The ideal world of bouncing, point-sized billiard balls fades into the real world of substance, of actual atoms and molecules. At a pressure of 1 atmosphere (1 atm), for example, helium liquefies at −268.9°C, or 4.1 K. The boiling points of some representative gases appear in Table 19.1. These are the temperatures at which the liquids boil to become real gases, and at which the real gases condense to liquids.

The relationship between the volume of an ideal gas and its temperature appears graphically in Figure 19.12. As with Boyle's Law, the kinetic-molec-

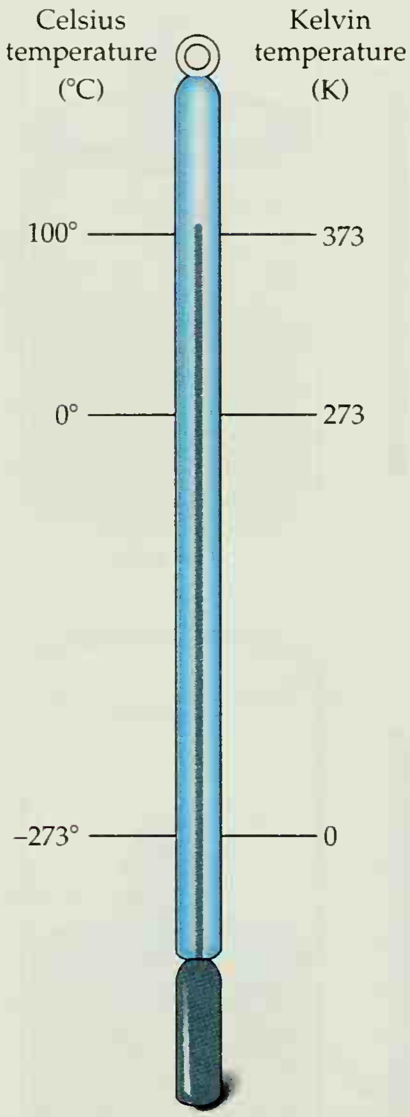


Figure 19.11
Celsius and Kelvin (absolute) temperature scales.

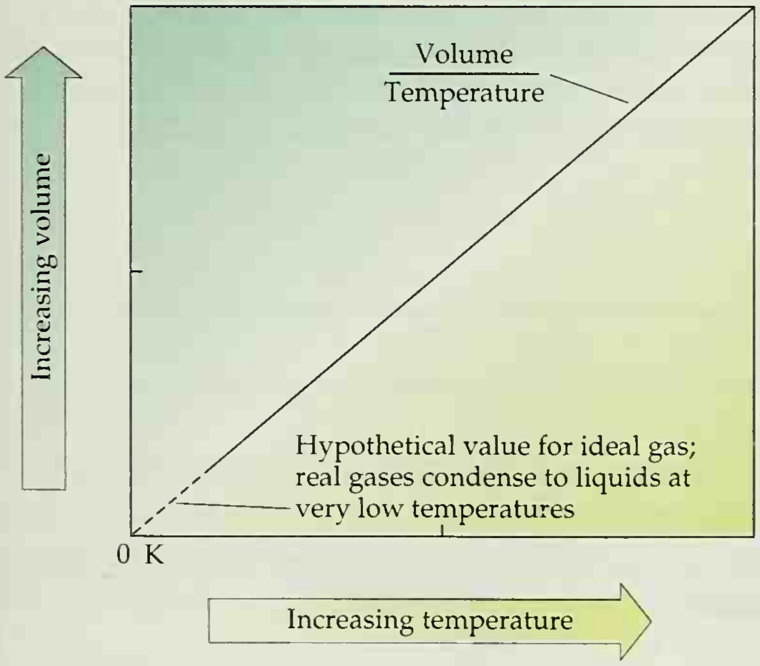


Figure 19.12
Charles' Law: the temperature–volume relationship for a fixed quantity of gas maintained at a constant pressure.

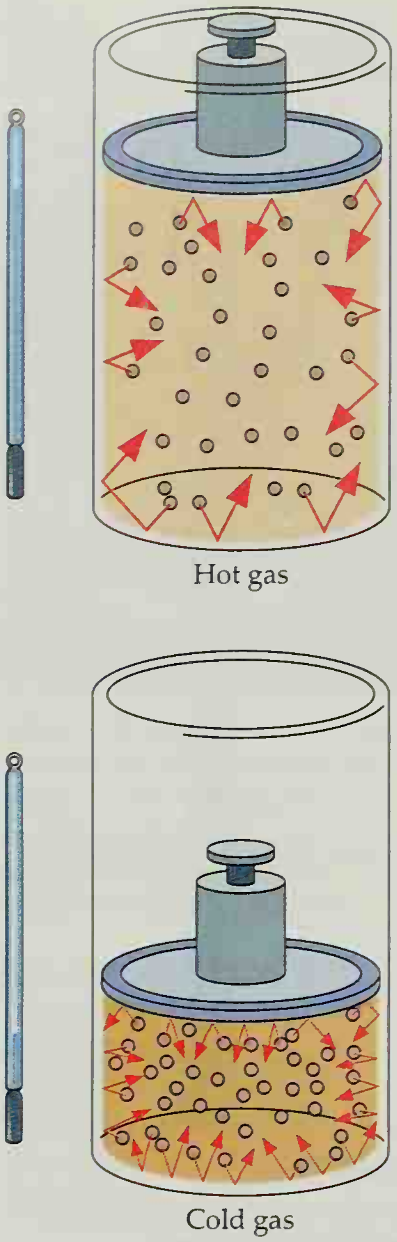


Figure 19.13
Charles' Law and the kinetic-molecular theory of gases: At constant pressure, as the temperature increases, so does the volume.

ular theory works nicely here too. As the temperature of a gas drops, so does the kinetic energy of its molecules. At the lower temperature they don't bounce off each other or off the walls of their container with quite as much energy or as often as they do at the higher temperature. To maintain the constant pressure on the walls of the container, the volume of the gas must shrink. On the other hand, as the temperature rises the energy and frequency of collisions also increase and so does the volume if the pressure is to remain constant (Fig. 19.13).

EXAMPLE THE SHRINKING BALLOON

As an illustration of Charles' Law, suppose we start by blowing up a balloon to a volume of 1 L at 27°C and then place it in a refrigerator kept at 7°C. Now we'll ask: What is the volume of the balloon when the gas in it cools to the refrigerator's temperature?

We can solve the problem with the same kind of ratio we used for Boyle's Law. Since $V_1 = k \times T_1$ and $V_2 = k \times T_2$, the ratio becomes

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

To find V_2 we'll use Kelvin temperatures of $(27°\text{C} + 273) = 300$ K for T_1 and $(7 + 273) = 280$ K for T_2. This gives us

$$\frac{V_2}{1\text{ L}} = \frac{280}{300}$$

$$V_2 = 1\text{ L} \times 280/300 = 0.933\text{ L} = 933\text{ mL}$$

QUESTION

Suppose that the smallest decrease in volume you could see easily is 20%. (That is, the balloon would have to shrink to 80% of its original volume for the decrease in volume to be visible.) To what *Celsius* temperature would you have to cool the balloon, filled at 27°C, so that you could actually see it contract? ____________

19.5 Putting Them All Together

So far we've seen two laws that describe the behavior of gases:

- Boyle's Law, which relates pressure and volume for a fixed mass of gas held at a constant temperature, and
- Charles' Law, which relates volume and temperature for a fixed mass of gas held at a constant pressure

Instead of treating these as two distinct laws, independent of each other, we can combine them into a single law that describes the interrelationship of the pressure, volume, and temperature of a fixed mass of gas. We can write this combination of Boyle's Law and Charles' Law in the following convenient form:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

EXAMPLE COUNTERACTING FORCES

To illustrate the use of the combined gas law, we'll return to Gay-Lussac's balloon voyage up 7000 m. At that height the atmospheric pressure drops to about 300 mm-Hg and the temperature could easily cool to a chilly −33°C. Let's suppose Gay-Lussac carried with him our small balloon, filled to 1 L at sea level with a pressure of 760 mm-Hg and a temperature of 27°C. What would its volume ultimately be when he reached a height of 7000 m?

This 1-L balloon would be subjected to two contrasting effects during the ascent. The pressure drop as it rose would tend to cause the balloon to expand, while the decrease in temperature would tend to make it contract. The answer to the question requires using the combined equation.

With

P_1 = 760 mm-Hg
V_1 = 1 L
T_1 = (27°C +73) = 300 K
P_2 = 300 mm-Hg
T_2 = (−33°C + 273) = 240 K

we can rewrite the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

as

$$\frac{760 \text{ mm-Hg} \times 1 \text{ L}}{300 \text{ K}} = \frac{300 \text{ mm-Hg} \times V_2}{240 \text{ K}}$$

Solving for V_2

$$\frac{1 \text{ L} \times 760 \text{ mm-Hg} \times 240 \text{ K}}{300 \text{ mm-Hg} \times 300 \text{ K}} = 2.03 \text{ L}$$

We find, then, that the decrease in pressure would produce a much greater effect than the decrease in temperature. The balloon's volume would almost exactly double.

EXAMPLE **WARNING!**

Labels on spray cans warn not to dispose of the empty can in an incinerator since it might explode (Section 19.2). Why would the can explode?

The answer comes from the combined gas law. Even when the can is "empty," a small amount of gas remains inside, at a pressure equal to atmospheric pressure. Since the can is sealed, the volume of this remaining gas remains constant, $V_1 = V_2$, and the combined gas law becomes

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

This tells us that as the temperature of the gas in the sealed can rises, so does the pressure. At some high temperature the pressure of the sealed gas would become great enough to rupture the can and produce an explosion.

QUESTION

Now let's take our 1 L balloon down to the bottom of Death Valley, California. It's the lowest point in the United States, 86 m below sea level, with a mean atmospheric pressure close to 770 mm-Hg. The hottest temperature ever recorded in the United States was in Death Valley: 57°C (135°F) on July 10, 1913. Suppose we take our balloon, filled at sea level on a pleasant day (760 mm-Hg and 27°C), and carry it to the depths of Death Valley on a day that equals the record for temperature (770 mm-Hg and 57°C). Will it expand or will it contract, and what will the new volume be? ________

19.6 Gay-Lussac Once Again

Gay-Lussac's Law states that when gases react with each other at constant temperature and pressure, they combine in volumes that are related to each other as ratios of small, whole numbers.

Even with his important work in relating volume to temperature and in studying the atmospheric composition, Gay-Lussac is probably better known for yet another discovery, one that now bears his name. **Gay-Lussac's Law** states that *when gases react with each other at constant temperature and pressure, they combine in volumes that are related to each other as ratios of small, whole numbers.* If the product is also a gas, its volume, too, is related to the volumes of the reacting gases as a small, whole number.

For example, if we set up conditions so that hydrogen gas and nitrogen gas react to produce ammonia gas, we'd find that the volume of the hydrogen that enters into the reactions is exactly three times the volume of the reacting nitrogen. We'd also find that the volume of the gaseous ammonia produced is exactly twice the volume of the nitrogen used. Notice that these proportions are not only small, whole numbers, but they're in exactly the same ratio as the numbers of the molecules present in the balanced equation for the reaction:

$$3H_2 + N_2 \rightarrow 2NH_3$$

QUESTION

When gaseous oxygen and gaseous hydrogen react to form water, in what volume ratio do the hydrogen and the oxygen react? (Writing a balanced equation for the reaction helps. See Chapter 9 for a review.) ______________________

19.7 Avogadro Carries Us Further Along

Every time you blow up a balloon or pump up a flat tire, you see still another gas law in action, one that's closely related to Gay-Lussac's. Amedeo Avogadro, born in Turin, Italy, June 9, 1776, less than one month before the Declaration of Independence was signed in Philadelphia, carried Gay-Lussac's reasoning one step further. Avogadro recognized that since the *volume* ratios of reacting gases are identical with the *molecular* ratios of balanced equations, the volume of a gas must reflect the number of atoms or molecules within it. This gives us **Avogadro's Law**: *Equal volumes of different gases (at the same temperature and pressure) contain equal numbers of atoms or molecules.* Put another way, at constant temperature and pressure the volume of a gas is directly proportional to the number of moles present, or

Avogadro's Law states that equal volumes of different gases (at the same temperature and pressure) contain equal numbers of atoms or molecules.

$$V = k \times n$$

where k is a constant and n is the number of moles. The more moles there are, the larger the volume. The more air we put into a deflated balloon or tire, the bigger it gets.

If we're using a hand pump to put air into a tire, the volume hardly changes after we've inflated it a bit. Under this condition of nearly constant volume, the pressure we're working against increases with each additional stroke and the pumping becomes harder.

QUESTION

You have a balloon that contains 2 L of hydrogen and 1 L of oxygen for a total of 3 L of gas. If the hydrogen and oxygen combine within the balloon to produce gaseous water (without bursting the balloon), will the balloon grow larger or smaller as a result? Remember, when the water forms there's no hydrogen or oxygen left. __________

19.8 John Dalton and William Henry Explain Why Soft Drinks Go Flat

John Dalton and William Henry round out our early explorers of the properties of gases. Dalton, who was born in northern England in 1766 and spent his life teaching mathematics and science in Manchester, stated what we now know as **Dalton's Law**: *The total pressure of a mixture of gases equals the sum of the partial pressures of each of the gases in the mixture.* The term **partial pressure** itself refers to the pressure each gas would exert, at the same temperature and in the same volume, in the absence of all the other gases.

Dalton's Law states that the total pressure of a mixture of gases equals the sum of the partial pressures of each of the gases in the mixture.

The **partial pressure** of each gas is the pressure each gas would exert, at the same temperature and in the same volume, in the absence of all the other gases.

TABLE 19.2 Partial Pressures of the Major Atmospheric Gases

Gas	Percentage of Atmosphere (by Volume)	Mole Fraction	Approximate Partial Pressure (mm-Hg)
Nitrogen	78.1	0.781	594
Oxygen	20.9	0.209	159
Argon	0.9	0.009	7
Carbon dioxide	0.03	0.0003	0.2

The total pressure of any mixture of gases, then, is

$$P(\text{total}) = p\text{A} + p\text{B} + p\text{C} + \ldots$$

where pA represents the partial pressure of gas A, pB represents the partial pressure of gas B, and so on. For air, the total pressure represents the sum of the partial pressures of each of its component gases—N_2, O_2, etc. Since the partial pressure of each component gas reflects the fraction of its molecules in the total number of molecules of the entire mixture, we can use the *mole fraction* of each component gas to calculate its partial pressure. (The *mole fraction* represents the ratio of the number of moles of each component to the total number of moles present.) Partial pressures for the gases that make up the air we breathe appear in Table 19.2.


John Dalton, who found that the pressure of a mixture of gases is the sum of the partial pressures of each of the gases in the mixture.

Here again we see that still another one of the gas laws, Dalton's Law, supports the kinetic-molecular theory of the ideal gas. As the particles of any particular gas bounce around within a container, unaffected by each other, they're equally unaffected by the chemical particles of any other gas that may be present. Each gas, acting independently of the others, exerts its own pressure, with the total pressure equal to the sum of each of the individual, partial pressures.

William Henry, our final gas law scientist, was born in 1775 in Manchester, the same city where John Dalton would later find his career as a teacher. Henry's discovery that, at a fixed temperature, *the quantity of a gas that dissolves in a liquid depends directly on the pressure of that gas above the liquid,* has become **Henry's Law**. That is, the higher the pressure of a gas above a liquid, the greater the amount of dissolved gas in the liquid. On the other hand, as the pressure of a gas above a liquid drops, so does the amount of the gas that's dissolved in the liquid.

Henry's Law states that at a fixed temperature the quantity of a gas that dissolves in a liquid depends directly on the pressure of that gas above the liquid.

Now we can explain nicely why there's a rush of gas when we open a bottle of soda, why effervescence begins after the container is opened, and why a bottle of soda eventually goes flat if it stands unstoppered. Knowing that the sparkle of a carbonated drink comes from its dissolved carbon dioxide, we can put the gas laws into operation:

1. *Henry's Law*: To put plenty of CO_2 into the drink, the container is sealed under a high pressure of the gas.
2. *Boyle's Law*: When we open the can or the bottle, the pressure above the liquid drops quickly to atmospheric pressure and the pressurized gas in

Henry's Law
High pressure of CO_2 in sealed container causes CO_2 to dissolve in carbonated drink.

Boyle's Law
When cap is removed the pressure drops to atmospheric, causing the gases to expand and escape.

Dalton's Law
Partial pressure of CO_2 above the liquid drops as well.

Henry's Law
With drop in partial pressure of CO_2 above liquid, the solubility of CO_2 in the drink also drops. With continued loss of CO_2, the drink eventually goes flat.

Figure 19.14
The gas laws and a carbonated drink.

the space immediately above the drink expands and escapes into the room with the familiar hissing sound.

3. *Dalton's Law*: With the decreased total pressure of all the gases above the drink, the partial pressure of the gaseous CO_2, which is part of that gaseous mixture, drops as well.
4. *Henry's Law, again*: The concentration of the CO_2 dissolved in the drink shrinks proportionately.

As the drink stands unstoppered the very low partial pressure of the atmospheric CO_2 (0.2 mm-Hg, Table 19.2) allows almost all of the CO_2 to escape from its liquid solution, causing the soda to go flat (Fig 19.14).

QUESTION

Henry's Law applies at constant temperature. If we vary temperature but keep pressure constant, we find that the solubility of any gas in a liquid drops with increasing temperature. What is the chemical composition of the bubbles that form in a heated pot of tap water long before it begins to boil? ______________________

19.9 Don't Shake a Warm Bottle of Soda; Also Some Advice About an Aquarium

Henry's Law tells us all we need to know about the actual solubility of a gas in a liquid, but it says nothing about how fast the gas dissolves or how fast it comes out of solution. It doesn't tell us anything about the rates of the two processes or how to change them.

We know from experience that a carbonated beverage loses its CO_2 slowly. We can watch the bubbles form on the sides and bottom of a glass and rise

A combination of the laws of gases, including their low solubility in a warm liquid, causes this to happen when you shake a bottle of warm soda before you open it.

to the top slowly, over a reasonably long period, before the drink goes flat and the entire process slows or stops. But shaking a bottle or a can of soda, especially a warm one in which the solubility of the CO_2 is low (see the question at the end of the preceding section), often causes the drink to foam up and spill out of the container when we open it.

This foaming results from a process called *nucleation*. Shaking the soda causes microscopic bubbles of the gas in the space above the drink to become trapped inside the liquid. These serve as nuclei around which dissolved CO_2 can come out of solution to form gas bubbles quickly as we open the can or bottle and the external CO_2 pressure drops sharply. With the sudden drop in the external pressure and the rapid formation of a large number of CO_2 bubbles around the gaseous nuclei, the drink foams up and gushes out.

Nucleation can also occur on the surface of a solid. Try adding a few crystals of table sugar to a freshly poured soft drink. As soon as the sugar granules enter the liquid, they provide a surface for nucleation and result in a rush of gas bubbles.

The reverse process, dissolving a gas, requires a high pressure or a large surface area, preferably both. At atmospheric pressure a large area of contact between the gas and the liquid helps speed the flow of the gas into solution. Like other animals, fish need oxygen for life; they depend on the atmospheric oxygen that dissolves at a partial pressure of 159 mm-Hg (for dry air; Table 19.2) through the surface of the waters of lakes, streams, oceans, and home aquaria. To provide plenty of oxygen for an aquarium containing several fish, it's usually necessary to pump air into the aquarium water as a stream of small bubbles. The smaller the bubbles the better, because as a sphere shrinks its volume decreases more rapidly than its surface area. Plenty of small air bubbles present a larger surface area, per volume of gas, than a few large ones. This high ratio of surface area to the volume of gas permits an effective transfer of the oxygen into the water.

Because of their higher ratio of surface area to volume, small bubbles of gas transfer their oxygen to water more effectively than large bubbles.

QUESTION

Which would you expect to produce more bubbles, faster, in a carbonated drink, a little granulated sugar or the same weight of powdered sugar? Why? ____________

19.10 The Art and Science of Breathing

The simple act of breathing provides us with the most common and the most important application of the gas laws to our everyday lives. We breathe simply to exchange the oxygen of the air for the carbon dioxide produced by the body's cells as they metabolize macronutrients. As an illustration we can use the cellular oxidation of glucose to carbon dioxide, water, and energy.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6O_2} \longrightarrow \underset{\text{water}}{6H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{6CO_2} + \text{energy}$$

A tank of compressed gas furnishes oxygen at a partial pressure high enough to allow normal breathing underwater.

Our cells use or store the energy that's generated, as we saw in earlier chapters, and the water becomes part of our general physical inventory. But the carbon dioxide, a waste product, has to be transported by the blood from the cells to the lungs so that it can be eliminated in exhaled breath.

In a normal, healthy adult, the blood reaches the lungs carrying its cargo of CO_2 at a concentration equivalent to what we'd find in a solution that's under a partial pressure of 45 mm-Hg of carbon dioxide at normal body temperature. Henry's Law tells us that at any specific temperature the concentration of a gas in a solution is directly related to its partial pressure above the fluid. Knowing this we can use pCO_2 = 45 mm-Hg (or simply "45 mm-Hg") to define the concentration of carbon dioxide in the blood reaching the lungs. (Here, pCO_2 represents the partial pressure of CO_2; Section 19.8.)

This blood coming into the lungs through the blood vessels also carries residual, unused oxygen at a concentration of 40 to 45 mm-Hg. Within the lungs the blood, with its dissolved gases, passes through the capillaries of the *alveoli*, the very small sacs that terminate the bronchial network. We'll leave the blood here in the alveolar capillaries for a moment as we examine the gases that fill the alveolar sacs themselves.

As we inhale, the pressure inside our expanding lungs drops slightly and the outside air, traveling from a region of higher, external atmospheric pressure to a slightly lower internal pressure, enters the lungs. Once inside, the air's oxygen moves continuously to regions of ever lower partial pressure until it comes, finally, to the interior of the alveoli. Here the gaseous oxygen's partial pressure is at its lowest, about 100 mm-Hg. Within the sac itself, and still moving from a region of higher partial pressure to one of lower pressure, the oxygen passes through the thin membrane of the capillary wall and enters the fluid (blood) that's moving within the blood vessel (Fig. 19.15). With the passage of oxygen across the wall and into the capillary, the concentration of oxygen within the blood increases from the 40 to 45 mm-Hg of venous blood to arterial blood's 100 mm-Hg.

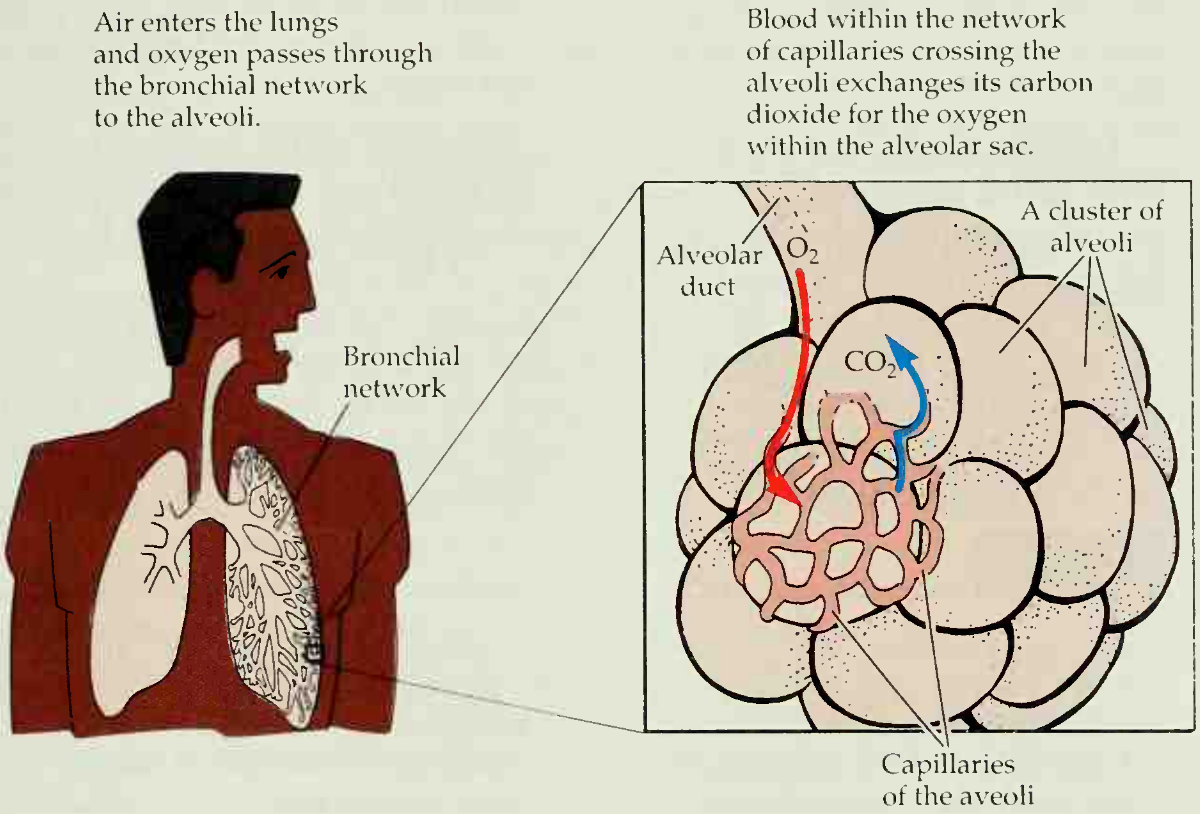
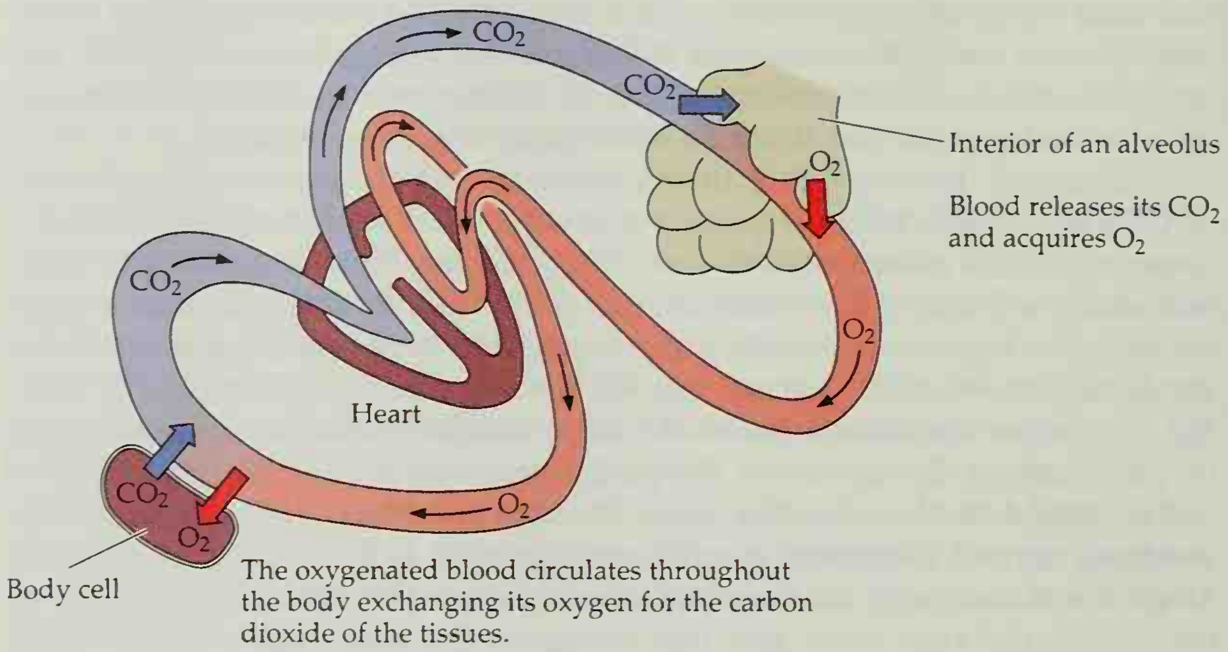


Figure 19.15
The lungs and the alveoli.

Figure 19.16

The movement of oxygen and carbon dioxide within the body.

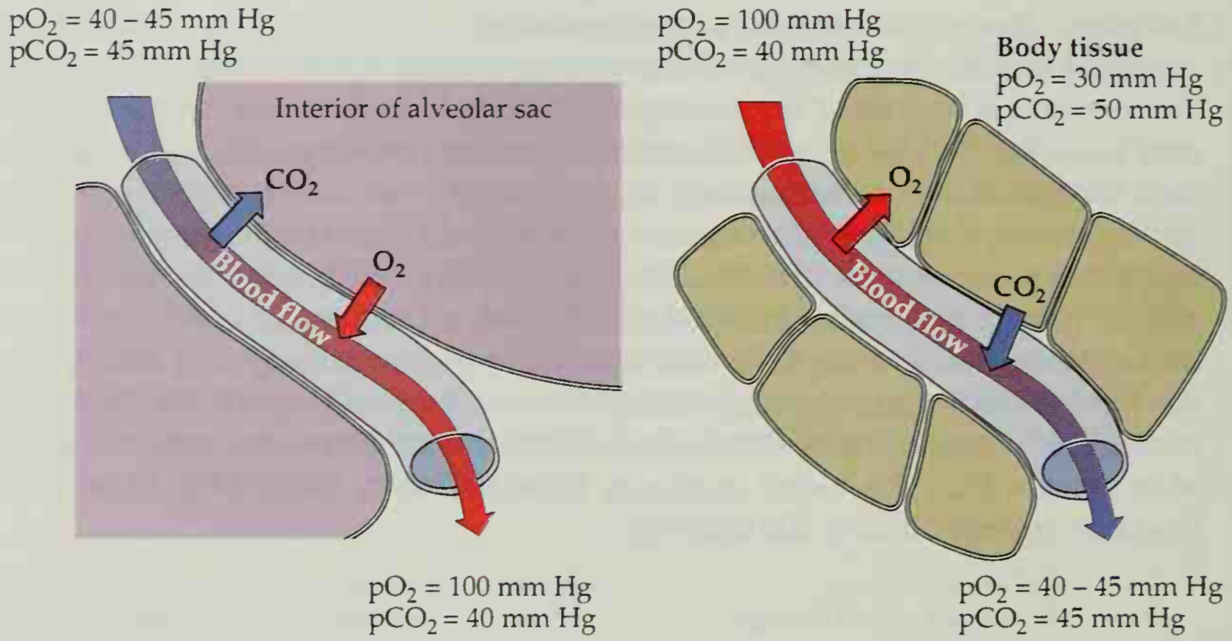


Blood releases its CO_2 and acquires O_2

The oxygenated blood circulates throughout the body exchanging its oxygen for the carbon dioxide of the tissues.

Figure 19.17

Partial pressures and gas flows to and from the blood. Both oxygen and carbon dioxide flow from regions of high partial pressure to regions of low partial pressure.



Meanwhile, the dissolved carbon dioxide travels in the opposite direction. With partial pressures of 45 mm-Hg in the blood and only a few tenths of a mm-Hg within the alveolar sac, the carbon dioxide passes through the membranes and into the alveoli to become part of the exhaled breath.

The blood itself, now enriched with oxygen and diminished in its carbon dioxide, leaves the lungs for its journey through the arteries to the cells, where it finds partial pressures of 30 mm-Hg or less for O_2 and at least 50 mm-Hg for CO_2. The process is reversed as the gases flow again from higher pressures to lower pressures, and the cycle is renewed (Figures 19.16 and 19.17).

QUESTION

Two gases constitute 99% of the (dry) air we inhale: nitrogen (78.1%) and oxygen (20.9%). Four gases make up virtually all of the air we exhale: nitrogen (74.9%), oxygen (15.3%), carbon dioxide (3.7%), and another gas that accounts for just over 6% of our exhaled breath. What is this fourth gas that makes up an even larger fraction of our breath than does carbon dioxide, and where does it come from? ______________

19.11 A Toxic Gas That Preserves Life

The atmosphere serves not only as our source of oxygen, as the repository of our exhaled carbon dioxide, and as the generator of our weather, but also as a shield protecting us from several unwelcome extraterrestrial events and forces. Virtually all meteorites, for example, burn up from the heat generated by atmospheric friction well before they reach the earth's surface. The atmosphere serves, too, as a protection against damaging and ultimately deadly ultraviolet radiation from the sun.

As we saw in Section 16.8, the sun's ultraviolet radiation converts the skin's 7-dehydrocholesterol into vitamin D_3. This vitamin formation may well be the only beneficial effect of ultraviolet radiation on human skin. This ultraviolet region of the solar spectrum is very high in energy and can easily destroy living cells and tissue. As anyone who has ever suffered a sunburn knows, acute exposure to these rays can produce severe and painful burns. A tan, sometimes considered a sign of good health or of easy living, is actually the skin's response to this damaging radiation. The darkening, which we interpret as a tan, acts to protect the skin from radiation damage. Nevertheless, long-term exposure to ultraviolet radiation, even at levels far below those that burn, can cause premature aging of the skin and unwanted and harmful changes to its structure, including cancer.

Sunburns and prematurely aged and cancerous skin are the effects of the relatively weak ultraviolet radiation that reaches the earth's surface. Exposure to *intense* solar radiation, unfiltered by the atmosphere, would present a lethal hazard to all forms of unprotected life, ranging from the lowly microorganisms that thrive on the surface of the oceans (and that serve as food to the larger creatures of the sea) to the exposed, higher land animals including humans. Fortunately these damaging ultraviolet solar rays themselves transform a zone of the stratosphere into a protective *ozone layer* that effectively screens out most of the remainder of the harmful solar radiation, thereby protecting the surface of the earth much as a tan protects the skin. Without this ozone layer life could never have emerged from the protection of the primordial seas; should the ozone layer vanish now, life as we know it could not survive on the surface of the earth. We'll examine the ozone layer after we look more closely at ozone itself and one of its undesirable effects on life.

Ozone is a triatomic form of oxygen with the molecular formula O_3. It contains more energy and is less stable than the more common, diatomic oxygen, and it's also better able to absorb ultraviolet radiation. Ozone forms in a variety of ways. As electrical currents pass through the air, from lightning or from a sparking motor or electrical appliance, they add energy to diatomic oxygen molecules, transforming them into unstable, triatomic ozone molecules. The same thing happens as ultraviolet radiation passes through the atmosphere and adds energy to oxygen molecules.

Ozone also forms as an indirect result of the operation of the internal combustion engine. It's part of a complex process that involves oxides of nitrogen as well. Among the pollutants of exhaust gases is a compound of nitrogen and oxygen called *nitric oxide*, NO. When nitric oxide enters the atmosphere it reacts with oxygen to produce *nitrogen dioxide*, NO_2, a red-brown gas.

$$\underset{\text{nitric oxide}}{2NO} + O_2 \longrightarrow \underset{\text{nitrogen dioxide}}{2NO_2}$$

A **thermal inversion** occurs when a layer of warm air lies above a layer of cooler air, trapping it and any pollutants within it.

Nitrogen dioxide is a particularly nasty air pollutant. It causes irritation to the eyes and the respiratory system. Even short exposures to concentrations near 200 ppm (Section 9.11) can cause death. Accumulation of nitrogen dioxide in the air above urban areas produces a red-brown haze often associated with air pollution. A haze of this sort is especially noticeable during periods of **thermal inversion**, which occur during abnormal weather. Normally, air temperature decreases with altitude, with warmer layers of air lying near the ground and cooler air above. Occasionally a layer of warm air moves over a cooler layer below it. This inversion of the normal temperature profile traps the cooler air and all the gases in it, including pollutants, until more normal atmospheric conditions return.

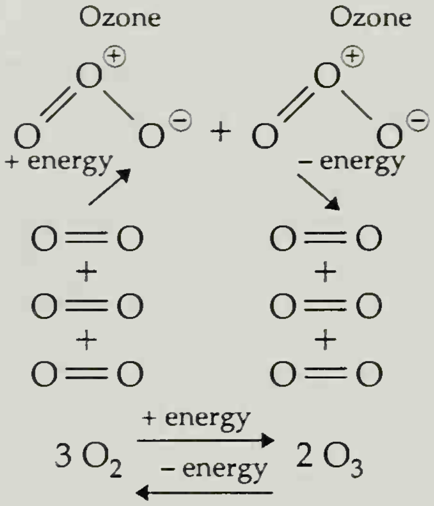


Figure 19.18

Oxygen and ozone. The addition of energy to oxygen molecules converts them to ozone molecules. The loss of energy from ozone molecules converts them to oxygen molecules.

Not only does NO_2 act as a pollutant itself, but it's also responsible for the formation of ozone, which is also an air pollutant. Under the influence of sunlight, a combination of nitrogen dioxide and atmospheric oxygen produces ozone (and other products as well). With time, the triatomic ozone molecules lose their added energy and decay back to the less energetic, more stable diatomic oxygen molecule (Fig. 19.18). As a result, concentrations of ozone in the atmosphere of urban areas reach their maximum during the day, with both intense automobile traffic and intense sunlight contributing to their formation, and drop at night.

Transient, relatively low atmospheric concentrations of ozone formed during electrical storms can add a pleasant, "fresh" quality to the air. But breathing ozone over a longer term, ranging from a few minutes to several hours, and at concentrations as low as 1 ppm in air (such as we might find consistently near sparking machinery, electrical generators, and some types of photocopiers), can lead to sore throats, general bronchial irritation, coughing, and fatigue. Much higher concentrations can kill. Ozone is also lethal to lower forms of life, including bacteria. In Europe ozone is widely used as a disinfectant for community water supplies, much as chlorine is used in the United States.

Like so many other chemicals we've examined, ozone can be beneficial or harmful, depending on the circumstances. It's an irritating, toxic gas that, ironically, shields surface life from the catastrophic effects of overwhelming ultraviolet solar radiation. In the air we breathe, especially in the air of urban areas with large numbers of cars, ozone is a pollutant; in the upper atmosphere it's a lifesaver.

The **ozone layer** is a layer of ozone lying within the stratosphere and centered some 30 to 35 km (about 20 miles) above the earth. It protects life at the surface of the earth by absorbing a portion of the sun's ultraviolet radiation.

A layer of ozone surrounds the earth within the stratosphere. This **ozone layer** is centered, roughly, some 30 to 35 km (about 20 miles) above the earth's surface. Its average altitude, shape, and dimensions vary over a large range with changes in latitude, the seasons, and the intensity of solar radiation. It forms as oxygen atoms, torn out of their diatomic molecules by the intense solar radiation at higher levels of the atmosphere, work their way downward into the stratospheric zone and combine with diatomic oxygen (Fig. 19.19). Absorption of ultraviolet radiation by an ozone molecule within the ozone layer regenerates an oxygen atom and a bimolecular oxygen molecule. Left undisturbed over the millennia, this cycling between the formation and de-

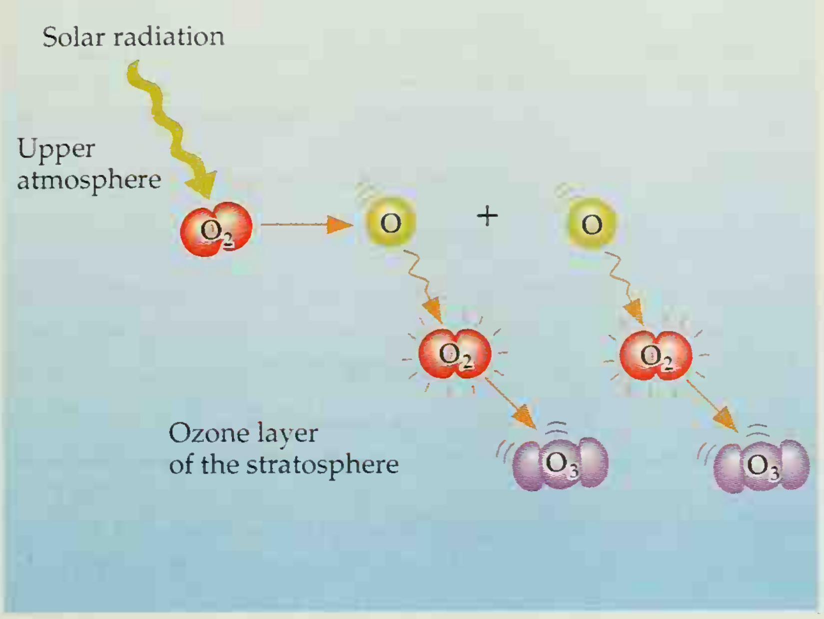


Figure 19.19
Formation of the ozone layer.

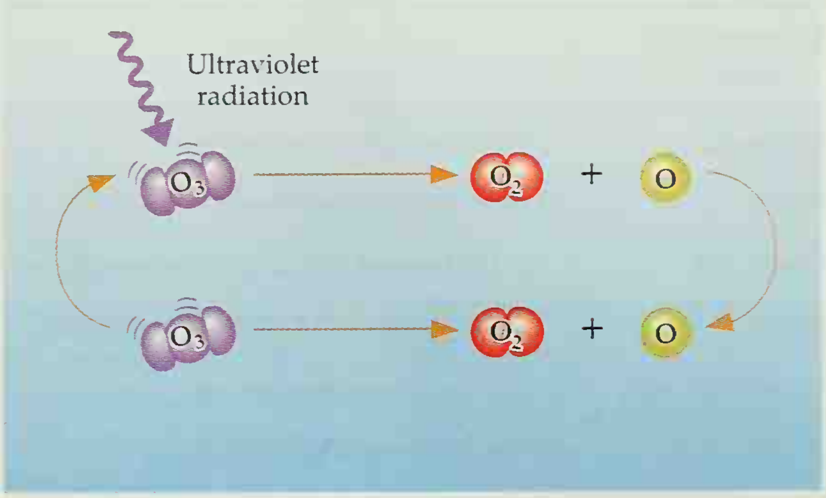


Figure 19.20
Ozone–oxygen cycling in the ozone layer.

struction of ozone molecules has produced a reasonably steady concentration of ozone that has allowed surface life to evolve and thrive under its invisible shield (Fig 19.20).

QUESTION

In what circumstance is ozone beneficial to life? In what circumstances is it harmful? ____

PERSPECTIVE: A Class of Wonder Gases Turned (Potentially) Lethal

Although a reasonably stable ozone layer has existed in the upper atmosphere for countless centuries as a result of a steady balance between the formation of ozone in the stratosphere and its natural decay to oxygen molecules, something new and unexpected seems to be happening. It appears that the widespread commercial use of a class of gases—the *chlorofluorocarbons* (CFCs) and closely related compounds known as *halons*—may be shifting the balance and eroding the ozone layer.

As consumers we recognize many of these chlorofluorocarbons (compounds of chlorine, fluorine, and carbon) by their more familiar commercial name, *Freon*. The word is a trade name of the DuPont Corporation, the corporate inventor of the CFCs (in the 1930s) and the world's leading producer (Table 19.3). (The halons are related compounds in which one or more bromine atoms replace the chlorines of the CFCs. Halons and CFCs are sometimes grouped together under the general term "halocarbon.") The CFCs and

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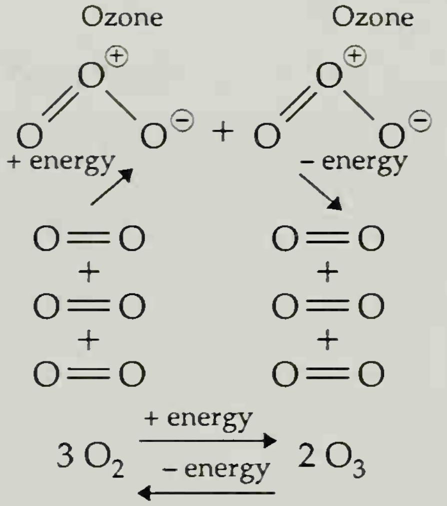

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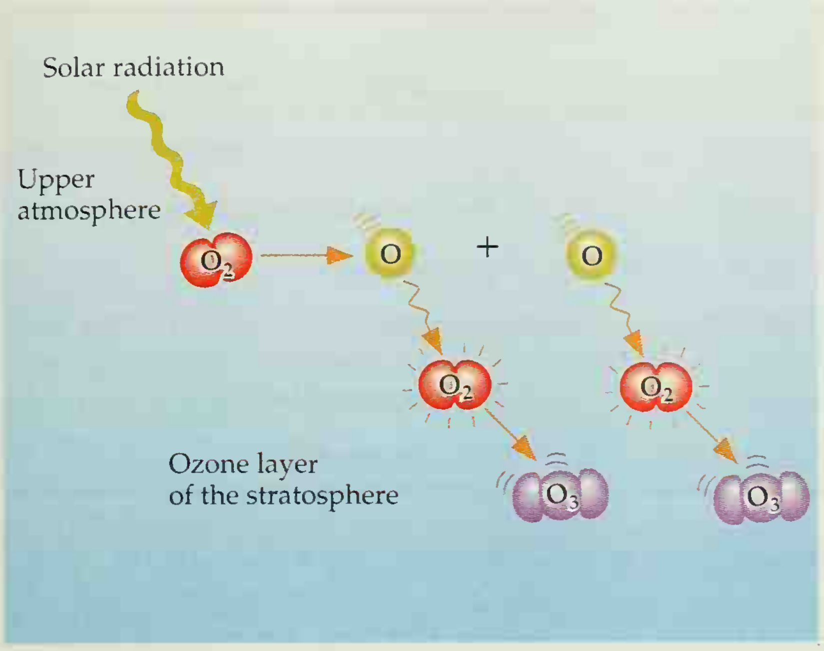

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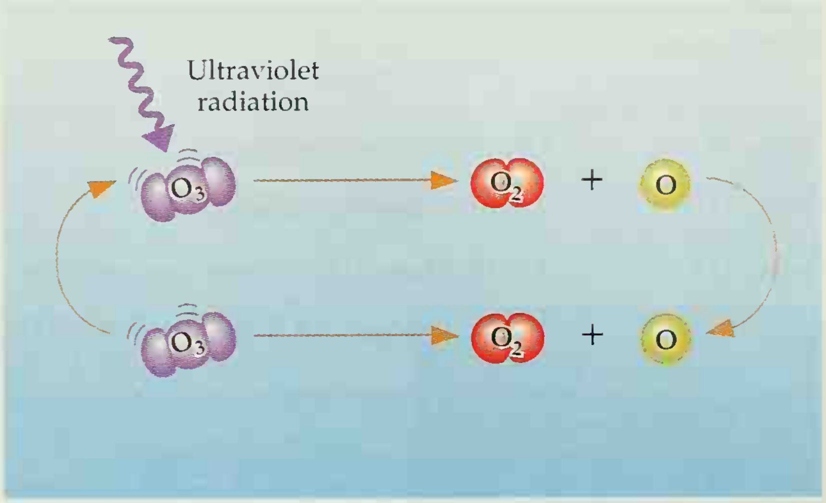

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TABLE 19.3 Typical Chlorofluorocarbons and Halons

Commercial Name	Chemical Name	Formula	Major Commercial Uses
Freon 12	Dichlorodifluoromethane	CCl_2F_2	Refrigerant, manufacture of foam
Freon 11	Trichlorofluoromethane	CCl_3F	Refrigerant, manufacture of foam
Freon 114	1,2-Dichloro-1,1,2,2-tetrafluoroethane	$CClF_2$—$CClF_2$	Refrigerant
Freon 113	1,1,1-Trichloro-2,2,2-trifluoroethane	CCl_3—CF_3	Solvent
Freon 13B1	Bromotrifluoromethane	$CBrF_3$	Fire extinguisher
Freon 1211	Bromochlorodifluoromethane	$CBrClF_2$	Fire extinguisher

A can of auto air conditioner refrigerant containing chlorofluorocarbons, CFCs.

halons are not at all flammable, show little toxicity, have little or no odor, are virtually inert under ordinary conditions, and are inexpensive to manufacture. With properties like these, they seemed at one time to be ideally suited to consumer goods.

By the mid-1970s CFCs, halons, and related compounds were almost universally used as aerosol propellants for the canned sprays and foams of consumer products ranging from insecticides to shaving foams and hair sprays. Additional physical and chemical properties made them ideal refrigerants for use in mechanical air conditioners and refrigerators, and as foaming agents in the manufacture of highly porous, lightweight plastics (such as containers for fast foods), plastic foams, and building insulation. Their solvent properties and lack of flammability were perfectly suited to use as solvents for cleaning circuit boards and similar electronic parts. In the year 1986 alone, a grand total of over 1 billion kilograms (about 2.5 billion pounds, or 1.25 million tons) of CFCs and halons were produced in the world. That's about half a pound of these compounds for every living person on earth. By now some 15 million tons of CFCs have been produced, every molecule of which has found or will eventually find its way into the atmosphere as all the aerosol cans are emptied; as all the cooling devices age, corrode, and leak; and as all the plastic foams crumble or are ground up as rubbish.

Because of their low chemical reactivity and very low water solubility, these halogenated compounds aren't easily decomposed by ordinary chemical reactions within the lower atmosphere nor are they washed back to the ground by rain. Instead they drift upward into the stratosphere and its ozone layer, in a journey that lasts 7 to 10 years. Once there they can remain for decades, even (for CCl_2F_2) more than a century, as they themselves absorb the sun's ultraviolet radiation and decompose into various chemical products, including chlorine and (for the halons) bromine atoms.

In this respect they mimic the ozone molecule as it decays to an oxygen molecule and an oxygen atom. But there's an important difference here. The *oxygen atom* that's produced through the interaction of ultraviolet radiation with *ozone* can recombine with a diatomic oxygen molecule to regenerate the protective ozone. The *chlorine* and *bromine atoms* of the CFCs and halons, though, react with ozone by a complex sequence of reactions to generate oxygen *molecules*, which do not regenerate ozone as readily as do the oxygen atoms produced from ozone by ultraviolet absorption (Fig. 19.21). The result

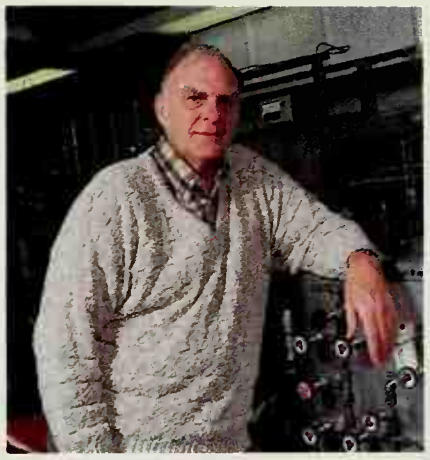
$$\text{Chlorofluorocarbons} \longrightarrow \underset{\text{Chlorine atoms}}{\mathrm{Cl}} + \text{Other products}$$

$$2\,O_3 \xrightarrow{\text{Catalytic action of chlorine atoms}} 3\,O_2$$

$$O_3 + O \xrightarrow{\text{Catalytic action of chlorine atoms}} 2\,O_2$$

is a net depletion of ozone. Through the chemical reactions that seem to operate in this conversion of ozone to molecular oxygen, a single chlorine atom or a single bromine atom that's split off a halocarbon molecule could, *in theory* (but hardly in practice, under the conditions of the stratosphere), destroy the entire ozone layer.

This ozone-destructive potential of atmospheric CFCs was recognized as early as 1974 by F. Sherwood Rowland, professor of chemistry at the University of California, Irvine, and his co-worker, Mario J. Molina. In response to warnings of possible damage to the ozone layer, the United States in 1978 banned the use of CFCs as aerosol spray propellants in consumer products. A decade later an international panel of scientists reviewing fluctuations in the ozone layer found evidence that it is indeed slowly shrinking, presumably through the action of halocarbons that have already entered the stratosphere. Although the decreases observed amounted to only a few percent, with an average loss of about 0.35% per year in the latitudes ranging from London in the northern hemisphere to the southern tip of South America in the south, the cumulative effect over many years could lead to increases in skin cancers and losses in food supplies. While the average, annual worldwide loss may seem small, ozone depletion over specific regions is alarmingly great. Over the continent of Antarctica, for example, ozone loss is so large that an actual hole in the ozone layer seems to be developing there.



F. Sherwood Rowland. He first warned of possible damage to the ozone layer by the CFCs.

To protect the ozone layer most of the major industrialized nations of the world have agreed by treaty to the need for restricting sharply the production and use of the halocarbons. Several, including Great Britain, the Netherlands, West Germany and nine additional nations of the European Economic Community, have endorsed a complete ban on all uses of the compounds by the year 2000.

Coming full circle, the DuPont Corporation, their inventor and chief producer, has also called for the complete abandonment of these halocarbons as commercial products and replacement by other, less hazardous materials. Among replacements under examination by the various manufacturers of the CFCs are compounds with molecular formulas such as $C_2H_3Cl_2F$ and $C_2HCl_2F_3$. While compounds of this sort resemble closely the CFCs and share many of their chemical and physical properties, the carbon–hydrogen bonds present in these replacement molecules make them much more likely to be destroyed by oxidation in the lower regions of the atmosphere. Thus, they would never reach the ozone layer itself.

The threat of CFCs to the ozone layer demonstrates once again that nothing is completely free of hazard; everything carries with it a risk of some sort. Noncorrosive, nonflammable, and with extremely low toxicities, the chlorofluorocarbons seemed for many years to be the ideal substances for use in aerosols and in a host of other consumer and industrial applications. The immediate, short-term risks associated with them were (and still are) small and completely acceptable. Yet we've found that on a time scale measured in years and perhaps decades—as the CFCs are released into the atmosphere and as they migrate slowly into the stratosphere and its ozone layer—the risks they present to us are completely unacceptable. In our search for safety, then, we find that the hazards we accept now are necessarily those we know of now, and that other hazards, unknown and unpredictable at present, may materialize far in the future. The search for safety has a time scale of its own.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

Earth's ______ consists of several layers or zones. The lowest, the ______ , is the region that carries the rain, wind, and clouds of our weather. Above this is the ______ , which contains the ______ , a zone of ______ molecules of ______ that shield us from the harmful effects of the sun's ______ radiation. Still higher is the ______ , whose ionized gases reflect radio waves and make possible long-range radio transmissions.

atmosphere
ionosphere
oxygen
ozone layer
stratosphere
triatomic
troposphere
ultraviolet

2. Complete this statement with the following words and phrases. Each is used once.

According to the ______ , an ______ consists of point-sized particles, with no ______ whatsoever, that bounce off each other in perfectly ______ collisions, without losing any ______ in the process. The ______ of a gas enclosed in a container results from the collisions of the particles with the walls of the container. If we increase the temperature of an ideal gas held in a container of constant volume, the pressure ______ and always remains directly proportional to the ______ . If we increase the pressure on a gas held at ______ , the volume of the gas ______ proportionately.

absolute temperature
constant temperature
decreases
elastic
energy
ideal gas
increases
kinetic-molecular theory of gases
pressure
volume

3. Explain, describe, or define each of the following:

a. absolute temperature
b. alveoli
c. atmospheric pressure
d. barometer
e. CFCs
f. mm-Hg
g. nitrogen dioxide
h. $p\text{CO}_2$

4. Match each of the names in the left column with the contributions described in the right column.

___ a. Amedeo Avogadro
___ b. Robert Boyle
___ c. J. A. C. Charles
___ d. John Dalton
___ e. Joseph L. Gay-Lussac
___ f. William Henry
___ g. F. Sherwood Rowland and Mario J. Molina
___ h. William Thomson, Lord Kelvin
___ i. Evangelista Torricelli

1. First recognized the ozone-destructive potential of chlorofluorocarbons
2. With the temperature and the number of moles of a quantity of gas held constant, the volume of the gas varies inversely with its pressure or $P \times V = k$
3. The total pressure of a mixture of gases equals the sum of the partial pressures of each of the gases in the mixture
4. Equal volumes of gases at the same temperature and pressure contain equal numbers of atoms or molecules
5. Invented the barometer
6. The quantity of a gas that dissolves in a liquid depends directly on the pressure of that gas above the liquid
7. Devised the absolute temperature scale

8. When gases react with each other at constant temperature and pressure they combine in volumes that are related to each other as ratios of small, whole numbers
9. With the pressure and the number of moles of a quantity of gas held constant, the volume of the gas varies directly with its temperature, or $V = k \times T$

5. Describe how:
(a) the volume of a gas varies with changes in pressure if the temperature is kept constant.
(b) the volume of a gas varies with changes in temperature if the pressure is kept constant.
(c) the pressure of a gas varies with changes in temperature if the volume is kept constant.

6. What determines the energy of the molecules of an ideal gas?

7. What gas makes up the largest percentage of the air we inhale?

8. Explain why shaking a bottle of soda causes it to fizz excessively when you open it.

9. Give the chemical name, molecular formula, and commercial use of a chlorofluorocarbon.

10. What are two hazards associated with NO_2 in the atmosphere?

11. From what hazard does the ozone layer protect us? Explain.

12. What hazard does ozone present to us?

13. Explain what a thermal inversion is and how it contributes to air pollution.

14. Why does replacing a halogen atom of a halocarbon with a hydrogen atom decrease the danger to the ozone layer?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

15. You have a certain volume of gas kept at atmospheric pressure. You increase the temperature of the gas by 100°C and find that its volume doubles. What was the original temperature of the gas?

16. Suppose you fill a cold tire to 32 psi (pounds/in^2) at 17°C and run it until it reaches a temperature of 37°C. What's the new pressure? (Assume that the volume of the tire doesn't change.)

17. A mountain climber fills three 1-L balloons with air at 760 mm-Hg and 27°C and carries each one to the top of Mt. Everest, the highest mountain in the world, Mt. McKinley, the highest mountain in the United States, and Ben Nevis, the highest mountain in the British Isles. Given the data below, calculate the volume of the balloon at the top of each of these mountains.

	Mt. Everest	**Mt. McKinley**	**Ben Nevis**
Height, m	8848	6194	1343
(ft)	(29,028)	(20,320)	(4,406)
Average atmospheric pressure, mm-Hg	221	345	647
Average temperature, °C	−42	−25	+7

For each peak, is the drop in pressure or the drop in temperature the dominant factor in determining the final volume of the balloon?

18. Avogadro's Law tells us that the more air we put into a balloon, the greater the numbers of molecules of gas there are within the balloon. This leads to an increase in the balloon's size and we might expect it to lead also to an increase in the pressure of the gas, as well. Yet it usually takes much more effort to start inflating a small party balloon than to continue once it's been blown up a bit. Why does the needed pressure *decrease*, at first, as more air enters the balloon?

(*Note*: The answer to this question has nothing to do with the gas laws. This question is included to illustrate an important point: Our everyday world displays many different, interwoven phenomena. The gas laws we have examined describe only one set of these phenomena. *All* the rules of the physical world, including the laws governing the behavior of stretching rubber and those of the gases, operate together to affect the way ordinary things act.)

THINK, SPECULATE, REFLECT, AND PONDER

19. If a helium balloon breaks loose, it rises into the atmosphere and at some point it bursts. Explain why.

20. If a gas behaved *exactly* like an ideal gas, at what temperature would it liquefy? Explain.

21. Which one of the gases in Table 19.1 behaves most like an ideal gas? Which one behaves least like an ideal gas? What can you conclude about the forces of attraction between the molecules of each of these two gases?

22. Explain why the partial pressure of a gas is an effective measure of the concentration of a gas in a solution.

23. It's sometimes necessary to carry out laboratory experiments in liquids that are completely free of dissolved gases. What simple technique should ordinarily free a liquid of all dissolved gases?

24. Gases move from regions of high pressure to regions of low pressure. What force keeps the gases of the earth's atmosphere from diffusing into interplanetary space, where the pressure is essentially zero?

25. Why is the air in jet aircraft flying at high altitudes pressurized?

26. Why are many small bubbles more effective than a few very large bubbles in maintaining a supply of dissolved air in a fish tank?

27. Why is it necessary for mountain climbers to carry a supply of oxygen and an oxygen mask with them on their ascent to a high peak?

28. Would you expect the average ozone concentration in an urban area for a 24-hour period to be higher in the summer or in the winter? Explain.

29. Some manufacturers of hair sprays have replaced CFCs with pressurized butane as a propellant in spray cans. Butane is not known to damage the ozone layer. What danger does pressurized butane present that the CFCs do not?

30. Given the following statements

a). Lightning produces extremely high temperatures and has been responsible for starting fires during thunderstorms.

b). Explosions are the result of the extremely rapid expansion of gases.

Use Charles' Law to explain the origin of thunder.

Polymers and Plastics

20

THE PLASTIC AGE

Compact discs. Plastic that stores sound.

Figure 20.1

Separating plastics of different densities with a mixture of isopropyl alcohol (rubbing alcohol) and water. The more dense plastics sink; the less dense plastics float.

Plastics, Water, and Rubbing Alcohol

Plastics are remarkably useful materials, but one of their greatest advantages over other materials, their durability, is also one of their greatest handicaps. They don't disintegrate. Once we dump them into the environment, they just stay there. Some plastics seem to last forever. One way to keep discarded plastics from overwhelming us is to recycle them, to use them over and over again. But there are different kinds of plastics, and one sort doesn't mix well with another. To reuse plastics we have to separate one kind from another so that we can combine all compatible plastics into one group and reprocess them as a whole. One way to sort them is by taking advantage of differences in the densities of different kinds of plastics (Section 11.1).

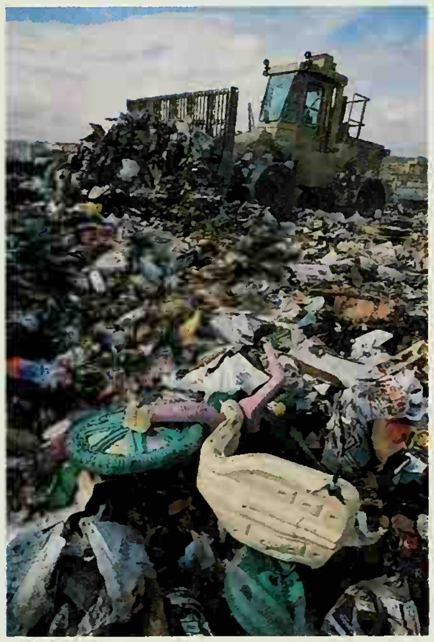
You can do this yourself by using some rubbing alcohol, water, and a few pieces of different plastics. For a good start, use the rather hard plastic of a milk bottle. Be sure to use a plastic bottle, not a waxed paper carton. Another good plastic to use here is a trash bag. Plastic milk bottles are made of a high density polyethylene, while trash bags are made of a low-density polyethylene. Made by one process, the polyethylene forms as a hard, rigid, high-density material well suited to bottles and other containers. Made in a different way, the polyethylene forms as a soft, flexible, low-density plastic that gives trash bags their desirable characteristics.

A mixture of one part water and two parts rubbing alcohol, by volume, provides a good start for separating the two. The milk bottle plastic should sink in this mixture and the trash bag should float. If both sink, add a little water to the mixture. If both float, add a bit of rubbing alcohol. Water is more dense than the isopropyl alcohol of the rubbing alcohol (Section 9.9). If both plastics sink, adding some water should force the less dense plastic to float. Adding the rubbing alcohol decreases the density of the liquid mixture and lets the more dense plastic sink.

Either way, by adding water or rubbing alcohol to adjust the density of the liquid, you can separate plastics of different densities. Once you learn how with the polyethylenes, try separating pieces of plastic taken from other containers (Fig. 20.1). Techniques of this sort can help us keep used plastics out of our trash dumps and put them back into consumer products.

20.1 The Age of Plastics

If an era is known by the kinds of materials its people use to build the world they live in, then the Stone Age, the Bronze Age, and the Iron Age have given way to our own Plastic Age. Plastics form much of our packing and wrapping materials, many of our bottles and containers, textiles, plumbing and building materials, furniture and flooring, paints, glues and adhesives, electrical insulation, automobile parts and bodies, television, stereo and computer cabinets, medical equipment, video and audio tapes, records and compact disks, personal items including pens, razors, toothbrushes, and hairsprays, and even the plastic trash bags we use to discard our plastic trash. Except for our food, air, and water, almost every ordinary thing we come in contact with each day contains some kind of a plastic somewhere in, on, or around it. Or it comes to us wrapped in plastic. So many of our throwaway goods are made of plastic that, despite its lightness, the material currently makes up an estimated 7% of the total weight of all solid municipal wastes and is expected to grow to 10% by the year 2000. What's more, plastics are a highly visible part of what we discard, making up roughly a quarter of the entire volume of our trash. We'll have more to say about the problem of plastic wastes in Section 20.22.



Plastic trash in a landfill.

In 1990 the U.S. chemical industry produced just over 30 million tons (a bit under 27 billion kilograms) of unprocessed, raw plastics of all kinds, valued at more than $20 billion. The total amount spent by consumers of all kinds on all of the finished products made of plastics comes to more than 3% of the total value of all the goods and services sold in the United States. About half of the plastics produced today go into packaging and into building and construction materials, with about another 8% into personal consumer products. Figure 20.2 shows the quantities of the major plastics and related ma-

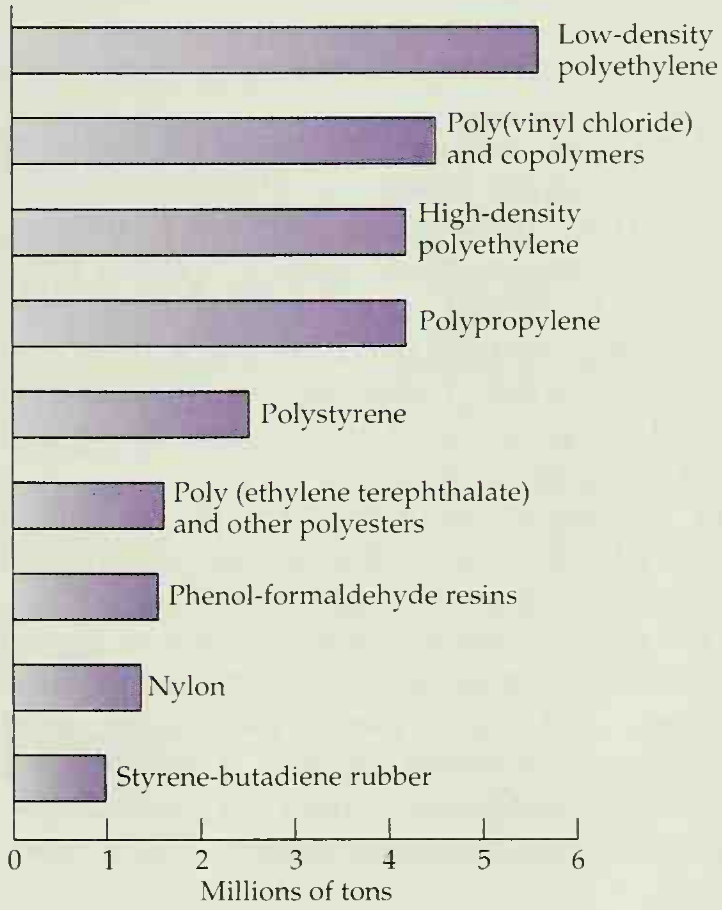
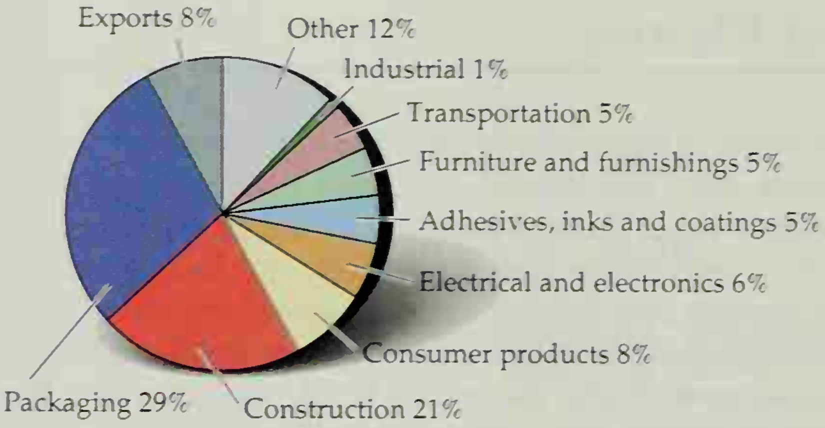


Figure 20.2

Production of selected plastics and related materials in the United States, 1990.

Figure 20.3
Applications of plastics manufactured in the United States.



terials manufactured in the United States in 1990, Figure 20.3 presents their major applications.

Durable or fragile, rigid or flexible, sturdy or flimsy, dense or light, strong or weak, plastics provide us with inexpensive materials of virtually unlimited properties. With chemical ingenuity we can transform them into almost whatever shapes we wish with almost whatever properties we desire. And at their root, in the *polymeric* molecules that make up these extraordinary substances of our everyday world, lies not only one of the shining achievements of modern chemistry but, as we'll see at the end of this chapter, perhaps even the secret of life itself. We'll begin, though, by examining the difference between the *plastics* of our world and the *polymers* that form them.

QUESTION

In 1990 what was the average cost of a kilogram of raw, unfinished plastic? What was the average cost per pound? ______________________________

20.2 Plastics and Polymers

Plastics, especially the plastics of our most common commercial products, are extraordinary kinds of materials that we can shape into virtually any form we want. The word itself comes from the Greek *plastikos*, "suitable for molding or shaping." We can form them into round, hard, resilient bowling balls, draw them out into the thin, flexible threads of synthetic fibers, mold them into intricately designed, long-running machine parts, or flatten them into flimsy but tough sheets of clinging kitchen film. Today, the word **plastic** refers mostly to a property of a material: its ability to be shaped into the myriad forms of today's commercial and consumer products.

A **plastic** is a material capable of being shaped into virtually any form.

A **polymer** is a molecule of very high molecular weight formed by the repeated chemical linking of a great many simpler, smaller molecules.

When we speak of a **polymer**, though, we return to the molecular level of matter. All the plastics of our everyday lives, as well as all the proteins and the starch and cellulose of our foods, the cotton, silk, and wool of our textiles, and even the DNA that carries the genetic code within the nucleus of the cell are formed of enormously large polymeric molecules. The combination of the Greek words *poly*, meaning "many," and *meros*, "parts," gives us the word for the molecules that compose these substances, *polymer*. A polymer is a molecule of very high molecular weight, composed of many—a great many—much smaller parts joined together through chemical bonds.

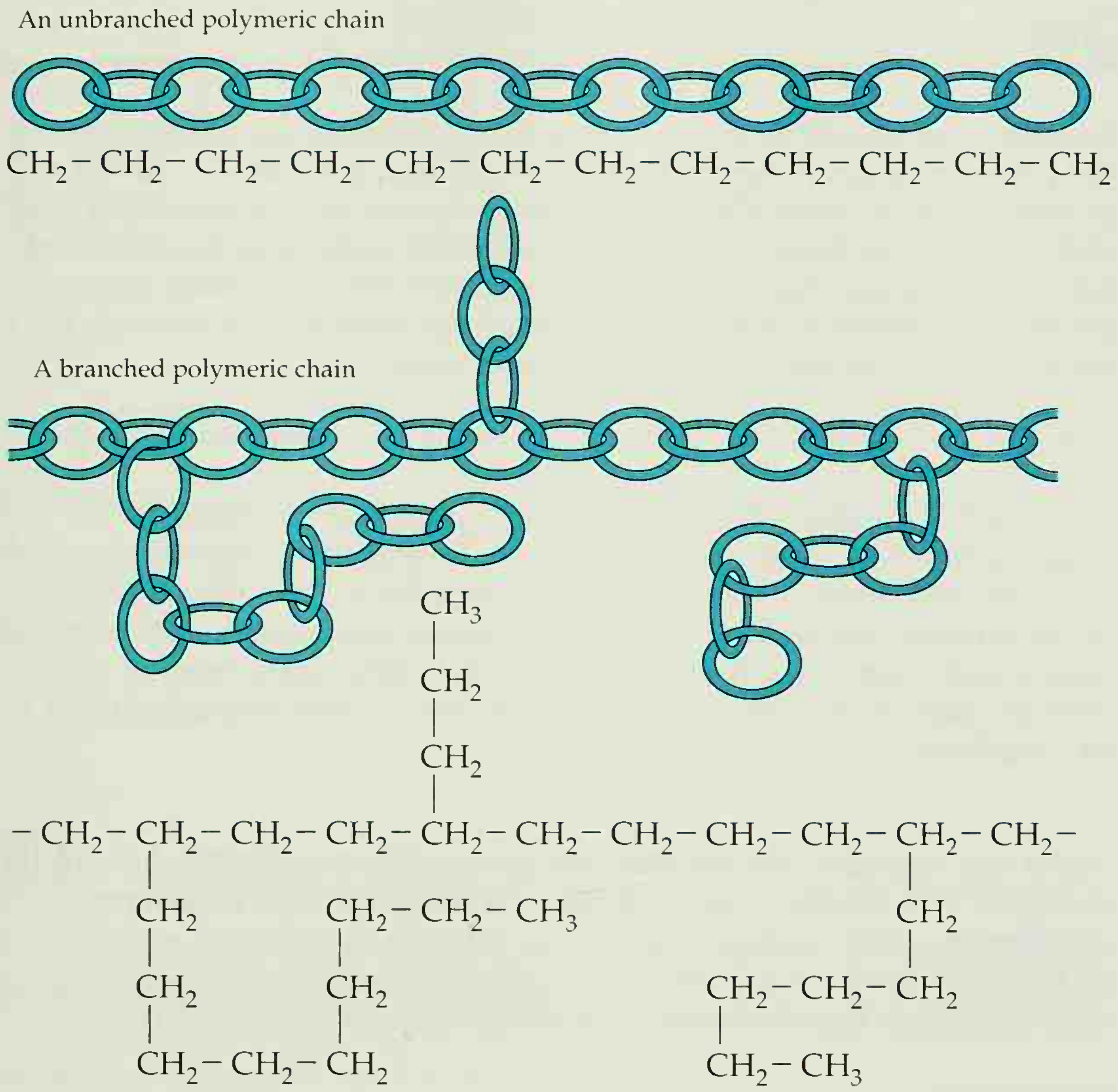


Figure 20.4
Chains and polymers.

As the word implies, polymers are extremely large molecules, sometimes called *macromolecules* to emphasize their very large size. The individual parts that combine to form them, **monomers** from the Greek *mono*, "one," join to each other in enormously large numbers to produce polymers with molecular weights ranging from the tens of thousands to millions of atomic mass units. Often the monomers unite to form an enormously long, linear molecular thread, very much like a long chain we might find in a hardware store. In other polymers the chains may be branched to various degrees, or they may be interconnected at occasional junctions, or so frequently that they form a web or even a rigid, three-dimensional lattice (Fig. 20.4). In any event, a *polymer* is a substance composed of huge molecules, sometimes in the form of very long chains, sometimes as sheets, sometimes as intricate, three dimensional lattices. A *plastic*, on the other hand, is a material that can be molded readily into a variety of shapes. All of today's commercial plastics are polymers, even though some of our most important polymers are not at all plastic.

Monomers are the individual structures that are linked to each other to form a polymer.

QUESTION

What is the difference between a plastic and a polymer? ______________________

20.3 A Polymeric Chain

In earlier chapters we've seen two examples of naturally occurring polymers, the polysaccharides (Chapter 14) and the proteins (Chapter 15). As we saw in Section 14.11, molecules of the polysaccharide *cellulose* consist of long chains of glucose rings (the monomers) joined to each other through β-linkages. Cellulose falls into the class of *homopolymers*, polymers whose monomers are mutually identical (Fig 20.5). If we represent each of its monomeric links simply as "X," we can show the polymeric molecule as

—X—X—X—X—X—X—X—X—X—X—X—X—X—X—X—X—X—X—X—X—

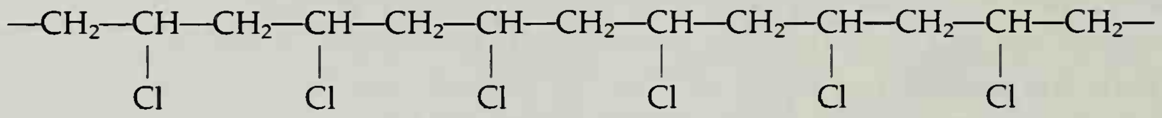
with the X's running off both sides of the page and continuing to the full length of the chain, from beginning to end. To simplify matters we can show the molecular structure just as well by writing *one* of these monomeric units in parentheses and adding a subscript *n*, which represents a very large but unspecified number of links. The short, horizontal lines running from X through each of the parentheses represent the covalent bonds linking X to its neighbors:

$$-\!(\mathrm{X})\!-_n$$

Using this approach, we can draw the structure of the cellulose molecule as in Figure 20.6. Protein chains are also polymeric, but with an assortment of 20 different amino acids serving as their monomeric units and appearing in an elaborate sequence along the chain, protein polymers are far more complex than the simple homopolymer of the cellulose molecule (Fig. 20.7).

QUESTION

In Section 20.14 we'll find the homopolymer *poly(vinyl chloride)*, which consists of the polymeric chain



$$\begin{array}{ccccccccccccc} -CH_2- & CH & -CH_2- & CH & -CH_2- & CH & -CH_2- & CH & -CH_2- & CH & -CH_2- & CH & -CH_2- \\ & | & & | & & | & & | & & | & & | & \\ & Cl & & Cl & & Cl & & Cl & & Cl & & Cl & \end{array}$$

What is the repeating unit of this polymer? How would you write its structure in the form $-\!(\mathrm{X})\!-_n$? ________________________________

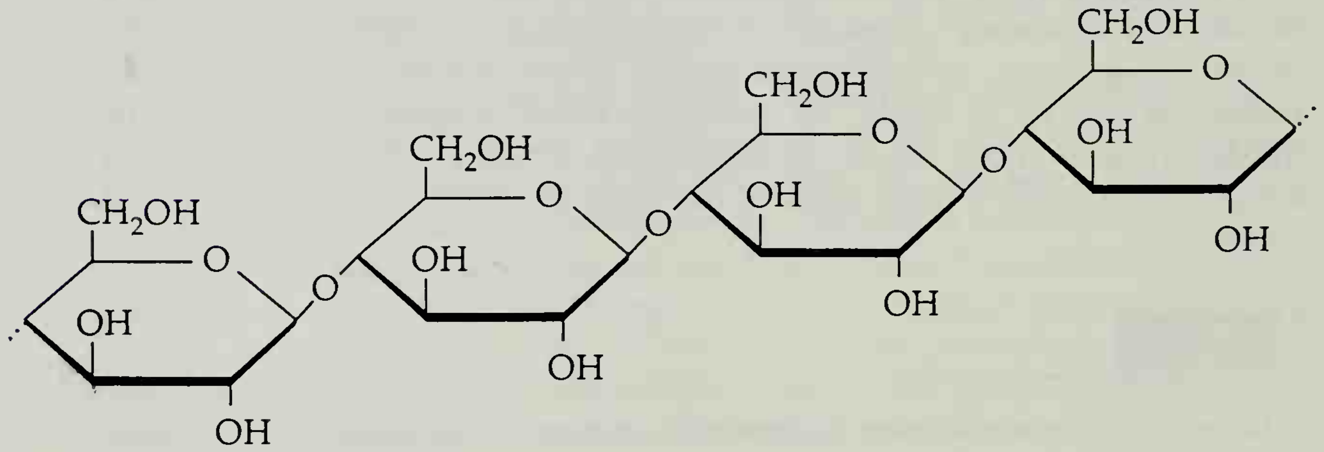


Figure 20.5
Cellulose as a homopolymer.

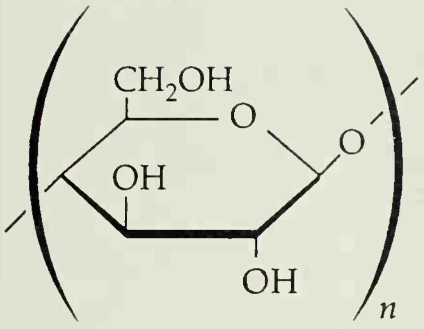


Figure 20.6
Cellulose.

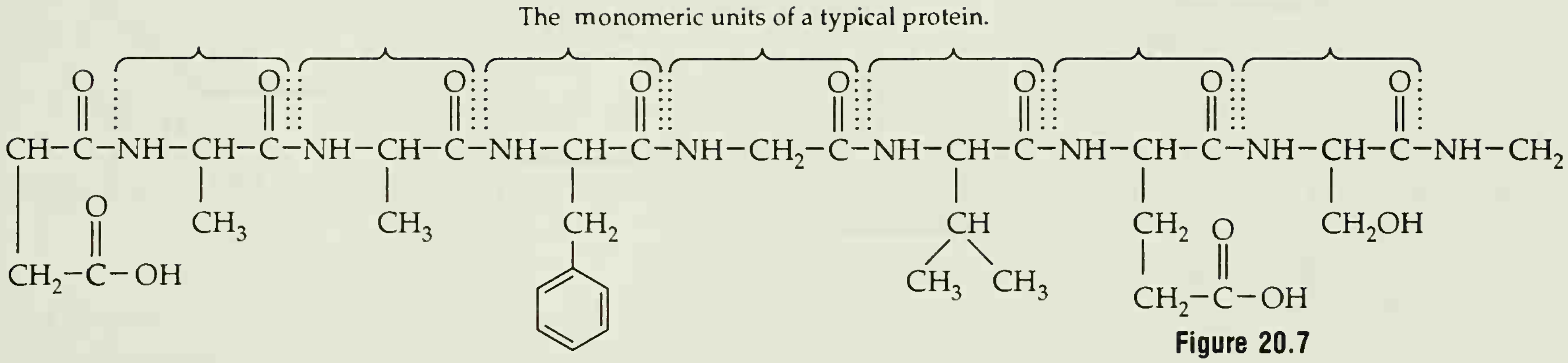


Figure 20.7
A typical protein as a polymer.

20.4 Condensation Polymerization

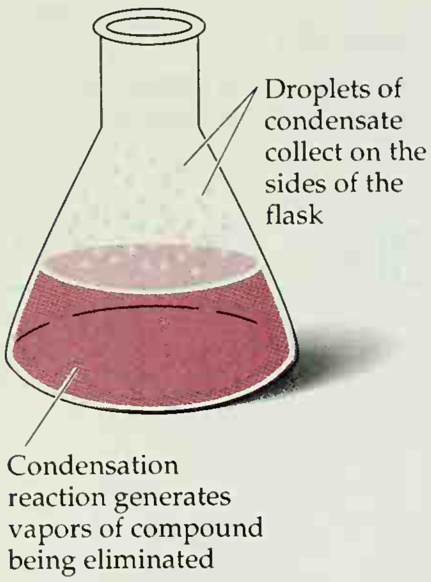
The actual linking of the monomers through covalent bonds occurs during **polymerization**, a chemical process easily divided into two broad categories: *condensation polymerization* and *addition polymerization*. The products are *condensation polymers* and *addition polymers*, respectively.

We'll look first at a few condensations polymers, then we'll return to addition polymers. The naturally occurring polysaccharides and proteins provide us with good examples of condensation polymers, even though they form through complex enzymatic reactions, far removed from the relatively straightforward industrial processes that produce our everyday polymers. Regardless of what kinds of chemical reactions actually produce them, these polysaccharides and proteins do provide us with fine illustrations of the *structures* of condensation polymers.

In a condensation reaction two molecules combine with the formation and loss of another, smaller molecule, usually water or a simple alcohol. [The general term *condensation reaction* probably originated as early chemists observed water or similar liquids forming droplets of condensate on the sides of flasks during this sort of reaction (Fig. 20.8).] Each of the condensing molecules contributes some portion of the smaller molecule being eliminated. Figure 20.9 shows segments of cellulose and of a typical protein as condensation polymers.

Polymerization is the process whereby individual monomers link together to form a polymer.

Figure 20.8
A condensation reaction.



QUESTION

Name a naturally occurring homopolymer, other than cellulose, that has the structure of a condensation polymer. ______________________

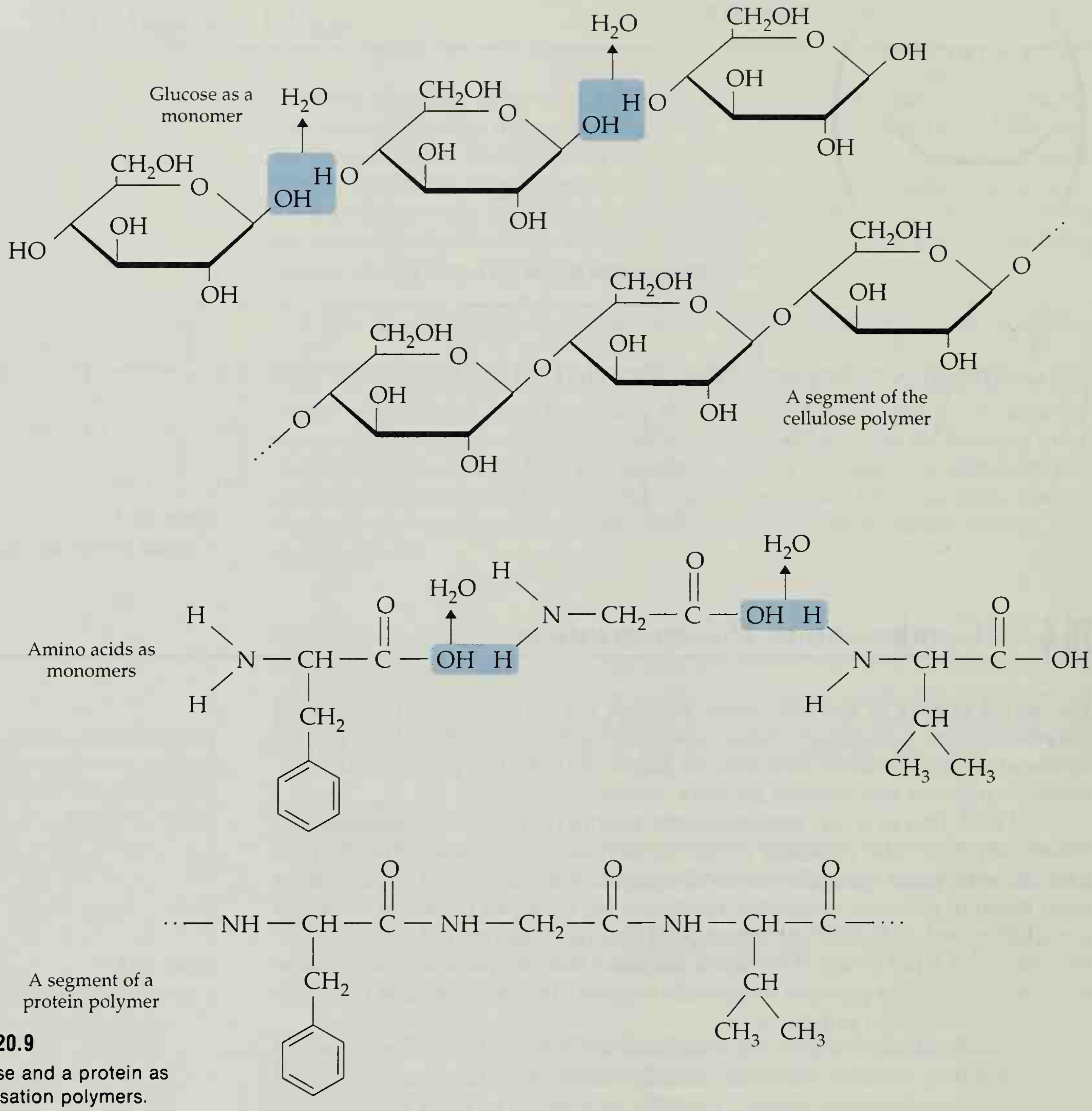


Figure 20.9
Cellulose and a protein as condensation polymers.

20.5 Nylons: The Molecules and the Stockings

The first and probably the best known of all the synthetic condensation polymers is *nylon*, a plastic developed by the DuPont Corporation. In 1928 Wallace H. Carothers (1896–1937), an Iowa-born chemist, left his post as instructor in organic chemistry at Harvard University to lead a research group in DuPont's Wilmington, Delaware, laboratories. There he began a program of fundamental research into polymers, studying how they form and what factors affect their properties. Within a few years he and his co-workers found

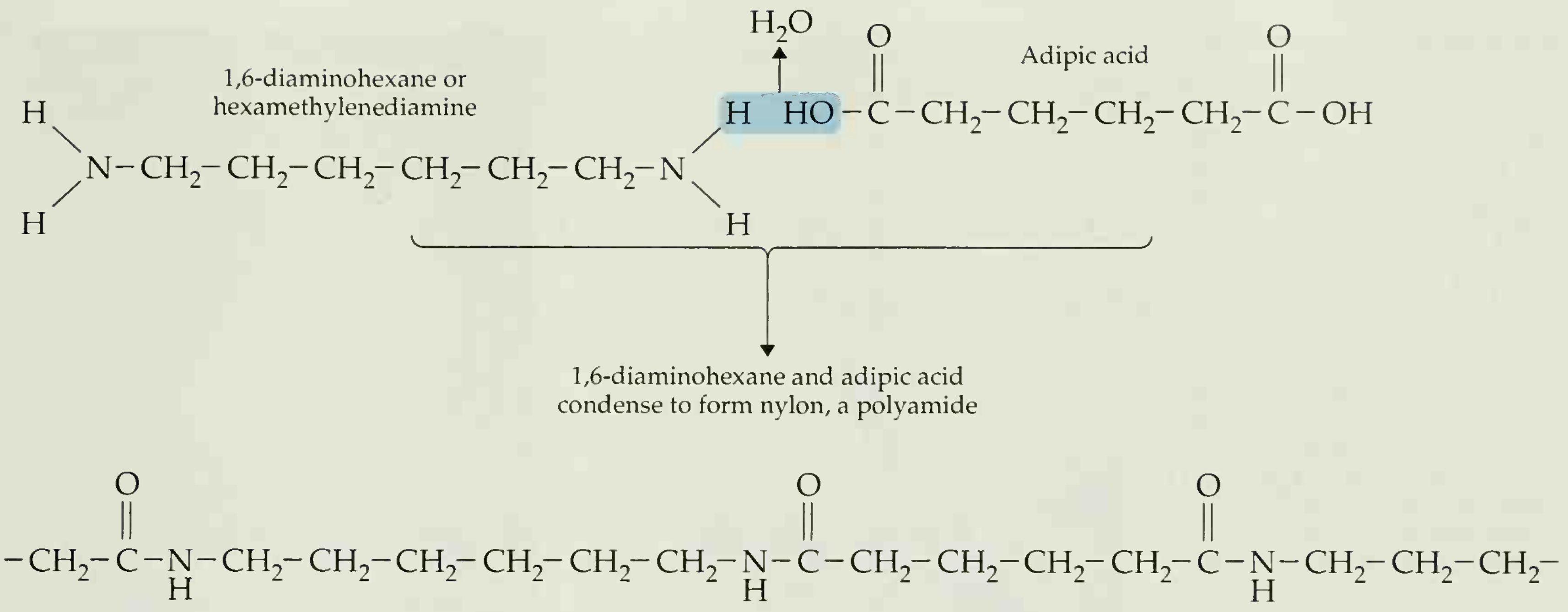
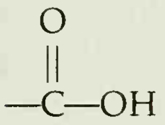


Figure 20.10
Nylon, a condensation polymer.

that by polymerizing a mixture of *adipic acid* and *1,6-diaminohexane,* they could produce a plastic (nylon) that can be drawn out into strong, silky fibers (Fig. 20.10).

Adipic acid is an example of a *dicarboxylic acid,* one containing two *carboxyl* groups (Section 10.18).



$$-\overset{O}{\overset{\|}{C}}-OH$$

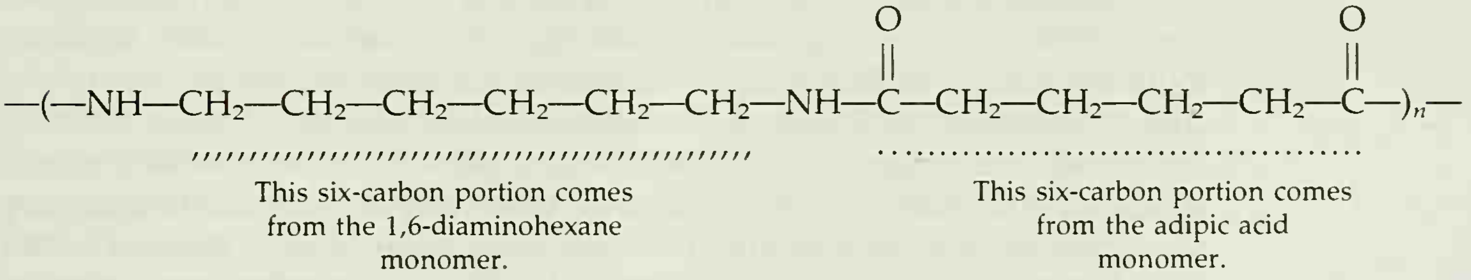
the carboxyl group

Wallace H. Carothers, the DuPont chemist who led the research team that invented nylon.

The name *adipic* comes from the Latin *adipem,* "a fat," and reflects the observation that adipic acid is one of the substances formed when fats are oxidized with nitric acid, HNO_3. Notice, in Figure 20.10, that the adipic acid molecule contains a chain of six carbons, which includes the two carboxyl groups at its ends. We'll refer to this shortly.

The other monomer is another six-carbon compound, 1,6-diaminohexane, with amino groups ($-NH_2$, Section 15.2), at the ends of a chain of six methylene groups ($-CH_2-$). Another useful name for this diamine is *hexamethylenediamine.*

With repeating units of the two monomers bonded to each other throughout the length of the chain, the structure of the polymeric molecule itself can be written as



$$-(-NH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-)_n-$$

This six-carbon portion comes from the 1,6-diaminohexane monomer.

This six-carbon portion comes from the adipic acid monomer.

Nylon

To emphasize the geometry of the molecule, which consists simply of a very long line of atoms (carbons periodically interrupted by nitrogen), with neither branching nor other structural diversions, nylon is known as a *linear* polymer.

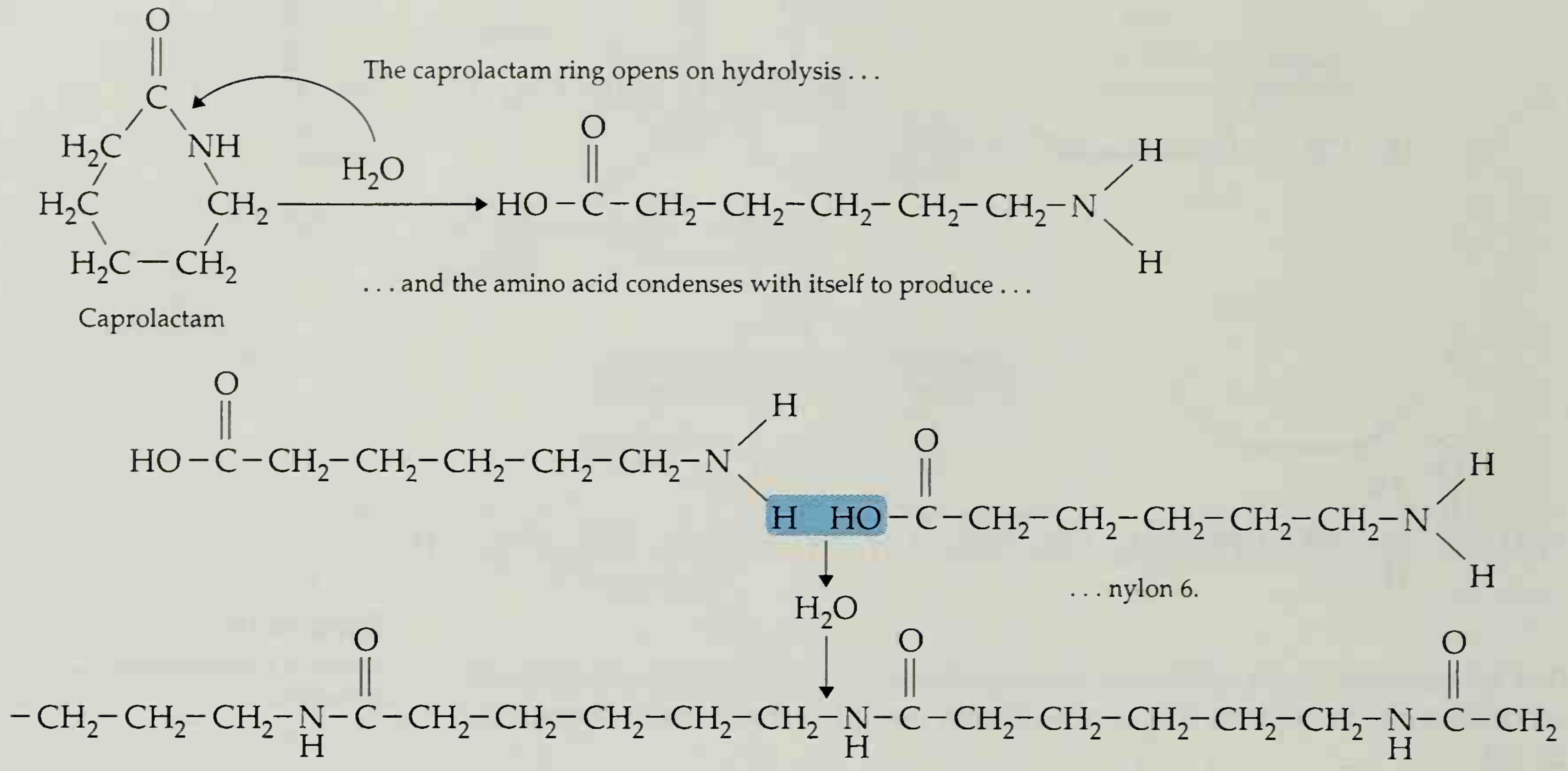


Figure 20.11
Nylon 6.

Unlike the homopolymers (cellulose, for example), nylon's linear chain is made up of *two* monomeric units, adipic acid and 1,6-diaminohexane. Polymers that, like nylon, are formed from two or more monomers are known as *copolymers*. In some copolymers the monomeric units alternate regularly, as they do in nylon; in others they appear randomly in the chain.

Carothers and his group produced several other nylons, each a *polyamide* (Section 15.7). To differentiate among all the newly formed nylons, the researchers coded each one for the number of carbon atoms in each of their monomers. The one produced from the six-carbon adipic acid and the six-carbon 1,6-diaminohexane, became *nylon 6,6*. (In fact, "66 polyamide" was its original name, before the term *nylon* was coined.) Another nylon, *nylon 6*, forms as the ring of *caprolactam* opens with the addition of water and the resulting amino acid undergoes polymerization (Fig. 20.11).

Nylon's first practical application to a consumer product came in 1938, when the new polymer was introduced to the public in the form of toothbrush bristles. But it was the polymer's use in stockings, first sold to consumers on a trial basis in October 1939, that made it an overwhelming commercial success. Similar to silk in its properties but far less expensive, nylon became the ideal replacement for the silk of stockings and other fashionable clothing. With the coming of World War II, fashion had to make way for the war effort. The government used most of the nation's limited supplies of nylon for making parachutes, ropes, and other military supplies. Since there wasn't enough nylon for both military and civilian uses, nylon stockings, which had become very popular and were in high demand, were rationed until the end of the war. During the war and shortly afterward, nylon stockings became a valuable item of barter in Europe and achieved the status of an informal currency. Not until the early 1950s was there sufficient production capacity to fill the popular demand for "nylons," as the stockings came to be known, and also to provide enough of the plastic for other consumer and commercial uses.

Left Photo: The formation of a strand of nylon 6,6 as two chemicals, dissolved in solvents that do not mix, react with each other. Hexamethylene diamine, H_2N-$(CH_2)_6$-NH_2, dissolved in water and adipoyl chloride, ClOC-$(CH_2)_4$-COCl, dissolved in another solvent, react to form nylon at the surface where the two solvents come into contact. The strand is pulled from the surface of contact.

Right Photo: A giant leg near Los Angeles, promoting the sale of nylon stockings after World War II.

(Nylon's name reflects, in a strange and devious way, one of the most appealing characteristics of the stockings made from the polymer: their resistance to snagging and running. An early name, suggested as a more popular replacement for the technical *66 polyamide,* was *norun,* referring to the appeal of the stockings. When that term was judged to be unsatisfactory by those at DuPont who were responsible for giving the polymer an acceptable trade name, it was first spelled backward as *nuron,* which was still unsatisfactory, and then finally converted to the acceptable *nylon.*)

QUESTION

In what important way are the molecular structures of nylon polymers and protein polymers similar to each other? ______________________

20.6 Addition Polymerization

Despite the immense initial popularity of nylon, a condensation polymer, a different class of plastics dominates today's chemical economy. *Addition polymers* such as *polyethylene* and several of its close molecular relatives account for more than half of all the plastics currently produced in the United States. These addition polymers form as their individual, unconnected monomers join together to form a polymeric chain in much the same way as people standing next to each other can form a human chain by holding the hands of those next to them.

Figure 20.12 shows a group of people lined up side-by-side, clasping their hands over their heads, and also a group of ethylene molecules (Section 7.9) arranged similarly, each with its two covalent carbon–carbon bonds. As we saw in Section 3.13, every covalent bond is actually a shared pair of electrons.

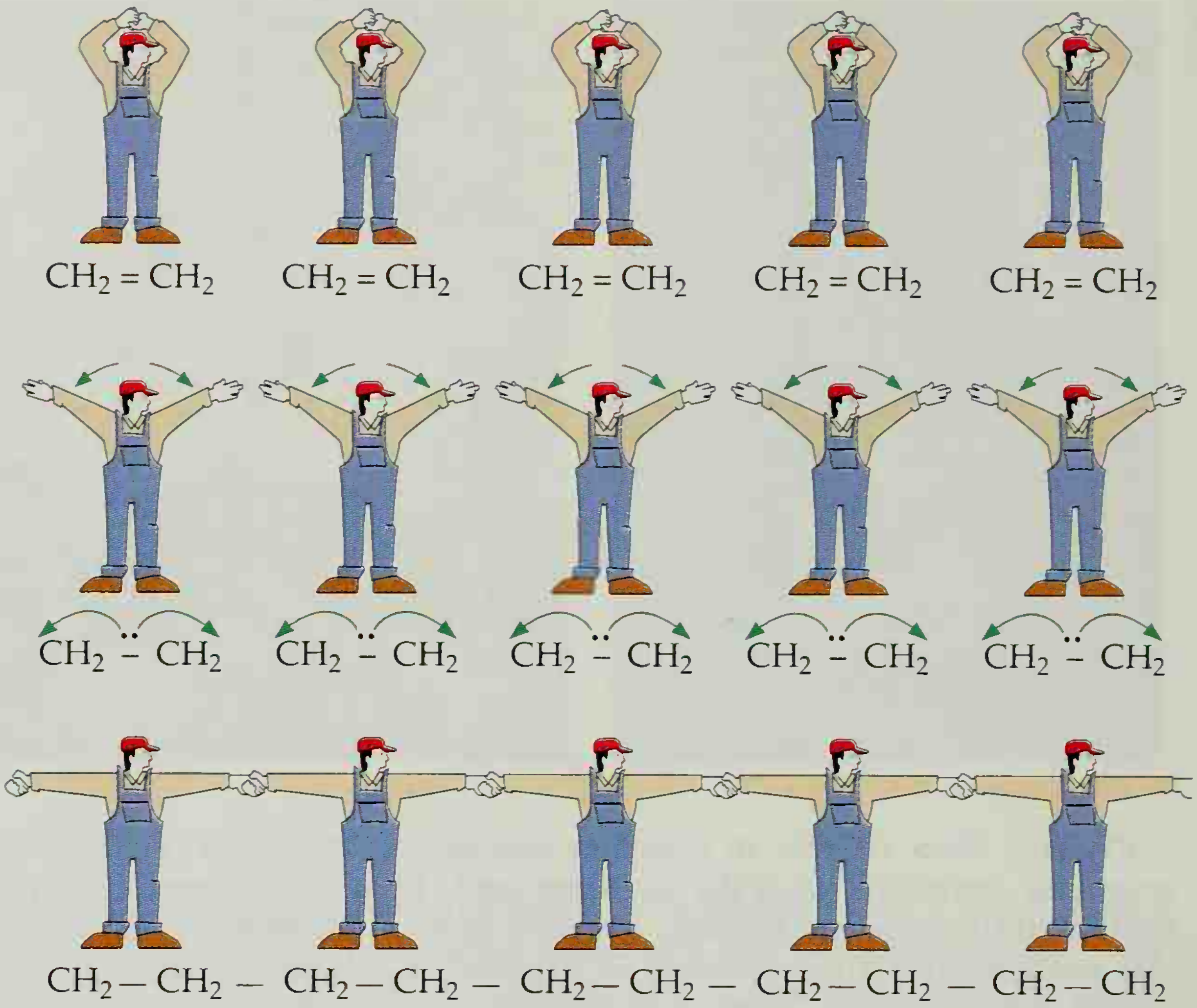


Figure 20.12
The addition polymerization of ethylene to polyethylene.

In a rough analogy, each pair of clasped hands in the figure corresponds to a pair of bonding electrons. Just as each person in the row can unclasp his or her own hands and link up with those on either side to form a human chain, each ethylene molecule, under the right chemical conditions, can swing the electrons of one of its bonds toward each of its neighbors to form a molecular chain. The result is polyethylene, an addition polymer.

The analogy isn't perfect. For example, polymerizations aren't limited to the specific sort of electron movements shown in Figure 20.12. Under different chemical conditions, both electrons can move in the same direction, as in Figure 20.13. In either case, though, the process is still polymerization and the product is still polyethylene, an addition polymer.

QUESTION

Polypropylene forms in the polymerization of propylene, $CH_2=CH-CH_3$, much as polyethylene forms in the polymerization of ethylene. Give the structure of polypropylene in the form $-\!\!\left(X \right)\!\!-_n$. ________________

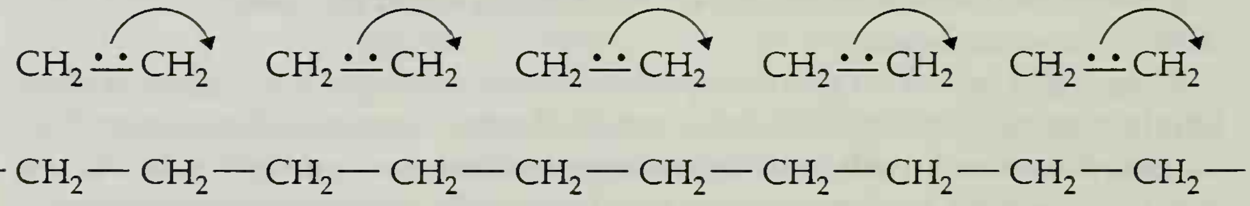


Figure 20.13
Another route for the polymerization of ethylene.

20.7 Thermoplastics and Thermosets: Plastics That Act Like Fats and That Act Like Eggs

We'll turn now from our survey of polymeric molecules to some of the materials in our everyday world that they form: plastics and closely related materials including rubber and synthetic fibers. We'll start with plastics.

Despite differences at the molecular level, nylon, which is a condensation polymer, and polyethylene, an addition polymer, show an important physical similarity in their behavior as bulk plastics: They both soften when heated and become firm again when cooled, much like the fats we examined in Chapter 13. What's more, they repeat this behavior as they are alternately heated and cooled. (We could draw an analogy to the cyclical melting and freezing of water as well, but plastics often tend to soften a bit before they melt, as do fats, rather than melt sharply like ice.) Plastics that respond to heating and cooling in this way are called **thermoplastics**.

A second category of plastics, the **thermosets** or *thermosetting plastics*, are soft enough to be molded when they are first prepared, but on heating they firm up permanently. Reheating may cause them to decompose but it certainly won't soften them again. Bakelite and epoxy resins are good examples of these thermosetting plastics. Since Bakelite is a strong material and a poor conductor of heat and electricity, it's used in making handles for cooking utensils and for molding parts for electrical goods, such as the familiar three-way adapter for electrical outlets. It is also used to make such diverse items as buttons and billiard balls. Epoxy resins are used for making fiberboard and plywood. While thermoplastics mimic fats in their response to heat, the thermosets are more like eggs. Heating produces irreversible changes in both thermosets and eggs.

Thermoplastics are plastics that soften when they are heated, then harden again as they cool.

Thermosets are plastics that hold their shape, even when they are heated.

Currently the thermoplastics are by far the more popular of the two, with about 6.5 tons of this class of polymer manufactured for every ton of the thermosets.

QUESTION

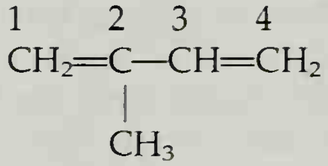
Which class of plastics would make a better handle for a frying pan? Which would make better frames for prescription glasses? Why? ______________

20.8 Compounds Related to Natural Rubber

Humans have used polymers since we first converted animal skins to leather (a protein) and wove fabrics of wool (another protein), silk (still another protein), and cotton (a polysaccharide). Christopher Columbus and his companions found the inhabitants of the newly discovered Western Hemisphere playing with still another natural polymer. The natives were fond of bouncing heavy balls made of a vegetable gum that Europeans eventually named *rubber* when, almost three centuries after Columbus's voyage, they found it was useful for rubbing out marks made by lead pencils. While rubber is plastic in the sense that we can mold, twist, stretch, and compress it into various shapes, rubber belongs to the class of polymers called **elastomers**, substances that stretch easily and return readily to their original shapes. It's the resilience of rubber that we value.

An **elastomer** is a substance that stretches easily and returns readily to its original shape.

Rubber itself is an addition polymer of a *diene* (a hydrocarbon molecule containing two double bonds) called *isoprene* or, applying the IUPAC rules of Section 7.7, *2-methyl-1,3-butadiene.* As shown below, we number the carbons of the unsaturated chain that contains the double bonds from 1 to 4, beginning at the end closer to the methyl substituent.



$$\overset{1}{\mathrm{CH_2}}{=}\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{C}}}{-}\overset{3}{\mathrm{CH}}{=}\overset{4}{\mathrm{CH_2}}$$

isoprene,
or
2-methyl-1,3-butadiene

With the methyl group as a substituent on carbon 2, the IUPAC name of the monomer begins "2-methyl- . . . ." Each double bond receives the smaller number of the two carbons it connects. The completed IUPAC name now reveals the position of the substituent (2- . . .), the structure of the substituent (2-*methyl-* . . .) , the position of the two double bonds (2-methyl-*1,3-* . . .), the number of carbons in the chain (2-methyl-1,3-*buta* . . , which comes from the name of the four-carbon alkane *butane*), and the presence of the two double bonds (2-methyl-1,3-buta*diene*). Notice that commas separate numbers from each other, and that hyphens separate digits from letters.

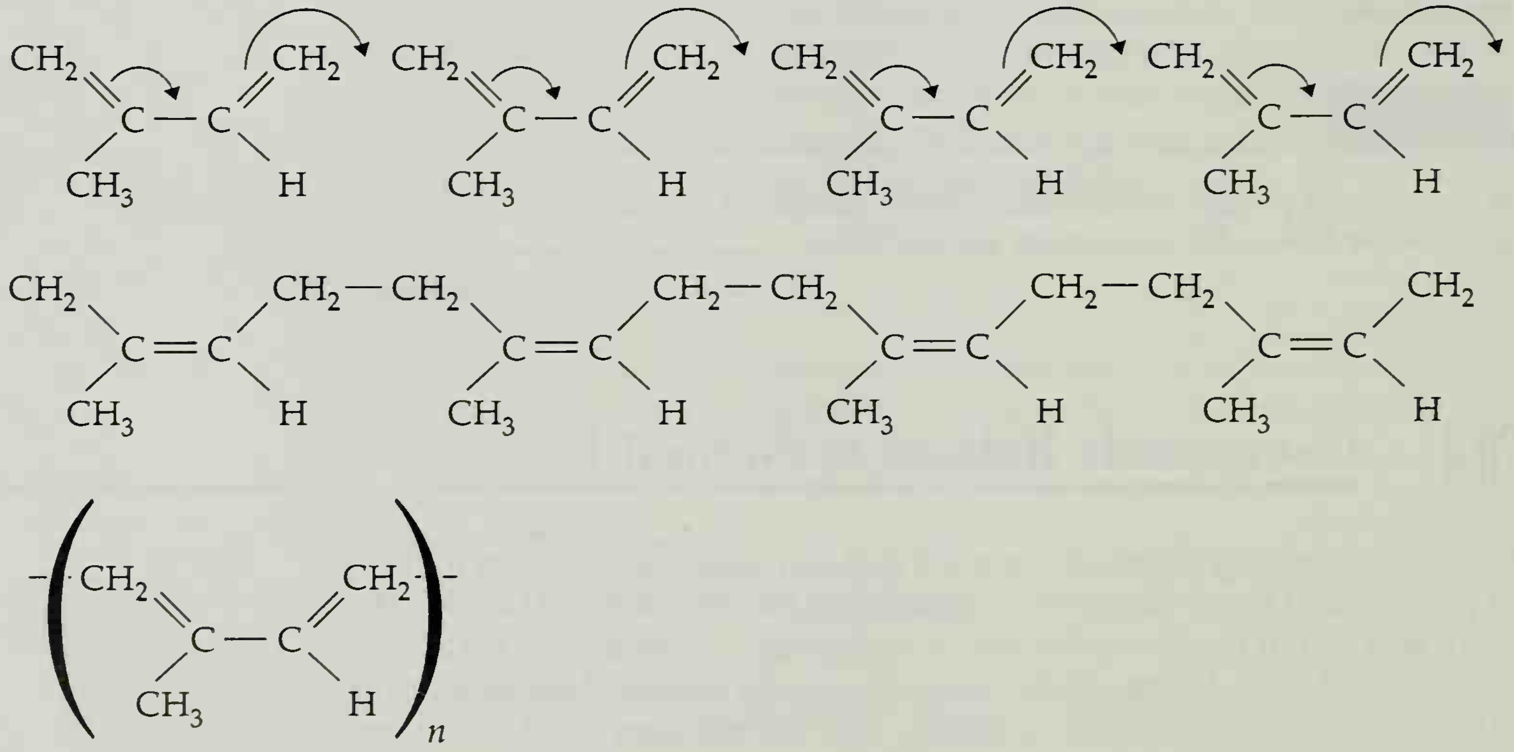


Figure 20.14
Rubber as *cis*-polyisoprene.

Like the carbohydrates and proteins, rubber forms in nature through a complex set of reactions. Nevertheless, we can view it as *polyisoprene*, an addition polymer of isoprene, and we can imagine it forming with electron movements similar to those that convert ethylene into polyethylene (Figs. 20.12 and 20.13). Double bonds remain in the polymeric chain of rubber and, moreover, fix each of the double bonds of the chain into the *cis* configuration, one of two possible shapes available to it (Fig. 20.14).

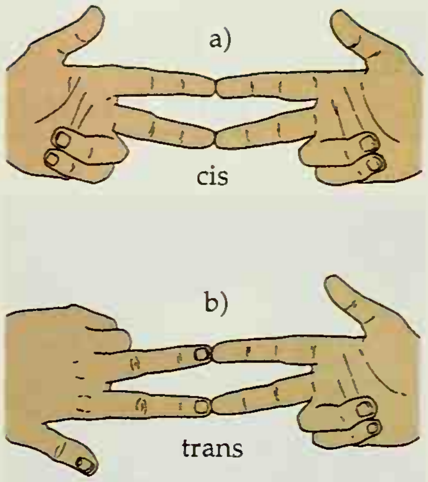


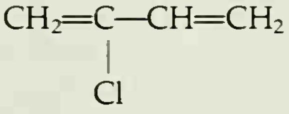
Figure 20.15
Geometric isomers.

As we saw in Section 13.6, a carbon–carbon double bond can secure an unsaturated molecule into a *cis* or a *trans* geometric configuration. You can form a good model of the two possibilities by putting your hands together as in Figure 20.15. With your extended thumbs representing methyl groups, Figure 20.15a shows your hands in a *cis* configuration. Here both methyl groups (thumbs) are on the same side of the double bond. The only way to get to the *trans* isomer (Figure 20.15b) is to flip over one of your hands. Of course this requires disconnecting the fingers that form the "double bond." At the molecular level this means the breaking and reforming of actual, covalent bonds, a high-energy process. Unless plenty of energy is available, as at a high temperature, for example, or in the presence of radiation, the *cis* and *trans* isomers don't ordinarily interconvert.

The uniformly *cis* configuration of all the double bonds in rubber's polyisoprene chain keeps the carbons of the chain on one side of the average line of the double bonds and the methyl substituents on the other, as in Figure 20.14. In *gutta-percha*, another naturally occurring polymer of isoprene, all the double bonds are in the *trans* configuration (Fig. 20.16). With an all-*trans* molecular geometry, gutta-percha isn't nearly as elastic as rubber. It does find uses, though, as a covering for golf balls, in surgical equipment, and as an electrical insulator, especially for underwater cables.

QUESTION

Give the IUPAC name of *chloroprene*, the monomer used in preparing *neoprene*, a synthetic rubber.



$$CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2$$

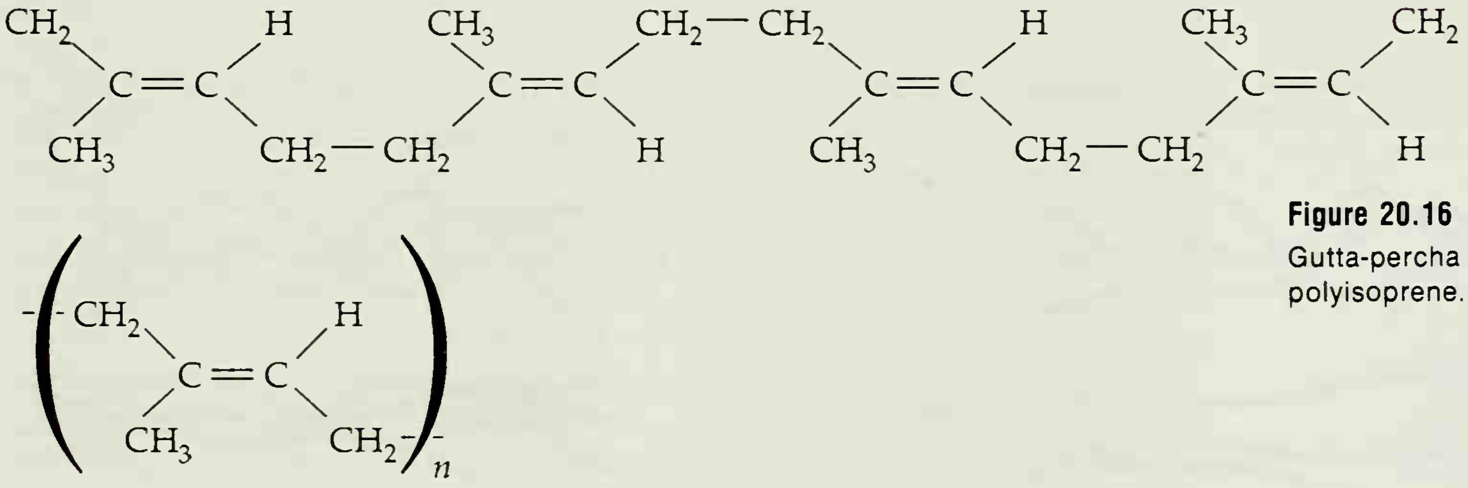


Figure 20.16
Gutta-percha as *trans*-polyisoprene.

20.9 A Brief History—Part I: The Roman God of Fire

When he accidentally dropped a mixture of natural rubber and sulfur on a hot stove, Charles Goodyear discovered the process that became known as *vulcanization.* We now know that the sulfur links the polymeric molecules of the rubber together so that the rubber retains its resilience even when it is hot.

In its elasticity, rubber illustrates the importance of molecular structure as a source of physical properties. Its elasticity originates in the way its molecules coil up, which allows them to stretch out when we pull on a piece of rubber and then to spring back when we release it. Heat a piece of pure, natural rubber, though, and you'll find that as it becomes warm it loses much of its resilience. Its usual bounce becomes sloppy and it turns sticky. That happens because at high temperatures the intertwined, threadlike polyisoprene molecules slide past each other a bit too readily when we stretch the rubber and they don't pull back to their original positions when we release it.

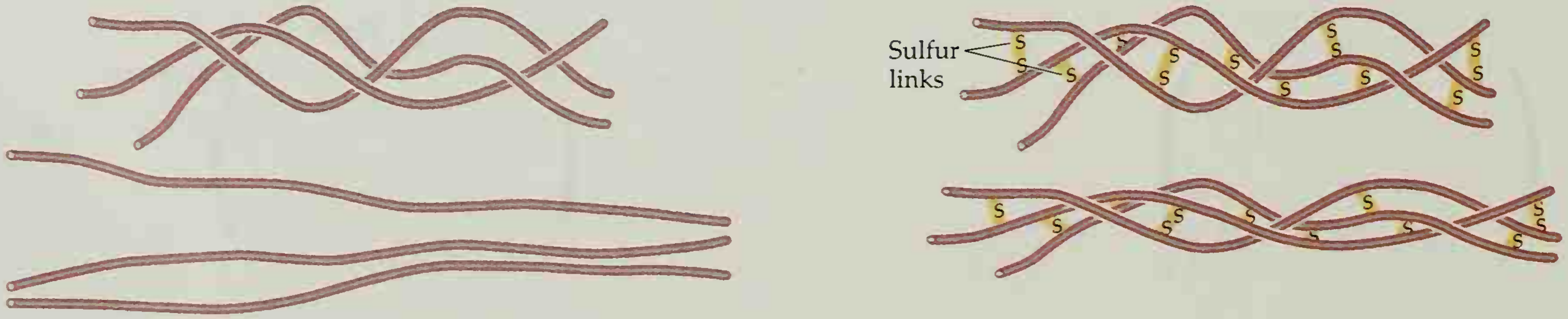
Charles Goodyear, born in 1800 in New Haven, Connecticut, four days after Christmas, solved the problem of sticky rubber partly by accident. He was an inventor and the son of an inventor, but he lacked the talents of a good businessman. He had already spent time in jail for his debts when he became obsessed with the idea of creating a rubber that retained its elasticity even when hot. He tried perfecting it for 10 years with little success until, one day in 1839, he accidentally dropped a mixture of crude rubber and sulfur onto a hot stove. When the charred mixture cooled a bit he found that it was nicely elastic, even though still warm. In 1839 neither Charles Goodyear nor anyone else knew anything about the molecular structure of rubber. Goodyear knew only that heating rubber with sulfur worked; he had no idea why. Once again we see the importance of serendipity in science (Section 4.2).

We know now that with heating, the sulfur and the polyisoprene molecules react to *crosslink* the polyisoprene molecules to one another. With this crosslinking the molecular structures became loosely bound to each other in a three-dimensional lattice. The sulfur links keep the long molecules from slipping past their neighbors at high temperatures and thereby keep the rubber resilient and prevent it from becoming sticky (Fig. 20.17).

Five years later Goodyear received a patent for the process, but financial success eluded him. Poor and debt-ridden, he tried unsuccessfully to make his fortune by manufacturing rubber in both England and France. Close to his 55th birthday, he was thrown into a Paris jail for debt. He returned to the United States and died in New York on July 1, 1860, still poor and still in debt. Someone else named his process *vulcanization* in honor of the Roman god of fire, *Vulcan.*

Figure 20.17

Vulcanized rubber.



Polymeric strands of unvulcanized rubber slip past each other when the rubber is heated and stretched.

Vulcanization connects the strands through links of sulfur so that the interconnected polyisoprene molecules retain their orientation when heated and stretched.

Today vulcanization forms the basis of a major industry. All natural rubber now used commercially is vulcanized, with most of it going into the production of auto tires. The name of Charles Goodyear is preserved in the Goodyear Tire and Rubber Company.

QUESTION

Is pure, natural, unvulcanized rubber an elastomer (a) when it is cold? (b) When it is hot? Repeat this question for vulcanized rubber. ______

20.10 A Brief History —Part II: Save The Elephants!

Charles Goodyear didn't invent a new polymeric molecule or a new elastomer; he accidentally modified a natural, polymeric elastomer and came up with an enormous improvement in its properties. John Wesley Hyatt and his brother Isaiah, on the other hand, consciously and deliberately converted a modified natural polymer into the world's first new, commercially successful synthetic plastic. They produced a plastic that hadn't existed earlier.

By 1863, three years after Goodyear's death, the slaughter of the world's elephants for their tusks had become a serious matter, as it still is today. In that era the disappearance of elephants was threatening to disrupt the world's ivory supply. Ivory, a valuable luxury item of the 19th century used for jewelry, ornaments, piano keys, and various other items, was becoming scarce and very expensive. Perhaps to protect the elephants but certainly to ensure a source of raw materials, the firm of Phelan and Collander, a New England manufacturer of ivory billiard balls, offered $10,000 to anyone who could devise a satisfactory substitute for the rapidly disappearing natural ivory. John Hyatt, a 26-year-old printer born in Starkey, New York, took up the challenge. He was helped by a startling discovery made years earlier by a chemist in Basel, Switzerland.

In 1846 a Swiss chemistry professor, Christian Schoenbein, had accidentally invented guncotton by spilling a mixture of nitric acid and sulfuric acid in the kitchen of his home and then wiping up the mess with his wife's cotton apron. He rinsed out the apron thoroughly with water and hung it up to dry near a hot stove. As it hung drying it disappeared in a sheet of flame.

The smokeless *guncotton* of Schoenbein's accident proved far superior to the very smoky *gunpowder* used at the time in warfare and it became a popular military item. More to the point, by inadvertently inducing a reaction between the mixture of nitric and sulfuric acids and the cellulose of the cotton apron, Schoenbein had successfully transformed the polymeric cellulose into *nitrocellulose*, a compound in which varying numbers of the hydroxyl groups ($—OH$) of the polymer are converted into nitrate groups ($—O—NO_2$). (The sulfuric acid serves to catalyze the reaction.)

John Hyatt won the $10,000 prize with a combination of *camphor*, a pungent substance obtained from the camphor tree, and a lightly nitrated form of

A burning ping-pong ball made of celluloid illustrates the flammability of the plastic.

Schoenbein's nitrocellulose. The mixture forms a thermoplastic so similar to ivory that it was known for some time as artificial ivory. We now call it *celluloid*.

With the help of his brother Isaiah, Hyatt began manufacturing celluloid in 1870 and became more successful financially than Goodyear. His synthetic billiard balls proved a bit too brittle to be useful, but the plastic did make fine dental plates, photographic film, brush handles, detachable collars, ping pong balls, and a host of other small products. Its major defect in consumer products is its tendency to burst into flames. Movie film was once made of this highly flammable celluloid and often ignited from the heat of the projector.

Although the Hyatts had produced celluloid, the world's first successful commercial plastic, they hadn't actually constructed a new polymeric chain. The plastic was, rather, a combination of camphor and chemically modified, naturally occurring cellulose. The credit for the world's first fully synthetic organic polymer goes to Leo Hendrik Baekeland.

QUESTION

The nitric acid in Schoenbein's accident reacted with free hydroxyl groups on each of the monomeric glucose links of the cellulose polymer. How many free hydroxyl groups does each of these monomeric units have available for this reaction? ____________

20.11 A Brief History—Part III: The First Synthetic Polymer

Born in Belgium in 1863, the same year that Phelan and Collander offered its $10,000 reward for an ivory substitute, Leo H. Baekeland became an active, productive, and successful academic and industrial chemist. As a young man he emigrated to the United States and became a citizen; eventually he was elected president of the American Chemical Society, the world's largest professional association of chemists. In 1909 he announced his preparation of the first fully synthetic polymer, a resin he called *Bakelite*. In the following year he founded the Bakelite Corporation to manufacture the material.

Left Photo: Leo H. Baekeland, inventor of Bakelite, a condensation polymer of phenol and formaldehyde.

Right Photo: Old phonograph records made of Bakelite. These records revolved at the speed of 78 revolutions per minute and were called "78-rpm" records.

Like nylon, Bakelite is a condensation copolymer; unlike nylon and unlike any of the other polymers we've examined so far, it is a thermosetting plastic rather than a thermoplastic. Bakelite forms as a mixture of *phenol* and *formaldehyde* (Section 14.4) polymerizes. As we see in Figure 20.18, each formaldehyde molecule bonds to *two* different phenol molecules, and each phenol ring bonds to *three* different formaldehyde molecules (with a molecule

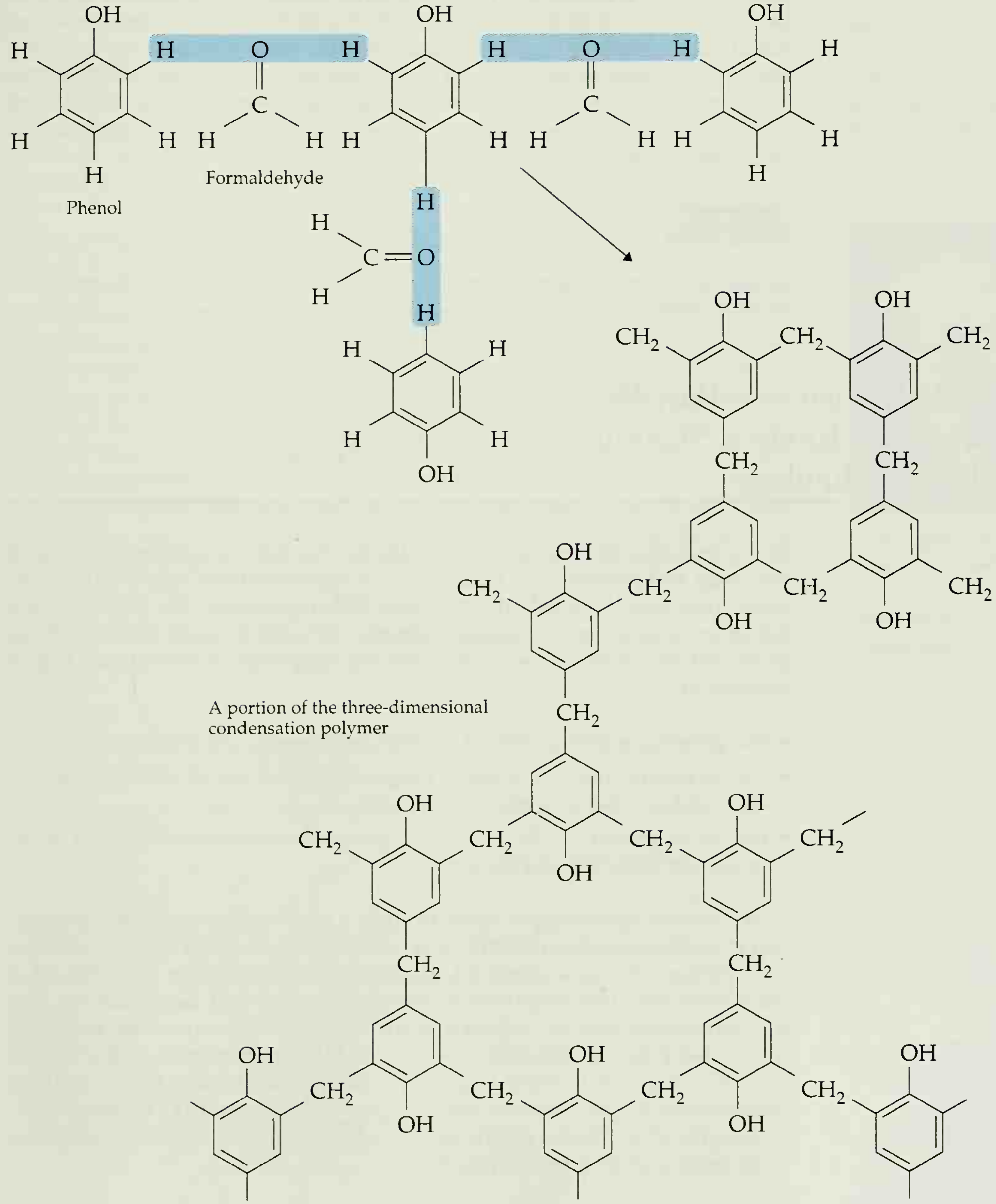


Figure 20.18
Bakelite.

of water lost for each combination of two phenols and one formaldehyde). The geometric possibilities available here produce an intricate, three-dimensional web of resinous polymeric material.

Bakelite is a hard, sturdy material, resistant to heat and electricity and not easily burned or scorched. With such properties, it's a good material for molding small household items such as handles for toasters and pots and pans, and for electrical insulators. The use of other aldehydes and of other phenols, bearing groups other than hydrogens here and there on the ring, produces variations on Bakelite and has created an entire class of *phenolic resins*. Today the primary uses of the phenolic resins are as adhesives and fillers in the manufacture of plywood and fiberboard and in the production of insulating materials. A little more than 45% of all thermosetting polymers produced today belong to this class of resin.

QUESTION

Is Bakelite (a) an addition polymer or a condensation polymer? (b) A thermoplastic or a thermoset? ____

20.12 A Brief History—Part IV: From the Kitchen Stove to High Technology

We've seen that the early advances in the development of commercially useful polymers and plastics were made by a few ingenious (and lucky) individuals, sometimes quite by accident, often with little equipment. The days of major advances in polymer and plastic chemistry arriving through small accidents on hot kitchen stoves came to an end in the early years of this century largely because of

- the growing sophistication of scientific equipment and techniques,
- the increasing rigor of research programs carried out in academic, industrial, and institutional laboratories, and
- the development, in the 1920s, of a comprehensive understanding of the molecular structure of polymers.

We've seen one example of the fruits of a highly organized, well-directed, and strongly supported research program in the discovery of nylon by Wallace Carothers and his co-workers at DuPont Corporation (Section 20.4). For other examples—one that contributed to winning World War II (Section 20.16), one that generated a flash of national mania (Section 20.17), and one that produced two Nobel Prizes in chemistry (Section 20.18)—we turn now to the field of *polyolefins* and closely related polymers. The plastics formed by the addition polymers we'll examine in the following several sections make up about 75%, by weight, of all plastics produced in the United States. They are among our most important commercial plastics.

20.13 Polystyrene

Olefin is another and much older name for the unsaturated hydrocarbons we now know as the *alkenes* (Section 7.9). It's a corruption of a name given to ethylene by several Dutch chemists in 1795 to reflect its character as an "oil-forming" gas in its reaction with chlorine. Since then, the term has been extended to include the entire category of hydrocarbons that, like ethylene, bear a single carbon–carbon double bond. By now the name is used as a synonym for "alkene" for the hydrocarbons whose molecular formulas adhere to the general formula C_nH_{2n}. Polymerizing any of these produces a **polyolefin**.

Polyolefins are polymers produced by the polymerization of alkenes and compounds closely related to them.

We've already seen that polymerizing ethylene, the simplest of all the alkenes, produces polyethylene, a polyolefin we'll examine in more detail in Section 20.16. Replacing one or more of ethylene's hydrogens by other substituents gives monomers useful for preparing polymers closely related to the polyolefins and sharing many of their important properties.

Replacing one of the ethylenic hydrogens by a *phenyl* group, for example, gives *styrene*, which polymerizes to the thermoplastic *polystyrene* (Fig. 20.19). The various techniques available for converting the raw polystyrene polymer into a finished product provide a wide range of useful properties for the resulting plastic. Inexpensive, clear, rigid drinking glasses are made of polystyrene. In a variation known as high-impact polystyrene, the plastic is used to make sturdy furniture, inexpensive tableware, and stereo, television, and computer cabinets. On the other hand, solid, lightweight polystyrene foams are good thermal insulators and shock absorbers, useful for making picnic coolers, egg cartons, clamshell containers for fast foods, disposable cups for keeping drinks hot or cold, and small polystyrene nuggets used as packing

Cups, plates, and containers made from polystyrene foam.

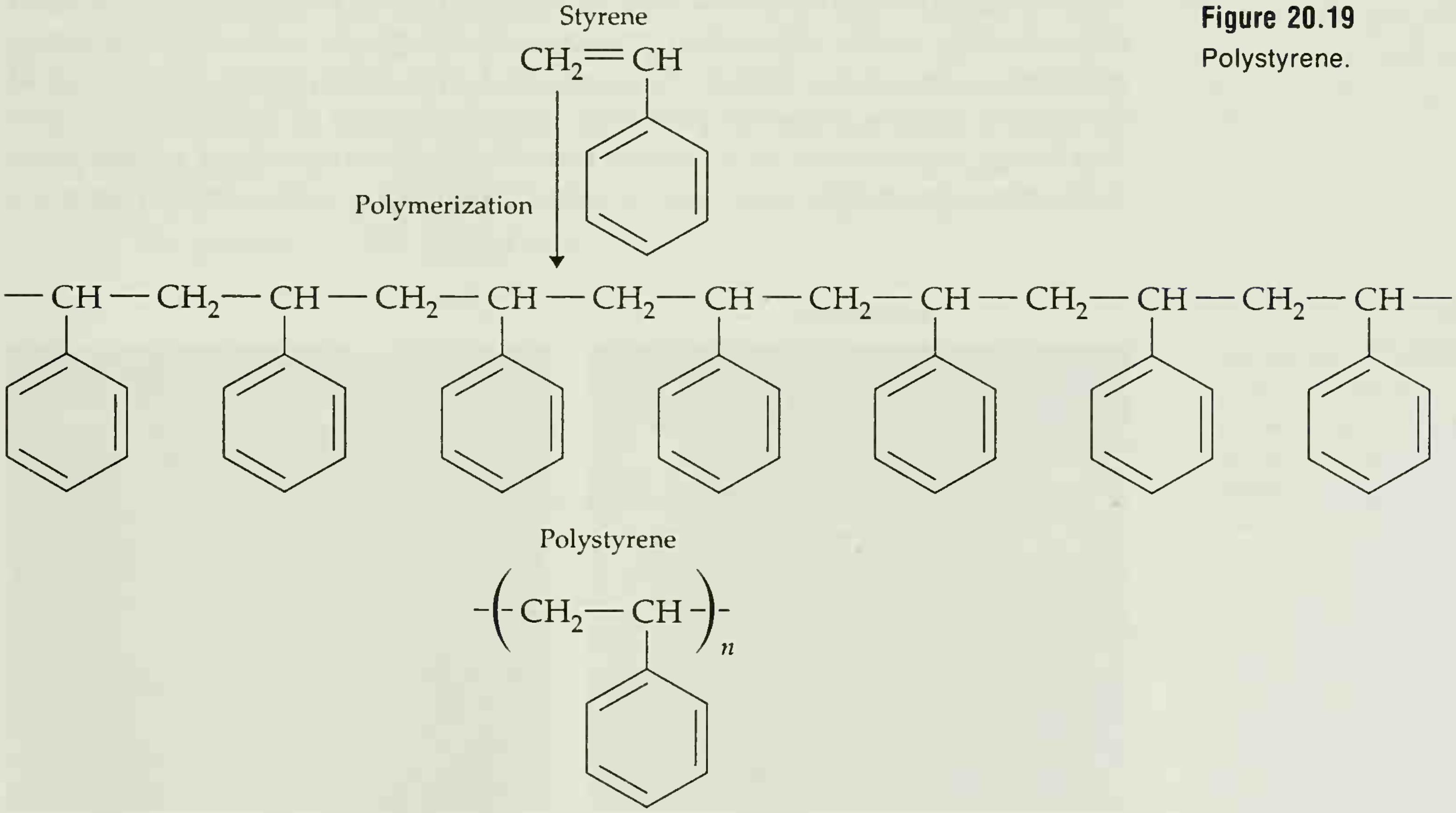


Figure 20.19
Polystyrene.

material. These foams, some of which are sold under the name *Styrofoam*, are made by using a gas to generate a foam of liquid polystyrene and allowing the frothy mass to cool. Chlorofluorocarbons (Section 19.12) were once used to generate the froth, but these have been replaced by other gases, including low-boiling alkanes. Today, well over half of all the polystyrene produced goes into inexpensive consumer products.

QUESTION

In what way does the molecular structure of styrene differ from the molecular structure of ethylene?

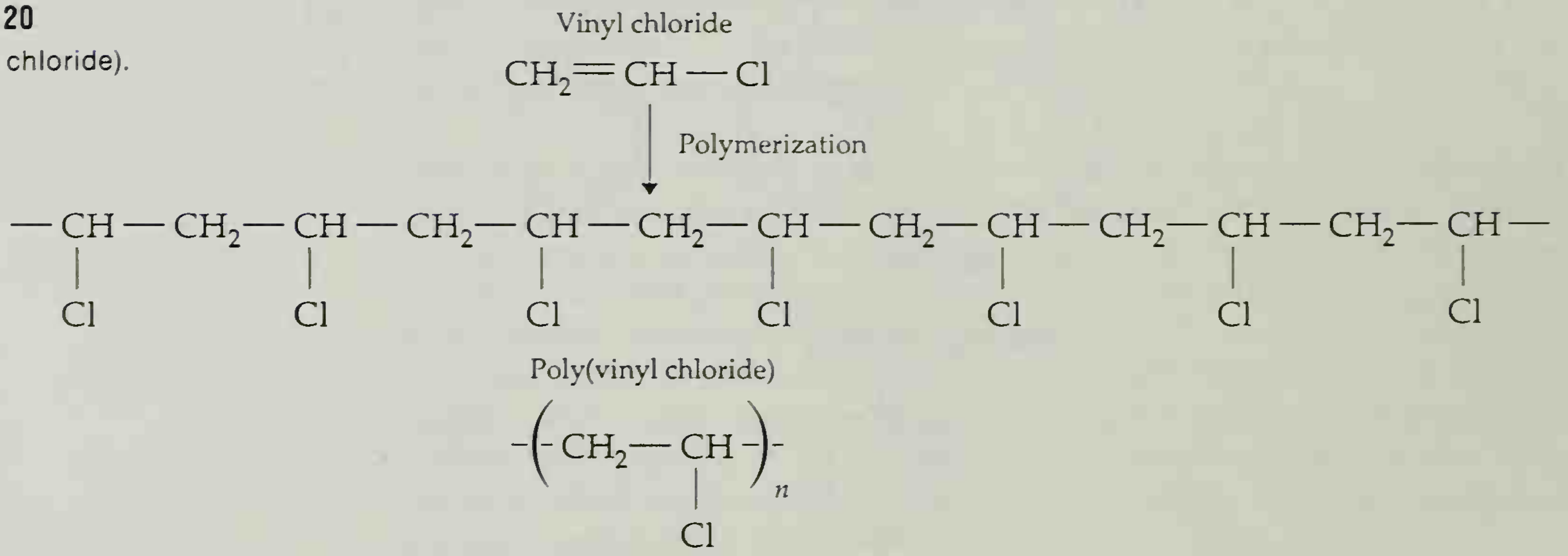
20.14 Vinyl . . .

In the realm of consumer products the word *vinyl* has come to mean a tough, flexible, and often smooth, shiny plastic that serves as a much less expensive substitute for leather. We often find vinyl purses, wallets, and jackets and other vinyl goods for sale at the lower-priced counters of stores.

To the chemist, though, *vinyl* represents a hydrocarbon group ($CH_2{=}CH{-}$) that can be formed by the removal of a hydrogen atom from ethylene, just as methyl group ($CH_3{-}$) and an ethyl group ($CH_3{-}CH_2{-}$) can be produced by the removal of a hydrogen atom from methane (CH_4) and ethane ($CH_3{-}CH_3$), respectively (Chapter 7). Moreover, just as $CH_3{-}Cl$ and $CH_3{-}CH_2{-}Cl$ represent *methyl* and *ethyl* chloride, $CH_2{=}CH{-}Cl$ is *vinyl* chloride.

The terms *poly(vinyl chloride)*, *polyvinylchloride*, and *PVC* all serve very nicely as names for the thermoplastic formed by the addition polymerization of vinyl chloride (Fig. 20.20). The polymer forms a tough plastic well suited to pipes, plumbing, electrical conduit, flooring, and both indoor and outdoor wall coverings. Among personal products, it's widely used in molding toys, garden hoses, and analog phonograph records (which are made of a copolymer containing about 87% vinyl chloride and 13% *vinyl acetate*, a monomer we'll

Figure 20.20
Poly(vinyl chloride).



$$CH_2{=}CH{-}Cl \xrightarrow{\text{Polymerization}} {-}\!\left(CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\right)_{n}\!{-}$$

examine in the next section). Well over half of all PVC production currently goes into the construction industry, with most of it used in piping, tubing, and similar extruded materials.

Because thin sheets of polyvinylchloride are relatively stiff and crack easily, it's necessary to add a **plasticizer** to give them the same sort of flexibility we expect from leather. Plasticizers are liquids that mix readily with a plastic and soften it. With time a plasticizer can migrate out of the plastic or otherwise deteriorate, allowing aged polyvinylchloride to stiffen and crack.

A **plasticizer** is a liquid that is mixed with a plastic to soften it.

QUESTION

What name would you give the plastic made from the addition polymer of $CH_2{=}CH{-}Br$? ______

20.15 . . . And Its Chemical Cousins

Other useful thermoplastics come from still other monomers closely related to ethylene, including *vinyl acetate, acrylonitrile, vinylidene chloride, tetrafluoroethylene, methyl methacrylate* (Table 20.1), and, of course, the styrene we examined in Section 20.13.

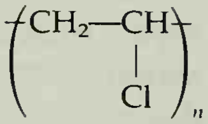
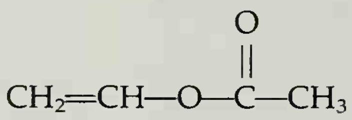
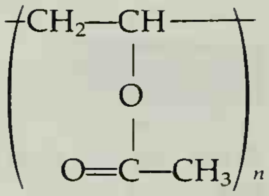
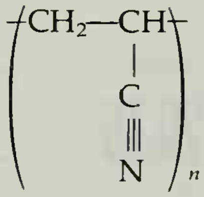
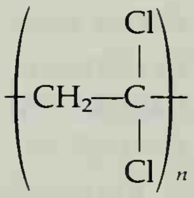
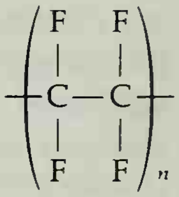
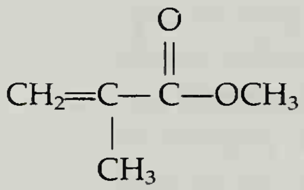
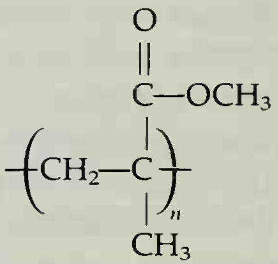
Polymerization of vinyl acetate produces *polyvinylacetate*, a plastic with a wide range of properties and an equally wide range of applications. As a thermoplastic with a low softening temperature it's useful in coatings and adhesives. A sandwich of two panes of glass bonded to a central sheet of the material forms a *shatterproof* or *safety* glass. While the glass can break, it won't shatter into dangerous slivers. Safety glass of this kind is used in car windows.

Mixed with sugar, flavoring, glycerine (for softening; see Chapter 17 Perspective), and other ingredients, polyvinylacetate replaces the chewy chicle of chewing gum. (Chicle itself is a rubberlike polymer obtained from the sap of the sapodilla tree.) Partially polymerized vinyl acetate serves as a *binder* in water-based house paints. As the water evaporates, the low-molecular weight polymer present in the paint polymerizes further, forming a tough sheet that "binds" the pigment to the coated surface.

Left Photo: A broken car window made of safety glass. A sheet of polyvinylacetate sandwiched between two sheets of glass prevents the broken glass from disintegrating into flying slivers.

Right Photo: Bubble gum made from polyvinylacetate.

TABLE 20.1 Addition Polymers

Monomer		Polymer	
ethylene	$CH_2{=}CH_2$	polyethylene	$\text{-}(CH_2{-}CH_2)_n$
vinyl chloride	$CH_2{=}CH{-}Cl$	poly(vinyl chloride) polyvinylchloride PVC	 $\left(CH_2{-}\underset{\underset{\displaystyle Cl}{\vert}}{CH}\right)_n$
vinyl acetate	 $CH_2{=}CH{-}O{-}\overset{\overset{\displaystyle O}{\Vert}}{C}{-}CH_3$	poly(vinyl acetate) polyvinylacetate PVA	 $\left(CH_2{-}\underset{\underset{\underset{\displaystyle O{=}C{-}CH_3}{\vert}}{\underset{\displaystyle O}{\vert}}}{CH}\right)_n$
acrylonitrile	$CH_2{=}CH{-}C{\equiv}N$	polyacrylonitrile Orlon Acrilan Creslan	 $\left(CH_2{-}\underset{\underset{\underset{\displaystyle N}{\vert\vert\vert}}{\underset{\displaystyle C}{\vert}}}{CH}\right)_n$
vinylidine chloride	$CH_2{=}CCl_2$	poly(vinylidine chloride) Saran	 $\left(CH_2{-}\overset{\overset{\displaystyle Cl}{\vert}}{\underset{\underset{\displaystyle Cl}{\vert}}{C}}\right)_n$
tetrafluoroethylene	$F_2C{=}CF_2$	polytetrafluoroethylene Teflon	 $\left(\overset{\overset{\displaystyle F}{\vert}}{\underset{\underset{\displaystyle F}{\vert}}{C}}{-}\overset{\overset{\displaystyle F}{\vert}}{\underset{\underset{\displaystyle F}{\vert}}{C}}\right)_n$
methyl methacrylate	 $CH_2{=}\underset{\underset{\displaystyle CH_3}{\vert}}{C}{-}\overset{\overset{\displaystyle O}{\Vert}}{C}{-}OCH_3$	poly(methyl methacrylate) Lucite Plexiglas	 $\left(CH_2{-}\overset{\overset{\overset{\displaystyle O}{\Vert}}{\overset{\displaystyle C{-}OCH_3}{\vert}}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}\right)_n$

Polyacrylonitrile, a thermoplastic that's drawn out into fine threads and woven into synthetic fabrics such as *Orlon, Acrilan,* and *Creslan,* comes from the polymerization of acrylonitrile ($CH_2{=}CH{-}CN$).

Putting two chlorines on the single carbon of ethylene converts it into *vinylidene chloride* ($CH_2{=}CCl_2$), the major monomer of *Saran.* Sheets of this polymer form a nearly impregnable barrier to food odors, which makes it useful for wrapping foods that are to be stored near each other in a refrigerator.

Teflon results from the polymerization of *tetrafluoroethylene* ($CF_2{=}CF_2$), a monomer obtained by replacing all of ethylene's hydrogens with fluorines. Teflon's great chemical stability, its resistance to heat, its mechanical toughness, and its nearly friction-free surface make it useful as a coating for bearings, valve seats, gaskets, and other parts of machinery that take heavy wear. Since things don't easily stick to it, Teflon makes a fine coating for cooking utensils such as pots and pans. Teflon was first prepared at DuPont in 1938; commercial production began 10 years later.

In molecular structure *methyl methacrylate* is a bit further removed from ethylene. Its polymer forms a very hard, very clear, colorless plastic that appears in consumer products as Lucite and Plexiglas. It's used in making glasses, camera lenses, and other optical equipment, in costume jewelry, and as windows in aircraft.

Food doesn't stick to cooking utensils coated with Teflon, a plastic made by polymerizing tetrafluoroethylene, $F_2C{=}CF_2$.

QUESTION

What property or combination of properties does each of the following polymers contribute to the consumer product associated with it: (a) poly(methyl methacrylate) as a camera lens; (b) poly(vinyl acetate) as a substitute for chicle in chewing gum; (c) polytetrafluoroethylene as a coating for pots, pans, and skillets; (d) poly(vinylidene chloride) as a food wrapper? ____________________

20.16 Polyethylene, the Plastic That Won the War . . .

With a total annual production of about 9.4 million tons, polyethylene is clearly the major polymer of the U.S. plastics industry. In its two principal commercial forms (high-density polyethylene and low-density polyethylene, which we'll examine shortly) it also illustrates very nicely the connection between the structure of a polymeric molecule and the properties of the plastic it forms. As we might imagine, the physical properties of a piece of bulk plastic depend partly on the molecular structure of the monomer that forms it and partly on the average length of its polymeric chains. As we'll see shortly, a third factor also comes into play: the way polymeric chains organize themselves as they constitute the bulk of the material.

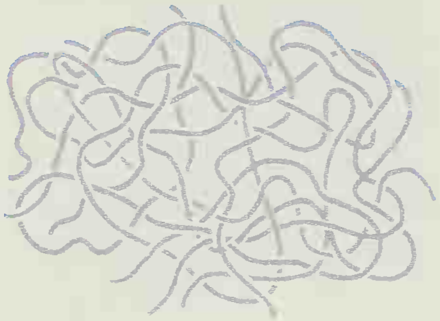


Figure 20.21
Disorganized polymeric strands of low-density polyethylene.

Polyethylene itself was first prepared in 1934 in the laboratories of Imperial Chemical Industries, in Great Britain. It went into commercial production there five years later, as World War II was about to begin. The first practical use of the plastic was as insulation on the electrical wiring of military radar sets. When we consider the critical importance of aircraft radar to the survival of Britain in the early years of the war, we could easily designate polyethylene as the plastic that won the war.

Trash bags made of low density polyethylene.

The techniques used for those early polymerizations produce what we now know as *low-density polyethylene* (*LDPE*). As the chains of LDPE form they branch sporadically into short offshoots from the main line of the polymer. These keep the major strands of the polymer from falling into anything resembling a coherent, well organized pattern. Instead they form a tangled, randomly oriented network of strands, somewhat like a large ball of fuzz (Fig. 20.21). The result is a low-density, soft, waxy, flexible, relatively low-melting plastic that accounts for about 55% of all the polyethylene produced in the United States. More of this LDPE goes into producing trash bags than into any other single product. Industrial and commercial packaging, food wrappers, and plastic shopping bags are close behind. As in World War II, the coating of electrical wires and cables remains a major use.

QUESTION

What are the two commercial forms of polyethylene? ____________

20.17 . . . And Gave Us a Significant Bit of Trivia

Polymerized by a different method, the polyethylene chains can grow on and on without branching, thereby generating *high-density polyethylene* (*HDPE*). This form of the plastic was first produced in the Federal Republic of Germany in the early 1950s by Karl Ziegler, a German chemist born near the end of 1898. Ziegler prepared HDPE by carrying out the polymerizations in the presence of certain highly specialized *organometallic catalysts*. These consist of combinations of organic molecules and metal atoms, joined to each other by covalent bonds, that control the way the monomers link to each other as they polymerize.

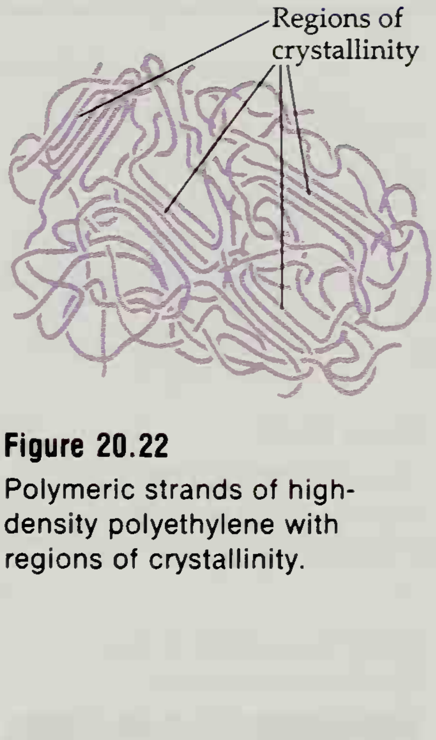


Figure 20.22
Polymeric strands of high-density polyethylene with regions of crystallinity.

In HDPE the long molecular chains aren't fixed into a tangled web as they are in the LDPE, and so they can align themselves into localized areas of tightly packed strands, mimicking here and there the orderly structure of crystals such as sodium chloride and sucrose. With many regions of close packing and a high degree of crystallinity, HDPE is a denser, harder, higher melting, and more rigid polymer than LDPE (Fig. 20.22)

We saw another example of this same sort of relationship between molecular structure and physical properties in the fats and oils of Chapter 11. Fats are solids with higher melting points than the liquid oils because the saturated side chains of the fatty triglycerides can pack more closely together and in a more orderly fashion than the side chains of the polyunsaturated oils, which are bent by the geometric requirements of their carbon–carbon double bonds (Section 11.10). This same kind of physical effect produces the differences in properties between the low-density and high-density polyethylenes, generated here by the orientations of long, polymeric chains.

Of the nearly 4.2 million tons of HDPE produced in the United States in 1990, most went into the manufacture of bottles and other containers designed to hold a variety of liquids, including noncarbonated drinks, bleach, antifreeze, and engine oil. It's also used in fabricating shipping drums and automobile gasoline tanks. Historically, HDPE's introduction into consumer products was as the Hula-Hoop, a large plastic hoop placed at the waist and twirled with hulalike motions. The craze swept the United States in the late 1950s; its memory survives today largely in collections of national trivia.

QUESTION

Would you use high-density or low-density polyethylene to manufacture each of the following: (a) rope, (b) disposable medical syringes, (c) utensils for use in microwave ovens, (d) plastic sheets to protect cars parked outdoors? ____________

20.18 A Nobel Prize for Two

We have seen repeatedly that the physical and chemical properties of a substance depend on the structure of its molecules or ions. For polymers, for example, we saw that the way individual glucose molecules are joined to each other determines whether they form starch or cellulose (Section 14.11), and that the geometry of the double bond in the polyisoprene chain determines whether it forms rubber or gutta percha (Section 20.8).

The effects of molecular structure on the properties of a plastic appear again in the polymerization of *propylene*. Figure 20.23 shows a small portion of the polypropylene chain, with emphasis on the orientation of the methyl substituents that appear on every other carbon of the polymer. There are three different ways these methyl groups can be arranged:

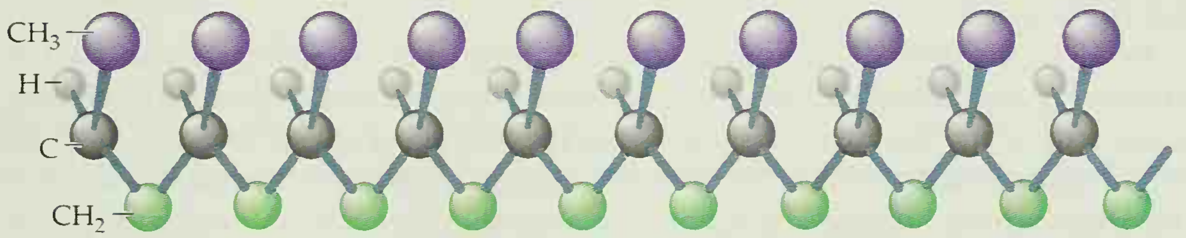
1. They can all protrude from the same side of the stretched-out, zig-zag molecular chain (*isotactic* polymer).
2. They can appear on alternating sides (*syndiotactic* polymer).
3. They can be oriented randomly (*atactic* polymer).

The terms for the three orientations come from the Greek *taktos*, "ordered," which is modified by the prefixes *iso-*, ("same"), *syndio-* ("two together"), and *a-* ("not").

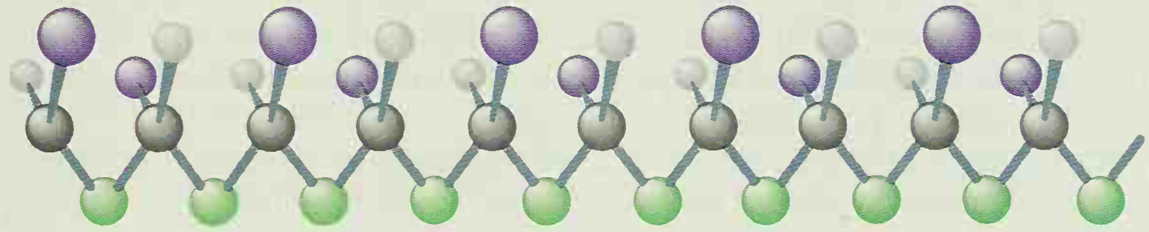
In 1953 Ziegler and Giulio Natta, Italian-born (1903) professor of industrial chemistry at the Milan Polytechnic, independently prepared the highly ordered polypropylenes, thereby creating the first *stereochemically ordered* polymers. For their pioneering work Ziegler and Natta shared the 1963 Nobel

Giulio Natta who shared the 1963 Nobel Prize in chemistry with Karl Ziegler for preparing stereochemically ordered polymers.

Isotactic (all on the same side)



Syndiotactic (alternating sides)



Atactic (random)

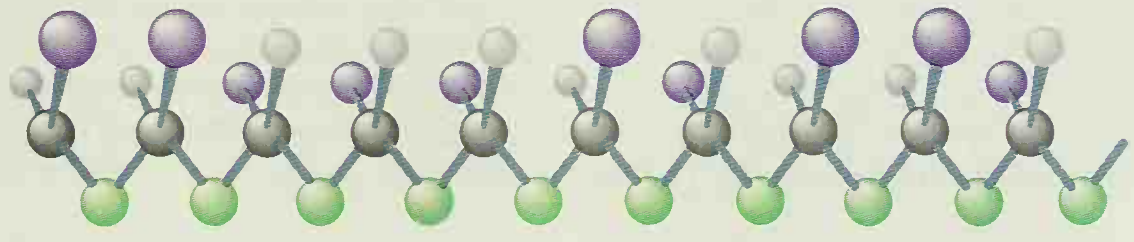


Figure 20.23
The polypropylenes.

Prize in chemistry. As we might expect from our knowledge of the effects of molecular order on the melting points of triglycerides and on the hardness of the polyethylenes, the highly ordered isotactic and syndiotactic polypropylenes are higher melting, more crystalline, and harder than the atactic.

Today more than 3.6 millions tons of polypropylene are produced in the United States each year, most of it going into the manufacture of automobile trim and battery cases, carpet filaments and backing, fabrics, small items such as toys and housewares, and the hard plastic caps used on containers made of other kinds of plastic.

QUESTION

Which of the polymers in Table 20.1 could exist in isotactic and syndiotactic forms?

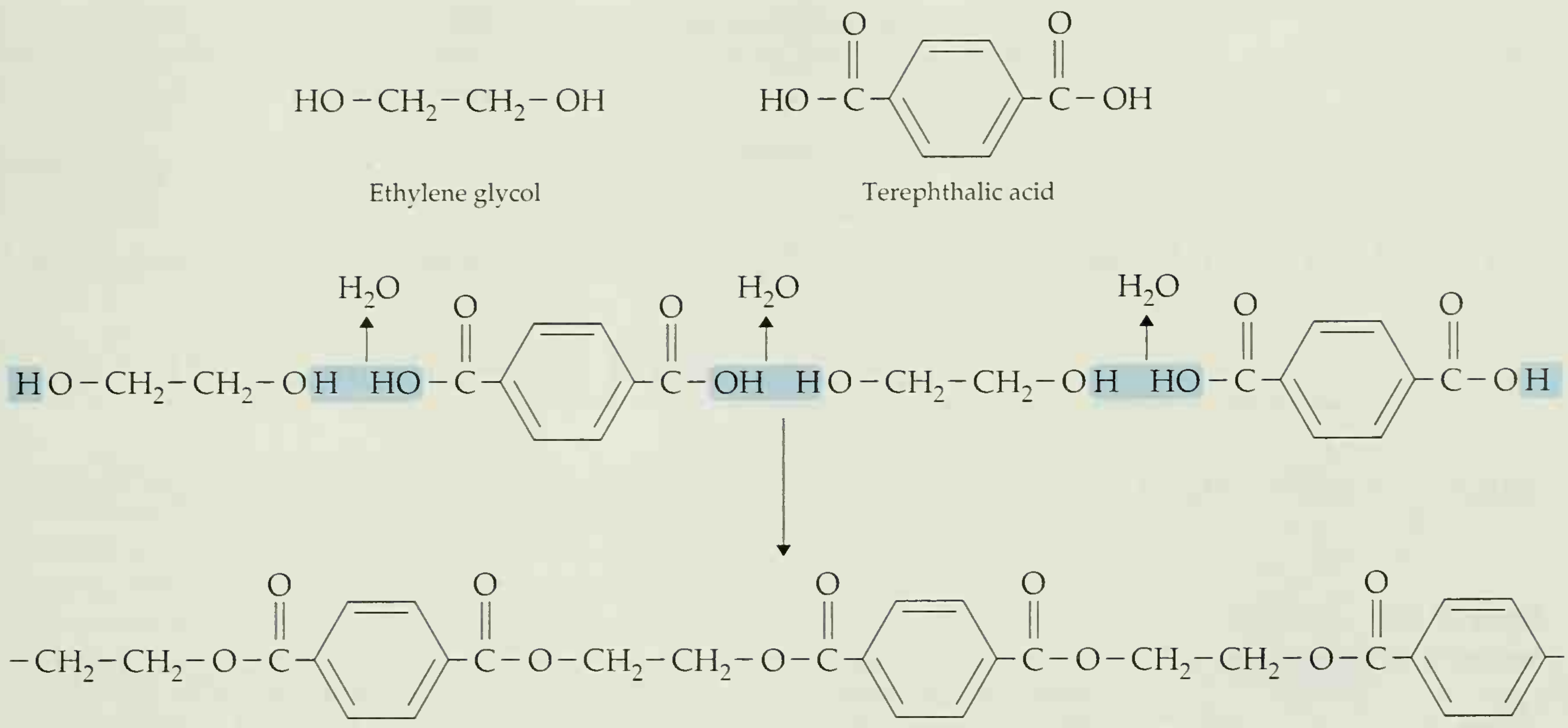
20.19 Condensation Polymers . . .

The polyolefins we've been examining in Sections 20.13 to 20.18 are all the products of addition polymerizations. We'll now survey some of the commercially important condensation polymers, the class of synthetic polymers that includes nylon (Section 20.5) and Bakelite (Section 20.11). The commercial leader in this class is *poly(ethylene terephthalate)*, a *polyester* also known as *PET*. We've already examined a *tri*ester in the triglycerides that form our fats and oils and that give us our soaps (Section 11.12; Chapter 13). In those compounds the three hydroxyl groups (—OH) of a single glycerol molecule are all combined with the carboxyl groups (HO_2C—) of the three carboxylic acids that form the triglyceride's side chains. Since each acid can contribute only one reactive group to the process, the reaction stops with the formation of the triglyceride.

In 1941 the British industrial chemist John Rex Whinfield succeeded in producing poly(ethylene terephthalate) by polymerizing a mixture of *ethylene glycol* and *terephthalic acid*. As shown in Figure 20.24, ethylene glycol has two —OH groups with which it can form esters. Unlike the carboxylic acids of the triglycerides, though, terephthalic acid also has *two* —CO_2H groups, allowing each one of its molecules to combine with *two different* glycol molecules. With this sort of combining power the two compounds form a copolymer whose monomeric units are linked to each other by ester groups. Chemically the process resembles the condensation of hexamethylenediamine and adipic acid to form the polyamide chain of nylon.

Poly(ethylene terephthalate) forms thin, tough films used for the backing on audio tapes and computer disks.

Drawing out the poly(ethylene terephthalate) into a filament produces the world's leading synthetic polymeric fiber, known as *Dacron* in the United States, as *Terylene* in Great Britain, and usually simply referred to as "polyester" when it's woven into a fabric. (Other, related polyester fibers include *Fortrel* and *Kodel*.) PET also forms an extremely thin and extremely tough film, *Mylar*, used as the plastic backing for audio and video tapes and computer diskettes, as well as wrapping material for frozen foods and bags for boil-in foods. In Western Europe PET has grown since the early 1980s into the dominant commercial plastic for packaging consumer goods.



Poly(ethylene terephthalate), a polyester

Figure 20.24
Poly(ethylene terephthalate).

[*Rayon* is a generic term for a group of fibers that are all derived from cellulose, largely by replacing one or more of the hydrogens of the —OH groups on the glucose rings with other chemical groups. Schoenbein's guncotton (Section 20.10) is one form of rayon.]

QUESTION

What chemical element occurs in fibers of nylon but not in fibers of Orlon?

20.20 . . . And Elastomers

As motorized vehicles replaced horses early in the 20th century, plentiful supplies of inexpensive rubber, needed especially for auto and truck tires, became critical to maintaining transportation and the effective distribution of goods and supplies throughout society. The two world wars produced a combination of increased military demands for rubber and the prospect of a loss of supplies from the plantations of Southeast Asia. This led the major industrialized nations of the West to develop various synthetic substitutes for rubber.

We'll round out our examination of the synthetic polymers with two of these elastomers that remain in large-scale production today, the homopolymer *neoprene* and the copolymer *styrene–butadiene rubber*. Neoprene comes from the polymerization of *chloroprene*, a monomer with a molecular structure resembling isoprene (Section 20.8), but with isoprene's methyl group replaced by chlorine (Fig. 20.25). Developed for commercial production by Wallace

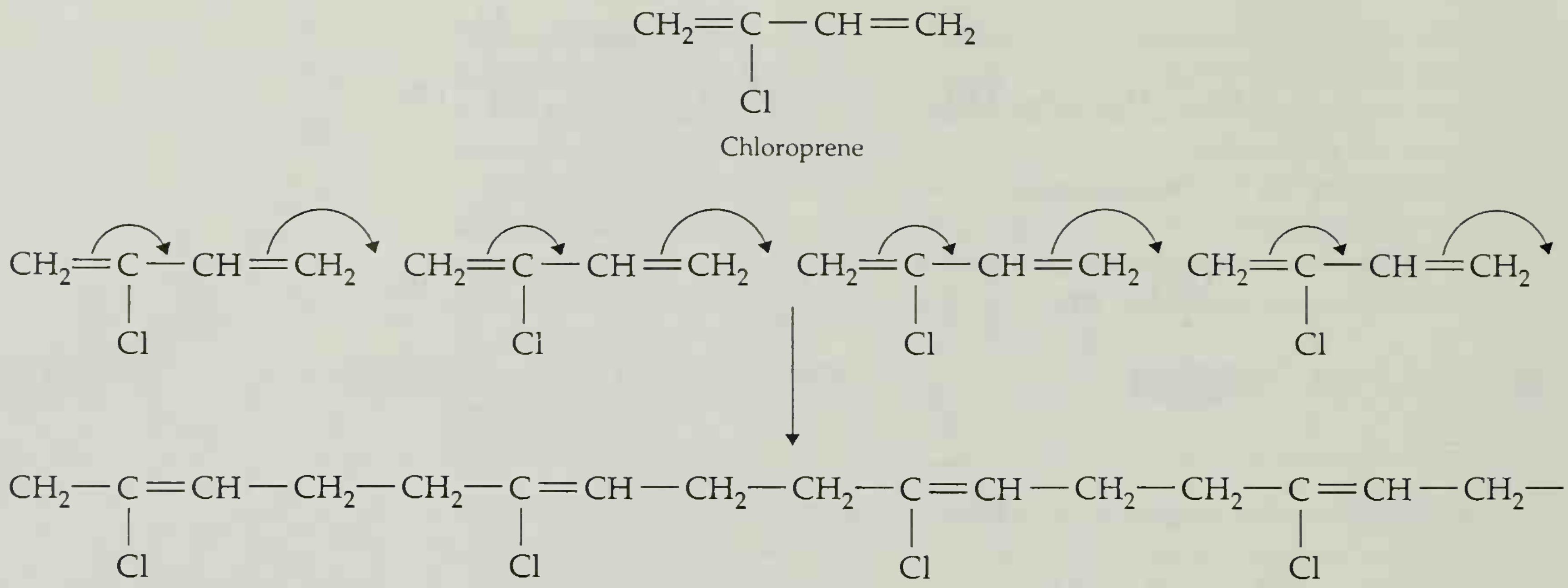


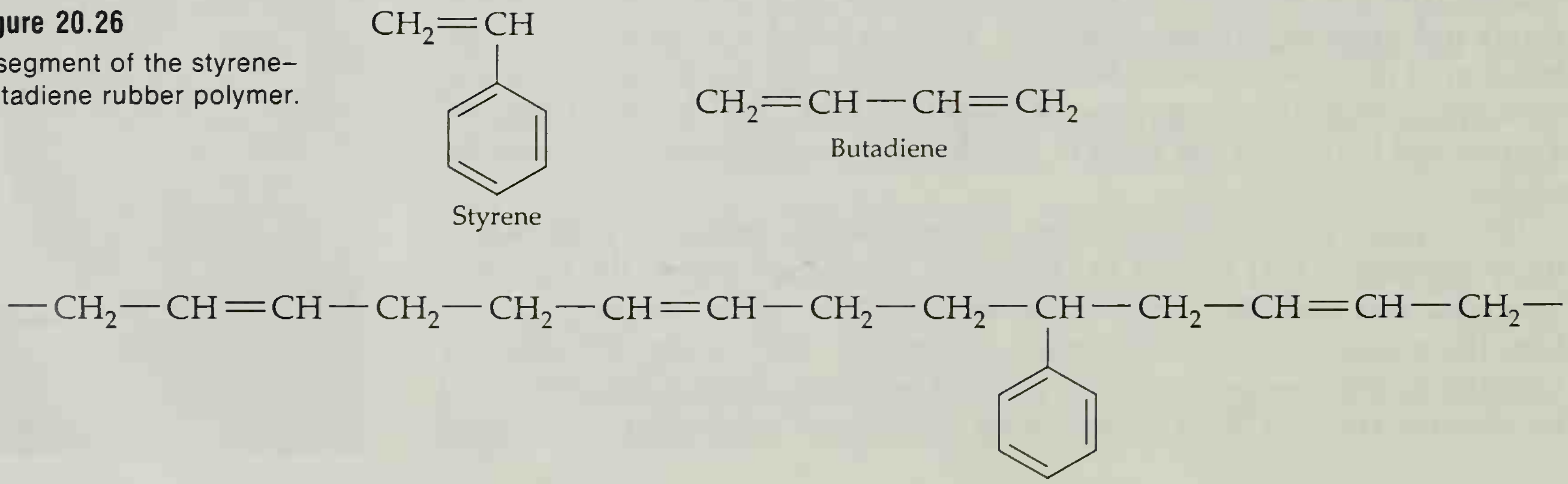
Figure 20.25
Neoprene, polychloroprene.

Carothers of nylon fame, neoprene resembles vulcanized rubber except that the synthetic substitute is much more resistant to heat and to the action of hydrocarbon solvents like gasoline and automotive greases and oils. Its properties are especially valuable in belts and other parts used in and around auto engines, in the hoses of gasoline pumps, in gaskets and filling material used in the construction of highways and bridges, and in the rubber stoppers found in chemistry laboratories.

Today's leading synthetic elastomer, *styrene–butadiene rubber*, was originated by German chemists in the early 1930s and developed further by Americans during and after World War II. It results from the copolymerization of a mixture of 75% butadiene and 25% styrene (Fig. 20.26), and it serves as a good substitute for natural rubber in the manufacture of various consumer goods, especially tires.

This ends our survey of the more important commercial plastics and related elastomers and fibers that make up the ordinary things of our everyday world. We'll conclude with an examination of a major societal problem they present to us, one we noted at the beginning of this chapter, their durability. Before we do, though, we'll examine two polymers that aren't plastics. They're not capable of being molded into useful products, they don't bounce or stretch,

Figure 20.26
A segment of the styrene–butadiene rubber polymer.



and we can't weave them into new kinds of synthetic fabrics or use them to wrap our goods. They have little or no commercial value. Yet they are perhaps the most important polymers of all.

QUESTION

Write the molecular structure of neoprene in the form $-\!(X)\!-_n$. ________________

20.21 The Most Important Polymers of All

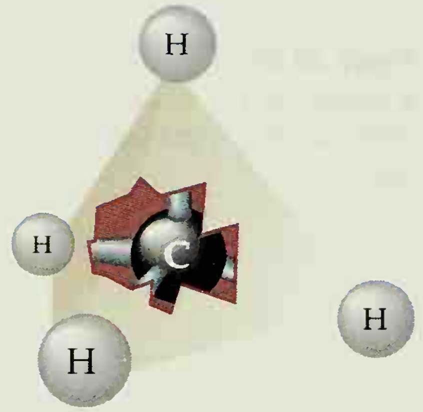
Except that they are both polymers, the two naturally occurring chemicals we examine here could hardly be more different from each other or from the synthetic polymers that make up the rest of this chapter. One, an inorganic polymer, forms the dead, dusty clay of the earth; the other, the beautifully intertwined and elegantly fashioned DNA molecule, spells out, more than any other single substance, the shape of life itself. We'll look first at the polymer (or, in some views, a set of similar polymers) that forms most of the surface of the earth. It's a compound of silicon and oxygen.

The clays, rocks, and inorganic soils of the earth's crust are made mostly of oxygen and silicon. On average, oxygen constitutes about 46% of the mass of the planet's outer layer of land and ocean bed; silicon, about 28%. Taking into account the difference in their atomic weights, this corresponds to a ratio of almost three atoms of oxygen for every atom of silicon.

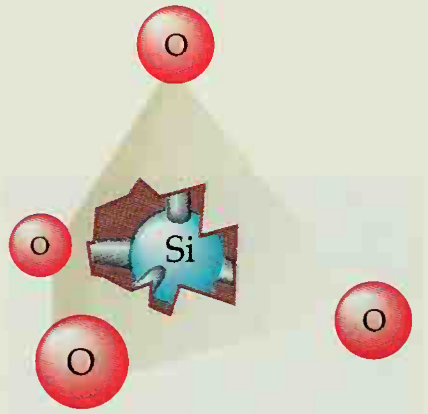
Most of the solid crust consists of polymers with repeating units of silicon dioxide (SiO_2) and of ionic aggregates such as SiO_3, SiO_4, Si_2O_5, Si_4O_{11}, and so forth. In these, four oxygens surround each tetracovalent silicon in much the same way as four hydrogens occupy the four corners of a tetrahedral methane molecule (Fig. 20.27). But while methane's hydrogens are monovalent, the oxygen atoms are divalent and so they either carry a negative ionic charge or bond to a second silicon atom. Bonding of any or all of the oxygens at the corners of the tetrahedra to still other tetrahedral silicons produces threadlike, sheetlike, and three-dimensional, inorganic, silicate polymers.

With the other elements of the earth's crust interspersed among them, these inorganic polymers form much of the substance of its rocks and minerals. One form of the mineral *asbestos* consists of a double strand of the tetrahedra (Fig. 20.28). Asbestos was once used in brake linings and cigarette filters and as insulation in houses, schools, and office buildings. Inhaling asbestos fibers has been shown to produce *mesothelioma*, a cancer of the lungs and the cavity of the chest and the abdomen. Since the mid 1970s the mineral has been abandoned as an insulating material in construction. Its use in consumer products is now prohibited by law.

Two-dimensional sheets of the polymer form micas, clays, and talcs, while quartz is a three-dimensional lattice of *silicon dioxide* (SiO_2). In the quartz lattice (Fig 20.29) every oxygen is shared by two different silicon atoms, one at the center of each of the two adjacent tetrahedra that are connected through the oxygen. Each silicon atom owns, in effect, exactly half of each of the four oxygens bonded to it (with the other half assigned to the other silicon atom bonded to the oxygen). With this arrangement, the molecular formula of quartz becomes SiO_2.



The tetrahedral carbon of methane



The tetrahedral silicon of the silicates (the oxygens either are anionic or they are bonded to another silicon.)

Figure 20.27
Tetrahedral carbon and tetrahedral silicon.

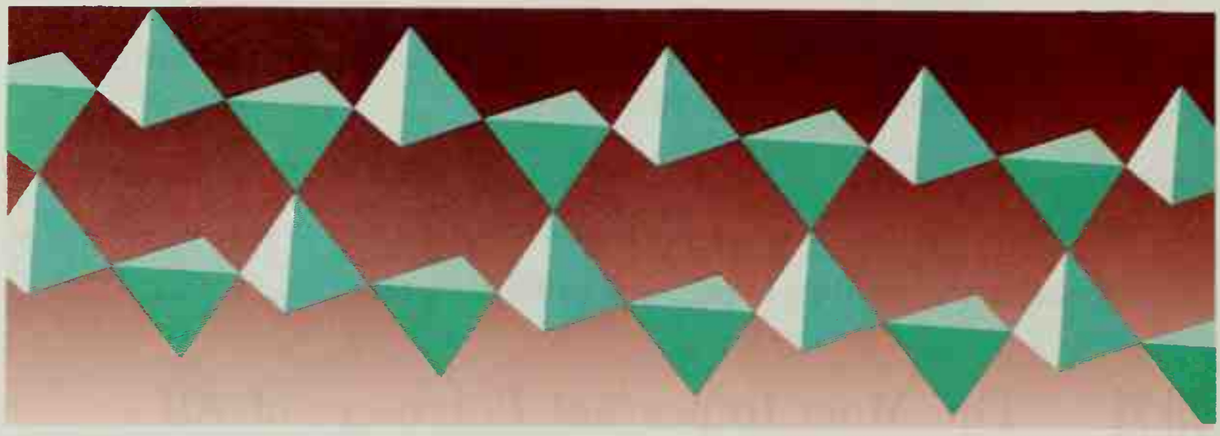


Figure 20.28
A double-stranded asbestos polymer.

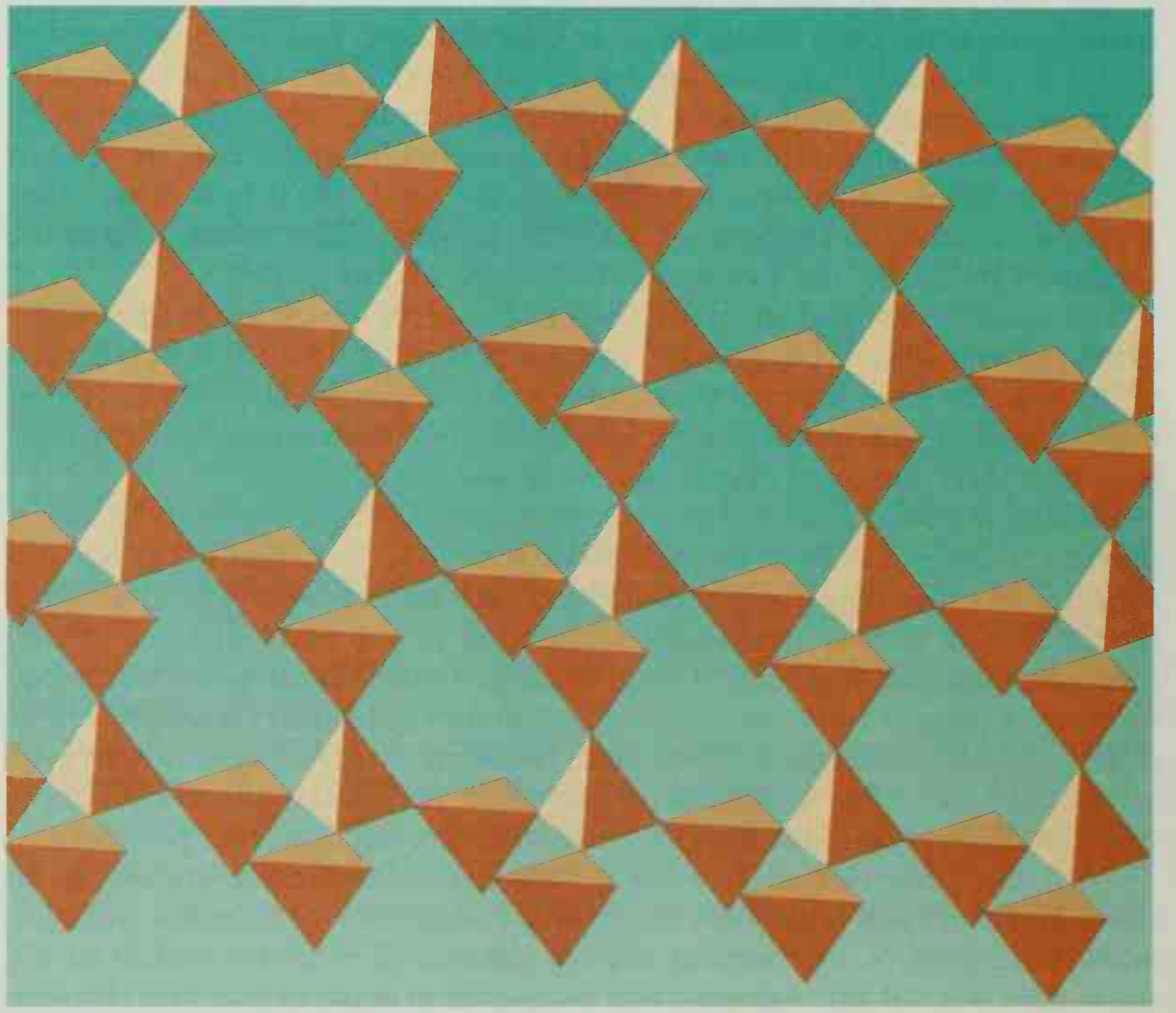


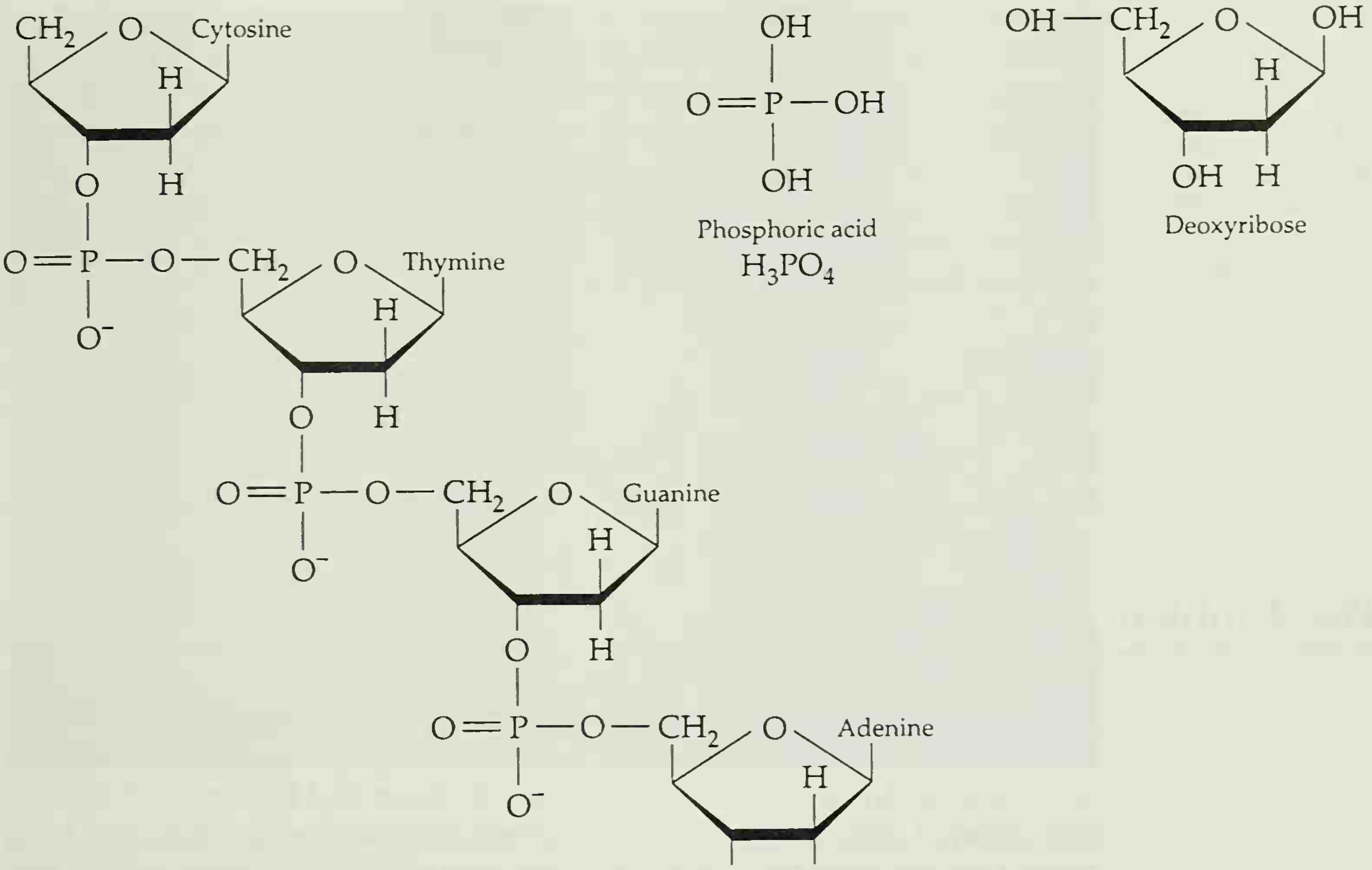
Figure 20.29
A portion of the three-dimensional crystal lattice of quartz.

Crystals of quartz, a polymer of silicon and oxygen.

DNA, or **deoxyribonucleic acid**, is a polymeric acid that resides in the nucleus of every cell and that carries in its structure the genetic code.

At the other end of the polymer spectrum, within the nucleus of each living cell, lies the *nucleic acid DNA*, which carries the genetic code of heredity throughout all generations of every living thing. Nucleic acids are, literally, acids that reside in the nucleus of every living cell, hence the generic name *nucleic acids*. The initials **DNA** represent the specific copolymer **deoxyribonucleic acid**.

Each strand of DNA consists of repeating units of *deoxyribose* (a structure closely resembling the monosaccharides of Section 14.3) and *phosphoric acid* (Fig. 20.30). These monomers are connected to each other through the same sort of chemical structures we find in the polyesters (Section 20.19), except that in DNA the acid is phosphoric acid rather than a carboxylic acid.



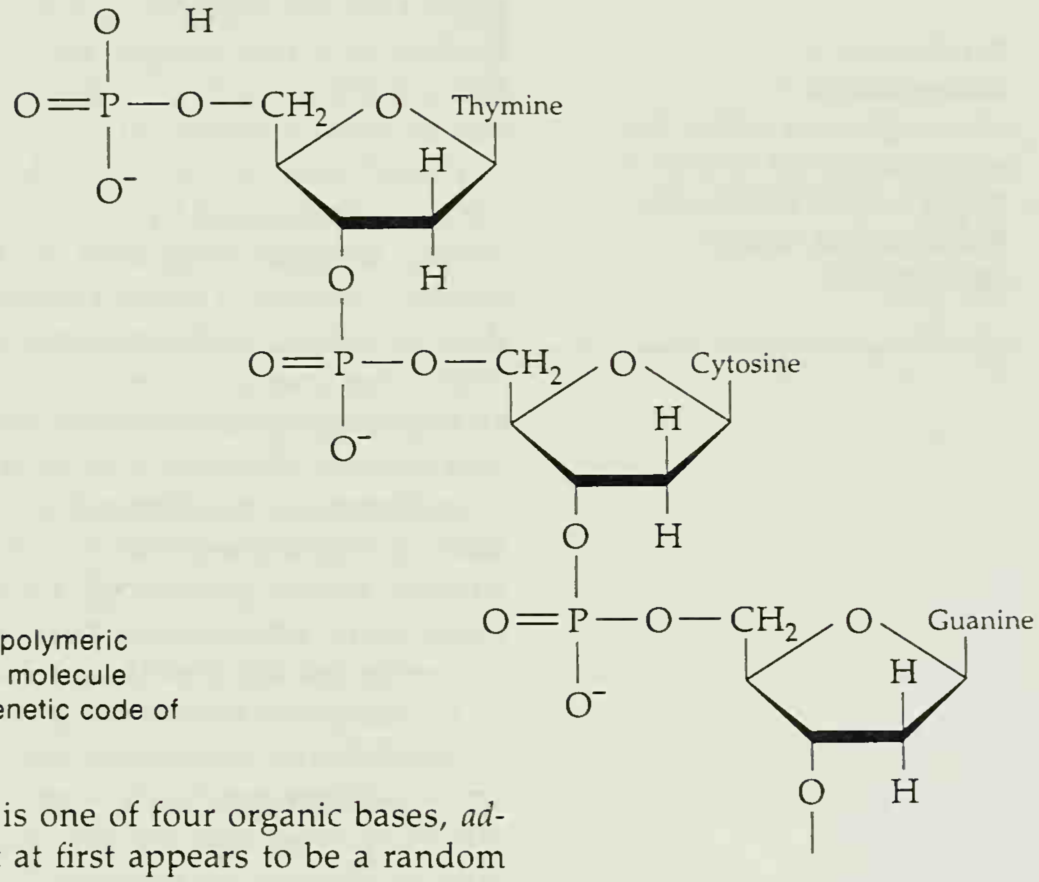


Figure 20.30
A typical segment of the DNA polymer.

A segment of the polymeric chain of DNA, the molecule that carries the genetic code of heredity.

Bonded to each of the deoxyribose units is one of four organic bases, *adenine*, *cytosine*, *guanine* and *thymine*, in what at first appears to be a random order. But the sequence in which these bases take their places throughout the polymeric chain is not random at all. Their exact sequence determines the arrangement of amino acids in the body's proteins, all of which are synthesized under the chemical direction of the DNA polymer. Generally, one or more specific sequences of three of these bases acts as a code or signal for each particular amino acid that is to be brought into the growing protein chain.

The **genetic code** is the genetic information contained in the sequence of four bases strung out along the polymeric nucleic acid, DNA.

The succession of the bases in the DNA molecules of each of our cells thus determines what proteins will form within our cells, what shapes our bodies will take, and how our bodies will function as our cells combine to form tissues and organs. The same is true for every other living thing: this **genetic code** of the base sequence on the DNA polymer controls the contour of life itself. In this sense, then, the foundation of all life is preserved in the fine threads of a condensation polymer, while polymeric networks of silicon and oxygen compose the crust of the planet that sustains it.

QUESTION

In what way(s) are asbestos and quartz alike? In what way(s) are they different?

20.22 The Problem with Plastics

A substance is **biodegradable** if microorganisms within the environment can convert it to the simpler substances that form our natural environment.

We'll return now to our commercial plastics and conclude with an examination of the major environmental problem they present, the persistence of waste plastic. Unlike metal, discarded plastic boxes and bottles don't corrode and decay. Unlike paper and cloth, plastic bags and wrappings aren't degraded by the weather or by the action of the microorganisms of the soil. Plastics, as a rule, simply aren't **biodegradable**. That is, the microorganisms that inhabit the soil can't degrade plastics to the simpler substances that form our natural environment.

Plastic litter lies by the side of the road and in our parks and beaches, virtually unchanged by weather or microorganisms, until it's gathered up for proper disposal. (An estimated 60% of all the debris collected from our beaches consists of plastics of one sort or another.) Even with proper disposal, though, plastic waste presents a growing societal problem as it accumulates, with other trash, in expensive landfills. These areas, where urban trash of all sorts is dumped and mixed into the land itself, are quickly filling to capacity and closing. About 80% of all our plastic wastes end up in landfills.

Incineration, an alternative approach used with about 10% of our plastic trash, is not only expensive, but potentially hazardous as well. Some plastics, such as Teflon, poly(vinyl chloride) and poly(vinylidene chloride), produce irritating or toxic gases when they burn. Added to this is the impact of incineration on the greenhouse effect (Section 7.13).

To attack the problem of growing deposits of plastic trash and litter, both in landfills and in public areas, various approaches have been proposed. In one legislative approach, some state and local governments have banned or otherwise restricted the use of plastics in consumer packaging. New York's Suffolk County, for example, forbids the use of plastics in the packaging of foods. In California, the city of Berkeley has banned the use of fast-food boxes made of plastics formed with chlorofluorocarbons (Chapter 19 Perspective) and requires, moreover, that all these containers be biodegradable. Florida requires that both the plastic bags used by retail business and the plastic rings of six-packs be biodegradable to nontoxic substances, and also prohibits the use of chloroflurocarbon-produced packaging materials of all kinds. Several

Covering 3000 acres, the Fresh Kills landfill on Staten Island is the world's largest. It lies 14 miles from Manhattan and receives about half of New York City's trash.

states have introduced deposit laws for plastic beverage bottles to encourage their return for recycling. At the federal level the Degradable Plastic Ring Carriers Act of 1988 carries the requirement for biodegradable six-pack rings to the entire nation.

PERSPECTIVE: Possible Solutions from Science And Technology

Science and technology offer some hope for solving the problem through two possible routes: recycling and degradability. Recycling waste plastics into new products, much as paper, glass, and metal wastes are recovered and recast into new and useful items, would certainly seem to be a promising approach. Yet, as we've seen, plastics come in a variety of molecular structures, with a variety of properties. Each synthetic plastic possesses its own particular characteristics that suit it to a set of specific applications. For effective recycling, the various plastics of our wastes would have to be sorted into a variety of individual piles, an expensive process, with each pile representing a separate category of properties. Tossing them all together, into a single batch, lowers the cost of the entire operation but produces a low-grade product known informally as "plastic lumber," a satisfactory substitute for wood in some of its rougher uses but hardly suitable for more specialized applications. In all, while about 30% of our waste aluminum and about 20% of our waste paper are recycled into new products, only about 1% of our plastic wastes is currently reused.

There are several reasons for this low recycling of plastics. One is the inherent difficulty in separating different kinds of plastic from each other so that each can be reused effectively. In the opening demonstration you used a mixture of isopropyl alcohol and water to prepare a liquid of just the right density to separate several different kinds of plastic. While achieving just the right liquid mixture for separating high-density and low-density polyethylene may have been easy, separating other kinds of plastics is far from simple. Another difficulty is that some plastic products just don't lend themselves to collection for recycling. The plastic liners of baby diapers probably offers the best example of this sort of problem.

In a second approach, through degradation to smaller molecules, the plastic is impregnated with a substance that promotes its decomposition without significantly affecting its properties. Incorporating a readily biodegradable form of starch, cellulose, or protein, for example, attracts soil microorganisms into the discarded plastic. As the microorganisms feed on these nutrients they also clip the long molecular chains of the polymers into shorter segments, causing the plastic to decompose. Alternatively, chemical activators can be added to the plastic so that continued exposure to sunlight leads to degradation.

Either treatment leaves the plastic suitable only for decomposition rather than for recycling and, therefore, does nothing to slow the introduction of plastics, or their degradation products, into the environment. What's more, the hazards of all the possible decomposition products produced by a large variety of plastic wastes are still uncertain and could pose a greater long-term threat to the environment than do the plastics themselves. Once again, the question of the safe disposal of long-lived plastics depends on which risks we as a society consider to be acceptable.

EXERCISES

FOR REVIEW

1. Complete this statement with the following words and phrases. Each is used once.

______ are macromolecules composed of long chains of structural units known as ______. If all of these units are identical in structure, the long chain is a ______; if they represent two or more different monomers, the result is a ______. The natural polymer ______, with its monomeric units of ______, represents a typical homopolymer. The synthetic polymer ______, with alternating units of ______ and ______, represents a typical copolymer. Cellulose and nylon are similar in that they are both ______ polymers. Another class of polymers, the ______ polymers, includes ______, which is produced in two forms. The ______ polymer forms branched chains and is used for manufacturing trash bags and other forms of wrapping, while the ______ product, a ______ polymer, is used in plastic bottles and other containers for soft drinks, antifreeze, bleach, and engine oils.

1,6-diaminohexane
addition
adipic acid
cellulose
condensation
copolymer
glucose
high-density
homopolymer
linear
low-density
monomers
nylon
polyethylene
polymers

2. Define, identify or explain each of the following:

a. DNA
b. HDPE
c. isoprene
d. isotactic
e. LDPE
f. PET
g. plasticizer
h. PVC
i. thermoplastic
j. vulcanization

3. Match each of the following with the contribution made to polymer chemistry:

___ a. Leo H. Baekeland
___ b. Wallace H. Carothers
___ c. Charles Goodyear
___ d. John and Isaiah Hyatt
___ e. Giulio Natta
___ f. Christian Schoenbein
___ g. John R. Whinfield
___ h. Karl Ziegler

1. discovered the process of vulcanization of rubber
2. first prepared poly(ethylene terephthalate)
3. shared a Nobel Prize with Karl Ziegler for preparing stereochemically ordered polypropylenes
4. prepared the first fully synthetic polymer from phenol and formaldehyde
5. invented celluloid
6. invented nylon
7. first prepared high-density polyethylene
8. accidentally invented nitrocellulose (guncotton)

4. Give the structures of each of the following pairs of compounds, name the polymer they form, and describe its use or importance:

a. adipic acid and 1,6-diaminohexane
b. phenol and formaldehyde
c. phosphoric acid and deoxyribose
d. styrene and butadiene
e. ethylene glycol and terephthalic acid

5. Identify the monomers used to make each of the following plastics:

a. Acrilan
b. Bakelite
c. Creslan
d. Dacron
e. Fortrel
f. Kodel
g. Mylar
h. Nylon
i. Orlon
j. Saran
k. Teflon
l. Terylene

6. Describe a consumer product in which each of the polymers in Exercise 5 is used.

7. Where possible, describe the properties of each of the polymers in Exercise 5 that make it particularly suitable for its commercial use.

8. In what polymer are *adenine, cytosine, guanine,* and *thymine* found? What function do they provide in this polymer?

9. What are three factors, operating at the molecular level, that affect the bulk properties of a plastic?

10. How do high-density and low-density polyethylene differ in (a) the structures of their polymeric molecules; (b) the forms or shapes that their molecules take within the bulk plastic; (c) the physical properties of the bulk plastic?

11. Give two examples of polymers that we eat.

12. What is the difference between a thermoplastic and a thermosetting plastic?

13. What was the first commercially successful synthetic polymer?

14. What is an *olefin*? How are olefins used in the manufacture of plastics?

15. Name a commercial plastic that contains (a) phenyl, (b) chlorine, (c) fluorine, (d) nitrogen, (e) acetate groups.

16. What is the principal environmental concern about the continued use of plastics?

17. In what two ways can science and technology help alleviate this concern?

18. What percentage of plastic wastes is currently recycled and reused?

19. Describe two factors that currently inhibit the effective recycling and reuse of plastics.

20. Name or describe one substance that can be added to a plastic to increase the likelihood that it will be biodegradable.

21. In addition to degradation by microorganisms, plastics can be degraded by another natural phenomenon. What is that phenomenon?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

22. In terms of the weight of the polymer produced annually in the United States, what is the leading commercial (a) addition polymer; (b) condensation polymer; (c) elastomer?

THINK, SPECULATE, REFLECT, AND PONDER

23. Why was the discovery of vulcanization so important to the development of the commercial rubber industry?

24. Give an example of the importance of geometric isomerism to the properties of elastomers.

25. Give an example of the importance of stereochemical order to the properties of a plastic.

26. Give *two* examples of serendipity in the discovery or development of a polymer.

27. Give examples of (a) a natural condensation homopolymer; (b) a natural condensation copolymer; (c) a natural addition homopolymer.

28. Give examples of (a) a synthetic addition homopolymer; (b) a synthetic addition copolymer; (c) a synthetic condensation copolymer.

29. What polymer would you use if you wanted to manufacture the following items:

a. skis with a coating that would make them slide over snow particularly easily
b. a wrapper for boxes of perfume that would not let the perfume's odor escape into a store or a room
c. automobile windows
d. an inexpensive, imitation silk fabric
e. an anchor for the ends of the heating elements of a toaster
f. an elastic, rubbery lining for gasoline tanks
g. a plastic film that's very thin, very strong and very resistant to stretching

30. Molecules of low-density polyethylene have the structure

$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

yet the shorthand form $\left(CH_2 \right)_n$ does *not* adequately describe the polymer. Explain why it does not.

31. Name two commercial products made of or containing plastic that you have used within the past 24 hours.

32. What structural characteristic must a molecule have if it is to be used as a monomer in an addition polymerization?

33. A plastic can be prepared easily by the polymerization of vinyl chloride, $CH_2=CH-Cl$. Can a plastic be prepared easily by the polymerization of ethyl chloride, CH_3-CH_2-Cl? Explain.

34. Describe the environmental problems generated by the production of synthetic plastics, their possible solutions, and the difficulties associated with each possible solution.

Cosmetics and Personal Care

21

LOOKING GOOD AND SMELLING NICE WITH CHEMISTRY

Cosmetic beauty through the ages.

Figure 21.1
The home permanent uses the chemistry of thioglycolic acid and hydrogen peroxide to change the shapes of the protein molecules of hair.

The Wave of Chemistry

If you ever give yourself a home permanent for waves or curls or to add a bit of body to your hair, you carry out some exceptionally interesting protein chemistry on the top of your head. Whether you use a kit that provides only the essentials, or the full treatment with a preperm shampoo and a postperm conditioner, you invariably go through two steps common to all. At some point in the process you use a waving lotion. Then after perhaps 10 or 15 minutes, you rinse out the waving lotion and apply a neutralizing solution.

The next time you have the packaging box in front of you, take a look at the list of ingredients. In addition to lots of chemicals to give the waving lotion a nice odor, a desirable sense of thickness, and the like, you'll probably find that it also contains a chemical with "thioglycolate" (or something resembling that) in its name. The neutralizing solution is likely to contain some hydrogen peroxide along with all of its perfumes, stabilizers, thickeners, and other assorted ingredients.

These two, the thioglycolate and the hydrogen peroxide, are what do the actual work. With the glycolate of the waving lotion you break a lot of covalent chemical bonds in your hair. But that's OK. Those are the bonds that hold strands of protein firmly in place next to each other. As soon as you break all those bonds the proteins that form your hair can shift around to accommodate your wishes, as you express them with the curlers.

After you wait a few minutes to let the molecules loosen up and slide past each other to conform to the curlers, you snap them into their new molecular shapes with the neutralizer. The hydrogen peroxide regenerates just about all the covalent bonds that the thioglycolate broke, but in new locations. Now the protein molecules are just where you want them, and there you are with the look that you want and that only chemistry can provide (Fig. 21.1). We'll examine the chemistry of the permanent, and also the wet wave, in Section 21.8.

If a home permanent is one of the ordinary things of your life, the chemistry that goes into it is truly extraordinary. How the cosmetics industry harnesses the chemistry of home permanents and other personal care products, for your pleasure and its profit, is one of the topics of this chapter.

21.1 The Universal Urge for Adornment

Each year consumers in the United States spend about $20 billion on chemicals designed to make us more attractive. That amounts to an average of roughly $80 a year spent by every individual man, woman, and child living in the United States for shampoos, toothpastes, colognes, perfumes, skin ointments and cleansers, hand and body soaps, lipsticks, deodorants, mouthwashes, antiperspirants, and related cosmetics and toiletries that are supposed to make us look and smell healthier, younger, and more fragrant (or perhaps less fragrant). Worldwide, the annual total comes to about $70 billion, or roughly $14 a year for each and every one of the earth's 5 billion inhabitants.

The urge to beautify ourselves—to look good and to smell nice, especially by applying chemicals to our bodies—is common to the entire human race, throughout the histories of all its civilizations. Peoples of all regions and of all times have painted themselves, sometimes with plant extracts, sometimes with powdered metals, to become more vivid and to appeal to the eyes of others. *Henna*, a hair dye extracted from the henna plants of Africa, India, and the Middle East and still in use today, colored the hair of Egyptians now mummified. Vases of cosmetics and unguents were sealed into the tombs of the kings of ancient Egypt to make them more presentable in the afterlife. The Bible tells of Jezebel painting her eyes when she heard of Jehu's arrival in Jezreel (II Kings, 9:30) and it speaks with scorn of those who paint their eyes and bedeck themselves with ornaments (Ezekiel, 23:40). The Hebrew *kakhal* ("to paint" or "to stain") and the Arabic *al-koh'l* (a fine powder used in coloring the eyelids), give us our own "alcohol" by a tortuous sequence of transformations.

In a subtle sense, the very word **cosmetic** is as universal as the materials it describes. The ancient Greek word *kosmos* served equally to represent "order", "adornment" and "the universe" itself. The connection among the

A **cosmetic** is a substance applied directly to the human body to make it more attractive.

Cosmetics for sale.

three meanings comes from the belief of the Greek philosophers that there is beauty in order and that the universe is an ordered place, and therefore beautiful. According to the Federal Food, Drug and Cosmetic Act (Section 17.8), a cosmetic is anything intended to be applied directly to the human body for "cleansing, beautifying, promoting attractiveness, or altering the appearance" (presumably for the better). According to the Act, soap is not considered to be a cosmetic. For our purposes we can consider that anything we apply directly to our bodies to make us more attractive is a cosmetic.

The growing appreciation that a healthy body is an attractive body can lead to confusion between a cosmetic and a medicine. We'll examine medicines more closely in Chapter 22, but for now we can say that while cosmetics make us more attractive, medicines are used specifically for treating diseases, illnesses, and injuries. Cosmetic companies that claim their products improve "health" must be able to verify their claims to the Food and Drug Administration (Section 17.7). Manufacturers of skin care products, for example, sometimes claim that their creams and ointments will lead to a "healthier" or "healthier-looking" skin. In fact, unless the substance can actually cure a disease of the skin, it is a cosmetic rather than a medicine.

QUESTION

Name a hair dye that was used by the ancient Egyptians and is still in use throughout the world today. ______

21.2 Rich Suds and Expensive Odors

Common to all personal care products are pleasant odors. Gram for gram, fragrances make up the smallest percentage of the weight of our personal care products and the largest percentage of their cost.

In the United States, four categories of cosmetics and toiletries account for a little over half the total sales of all these highly personal consumer chemicals:

- Hair care products
- Perfumes and colognes
- Skin care products and emollients (skin softening and smoothing products)
- Hand, face, and body soaps

(In Western Europe, half of all cosmetic sales come from hair care and body fragrances alone.)

The manufacture of these personal care products can be a rewarding activity. Overall, only about 10% of the retail cost of the average cosmetic or toiletry goes toward its raw materials, the chemical dyes, detergents, perfumes, moisturizers, solvents, and the like that make it up. The remainder pays for packaging, advertising, research, labor, and similar expenses, and, of course, profit.

Of all the chemicals used in these formulations, two classes, aside from water and common solvents, stand out. Synthetic detergents and other surfactants constitute the largest single category of chemicals used in their manufacture. They are important components of our hair shampoos, body and hand soaps, toothpastes, and related cleansing toiletries. Each year, about

275,000 tons of synthetic surfactants manufactured in the United States end up in these personal care products.

The other important class of chemicals, significant from both an aesthetic and an economic standpoint, are the fragrances that add their pleasant odors to virtually every one of these products. Although these compounds contribute less than 1% to the total weight of all our personal care products combined, the costs of these fragrances make up about 25% of the total value of all the raw materials used in the manufacture of cosmetics and toiletries. Gram for gram, the fragrances are by far the most expensive of all the ingredients.

QUESTION

What kind of chemical makes up the largest category of compounds used in the manufacture of personal care products? ______________________________

21.3 To Satisfy the Consumer

You wouldn't want to wash your hair with toothpaste or brush your teeth with shampoo, but the active detergent is very likely to be the same in each. This shouldn't surprise us when we recognize that the surfactant that forms the suds in our hair can foam up in our mouth or on our hands just about as well.

Of course, we don't wash our hair with toothpaste or brush our teeth with shampoo, and with good reason. Aside from the particular odors and flavors we associate with the two products, we expect a shampoo to do more than simply remove greasy dirt from hair—an ordinary hand soap can do that—and we expect a dentifrice to do more than merely clean our teeth.

To meet our broader expectations, each of our cosmetics and toiletries is formulated to perform a set of at least three different kinds of tasks, each important to the commercial success of the product. To formulate a product that does each one well requires a skillful blending of carefully selected chemicals, each lending its own characteristics to the jobs at hand.

First comes the principal function. We expect shampoos and toothpastes to produce suds and to clean. For the production of a rich foam their most important active ingredient is a detergent not much different chemically from those described in Chapter 11. (Actually, the detergent in a good dentifrice isn't nearly as important as the abrasive, but we'll come to that in Section 21.9.) Next there's a set of secondary activities that relate directly to its specific application on our hair, teeth, skin, or nails. We expect our shampoos, for example, to provide body and luster to our hair, as well as to clean it thoroughly without drying it of all its oils; we expect our toothpastes to give us a fresh-tasting mouth and clean-smelling breath along with clean, cavity-free teeth and healthy gums.

Finally there are the more subtle qualities of our personal care products. To produce consumer satisfaction they must be convenient to use, and their odors, colors, and general appearance must convince us that they do their jobs well and effectively. Otherwise they lose out in a competitive marketplace. Hair shampoo that looks like muddy water or toothpaste that reminds us of garlic would hardly be commercial successes no matter how clean and sparkling their chemicals might get our hair and our teeth. Along with all this we also get a reinforcement of our self-image. But that lies in the realm of advertising and packaging rather than chemistry.

QUESTION

What do you expect as the primary quality of an antiperspirant? What other, secondary qualities do you expect? ____________________

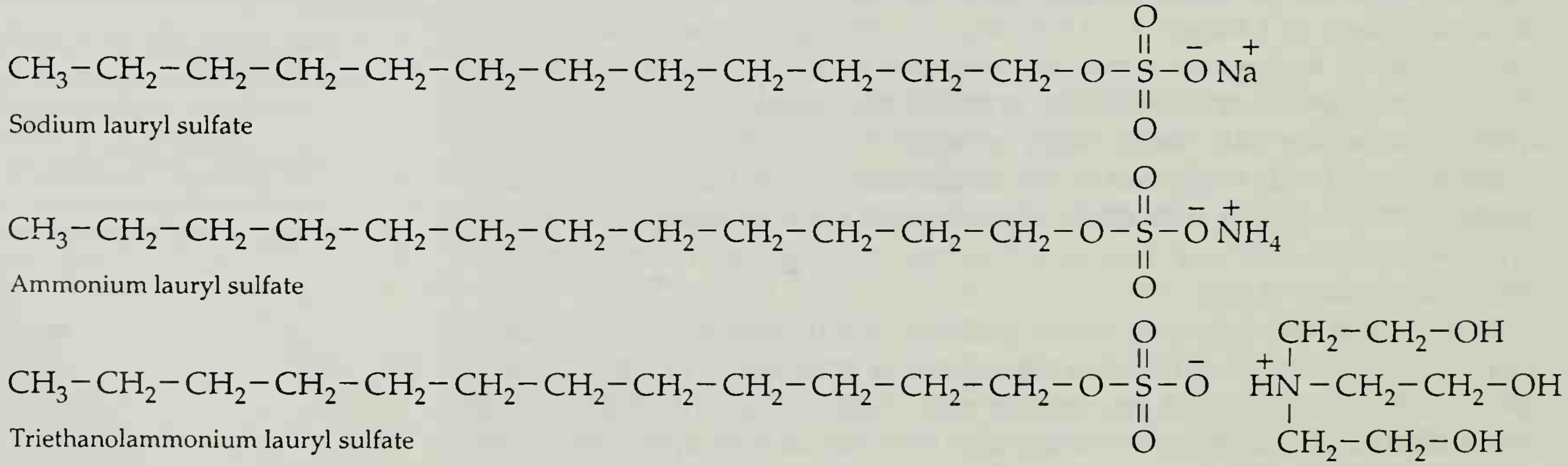
21.4 Personal Care Surfactants

As you read the list of ingredients of your favorite shampoo or toothpaste, it's likely you'll find among them a *sodium lauryl sulfate* or an *ammonium lauryl sulfate*. These are surfactants, with hydrophilic heads and hydrophobic tails, not much different in molecular structure from the soaps and synthetic detergents that clean our bodies and our clothes. As they appear in Figure 21.2, all the lauryl sulfates contain identical anionic portions and differ only in the cation that balances out the anion's negative charge. Since it's the anion of each that's the active surfactant, with its combination of hydrophilic head and hydrophobic tail, they are all *anionic surfactants* (Section 11.14).

Lauryl hydrogen sulfate, the parent compound, is manufactured through several different chemical reactions, principally by the action of *chlorosulfonic acid* on *lauryl alcohol* (Fig. 21.3). In the process the alcohol and the acid combine with the loss of a molecule of HCl. Replacing the acidic proton of the lauryl hydrogen sulfate with another cation, such as the sodium ion or the ammonium ion, generates the particular lauryl sulfate used in the toiletry formulation.

The sodium salt of lauryl hydrogen sulfate, *sodium lauryl sulfate*, the surfactant of many dentrifrices, is relatively insoluble in cold water. This decreases its appeal for hair shampoos since in cold weather the salt tends to come out of solution and produce a slight cloudiness. While a bit of turbidity hardly affects the appearance of most toothpastes, watching a bottle of what was

Figure 21.2
Surfactants of toothpastes and shampoos.



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-\overset{-}{O}\ \overset{+}{Na}$$

Sodium lauryl sulfate

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-\overset{-}{O}\ \overset{+}{NH_4}$$

Ammonium lauryl sulfate

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-\overset{-}{O}\quad \begin{array}{l} CH_2-CH_2-OH \\ \overset{+}{H}N-CH_2-CH_2-OH \\ CH_2-CH_2-OH \end{array}$$

Triethanolammonium lauryl sulfate

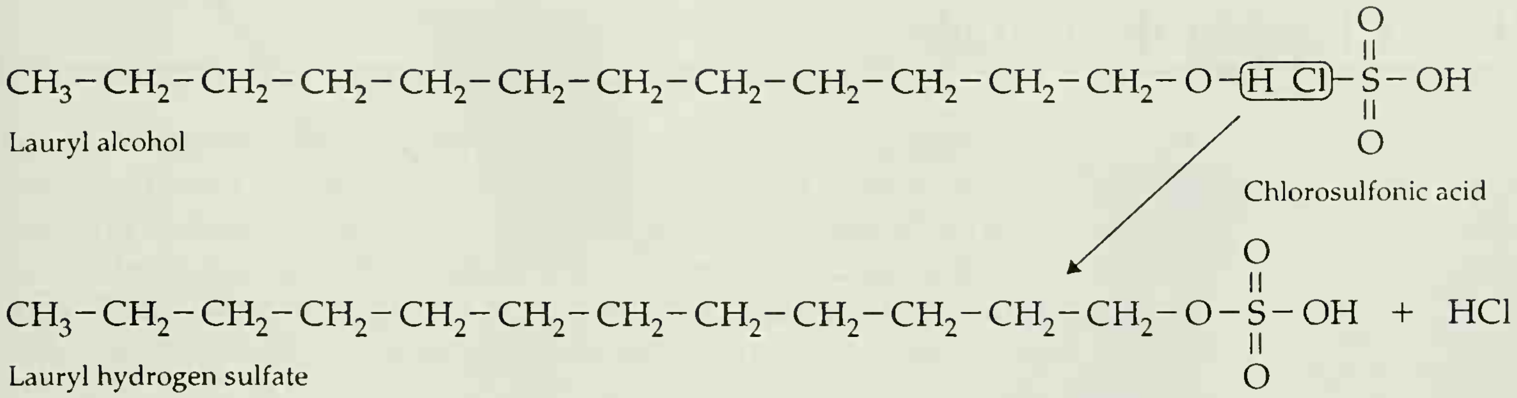


Figure 21.3
Synthesis of lauryl hydrogen sulfate.

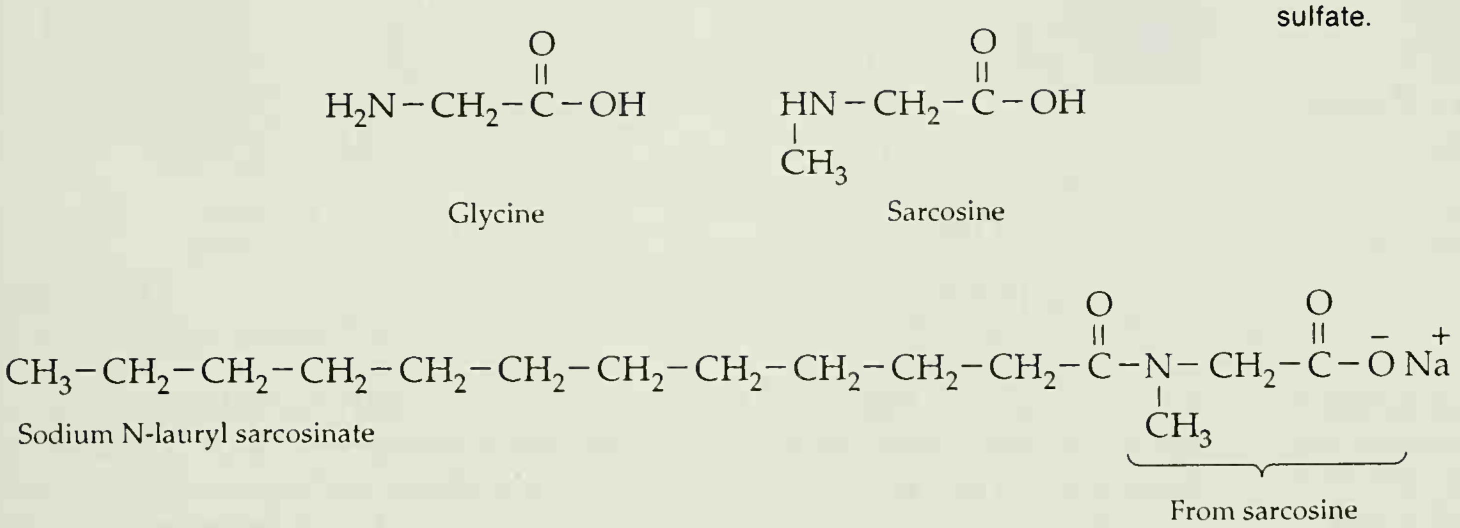
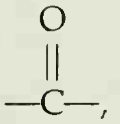


Figure 21.4
Sodium N-lauroyl sarcosinate, an antienzyme toothpaste surfactant. (Glycine and sarcosine are shown for comparison.)

once a clear shampoo turn strangely cloudy in cold weather could cause a consumer to switch brands. You're more likely to find *ammonium lauryl sulfate* or *triethanolammonium (TEA) lauryl sulfate* listed as an ingredient in your shampoo. They're more soluble in cold water and, as an added benefit, they don't dry out the hair quite as much as the sodium salt.

An example of a more highly specialized surfactant is the sodium salt of *N-lauroyl sarcosinate*, another toothpaste detergent. (The *N* of its name tells us that the lauroyl group is bonded directly to the nitrogen of the acid *sarcosine*; the "o" in lauroyl points out the presence of the carbonyl group,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-,$$

at the end of the hydrocarbon chain.) As shown in Figure 21.4, it's an amide derived from *lauric acid* and a compound closely related to the amino acid *glycine*. In addition to producing foam, sodium *N*-lauroyl sarcosinate also inactivates enzymes associated with tooth decay. It's used in toothpastes under the trade name Gardol.

QUESTION

Using techniques of nomenclature described in this section, name *sarcosine* as a modified amino acid. ______________________________

21.5 Hair: Cleaning the Cuticle

Hair itself is a lifeless structure composed of a protein called *keratin*. A strand of hair contains no more living tissue than do our nails or the keratin-containing claws, horns, hoofs, or feathers of other animals. Like all human proteins, keratin is a polypeptide with monomeric units consisting of a combination of the 20 amino acids of Table 15.1. In this particular protein one amino acid, *cystine*, dominates the polymer and accounts for somewhere between 14% and 18% of keratin's amino acids. The sulfur–sulfur bonds of the cystine give hair much of its strength by connecting the parallel strands of protein to one another, as shown in Figure 21.5.

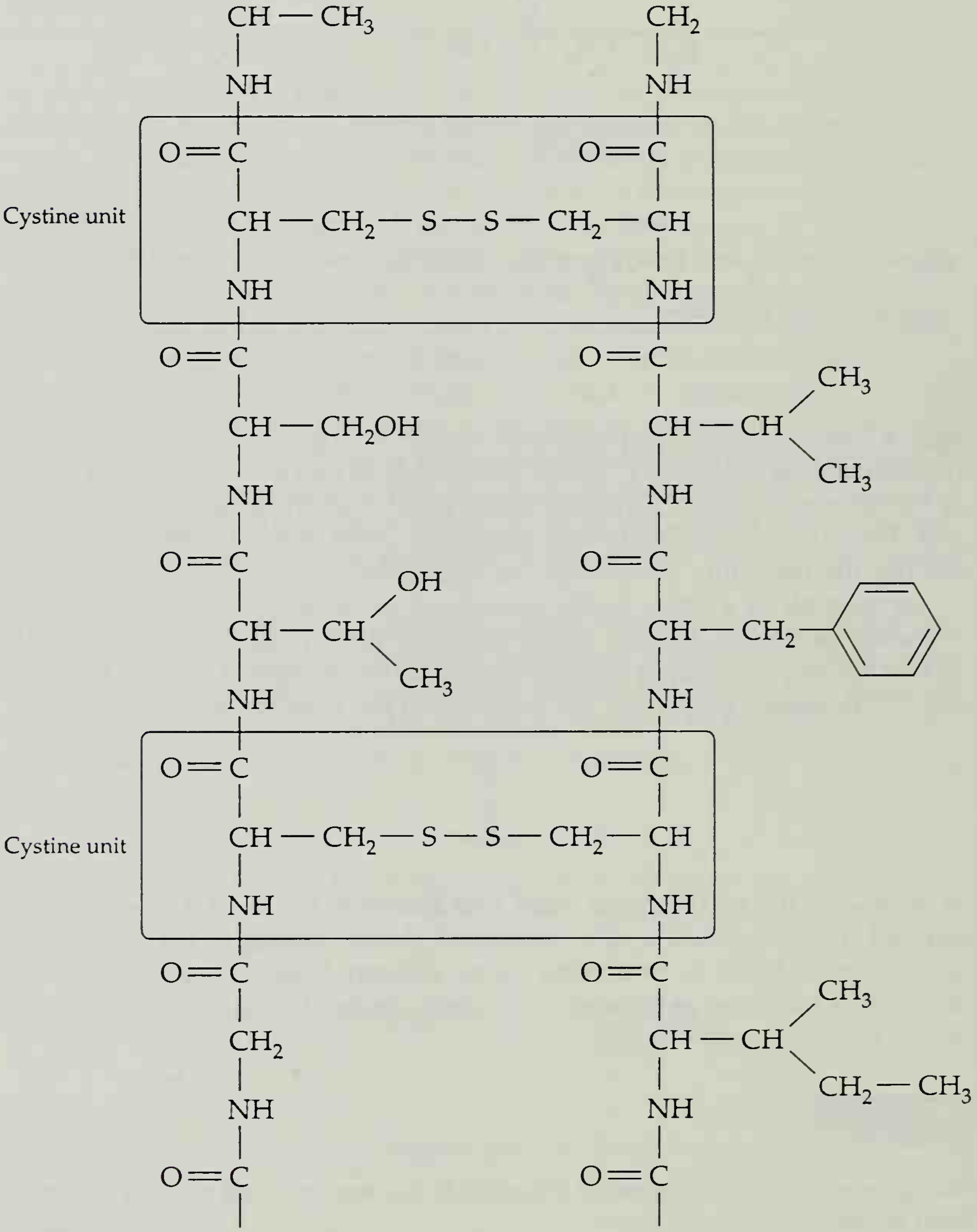


Figure 21.5
Sulfur–sulfur links in a typical segment of keratin.

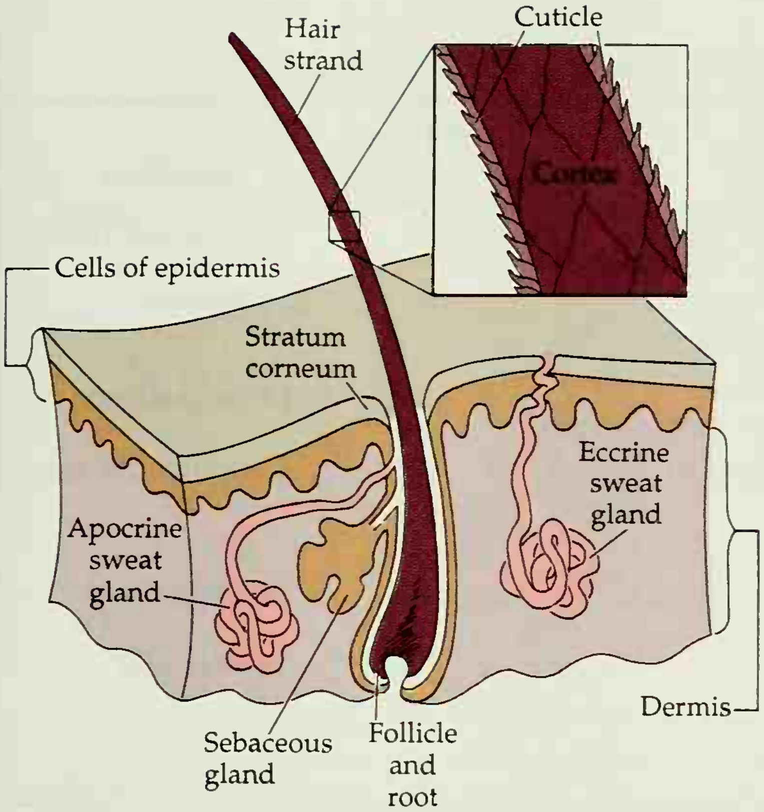
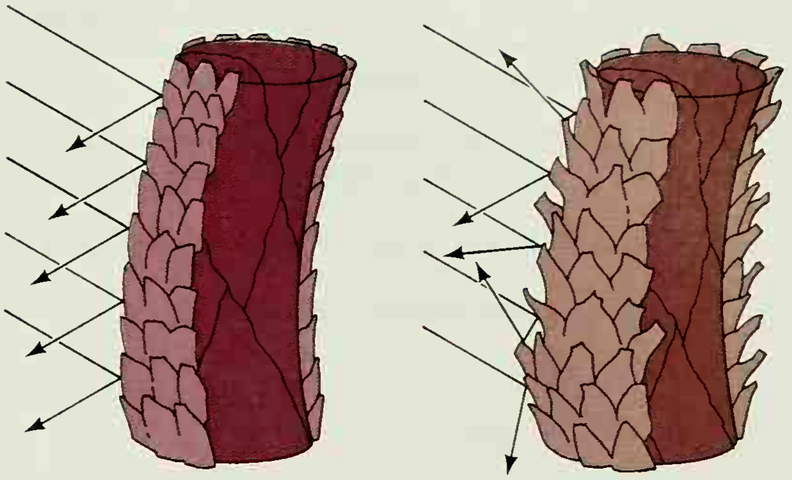


Figure 21.6
A typical section of skin, hair, and glands.


At pH 4-6, tight cuticle reflects light coherently, giving hair a luster.

At higher pH, ruffled cuticle scatters light making hair look flat and dull.

Figure 21.7
pH and the radiance of hair.

Each strand grows from a living root embedded within microscopic sacks or **follicles**, which are buried under the surface of the skin. The hair of the scalp grows outward at about one centimeter each month, or about a tenth of an inch per week. After 4 to 6 years of steady growth each strand falls out, replaced by a new one as it begins its own growth.

Typically each strand of hair consists of a central core, the **cortex**, which forms the bulk of the fiber and contains its coloring pigments. Enveloping this cortex is a thin, translucent, scaly sheath, the **cuticle**. **Sebaceous glands** lying in the skin near the follicle lubricate the emerging shaft with an oily **sebum**, which gives the hair a gloss, keeps the scales of the cuticle lying flat, and prevents the strand from drying out (Fig. 21.6). Too much sebum and the hair feels greasy and dirty; too little and it's dry, dull, and wild. The detergent of a hair shampoo, then, must remove dirt from the hair and scalp, as well as enough accumulated sebum to keep the hair looking clean, but not so much as to remove all of the oil. The moderate detergent action of the lauryl sulfates and related surfactants accomplishes this tightrope act very nicely. Many shampoo formulations contain added conditioners to replace at least part of the lubricant that might be lost in the washing.

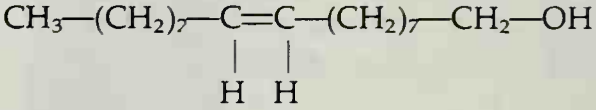
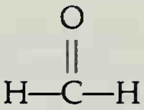
Other shampoo ingredients help stabilize the foam, act as preservatives, give the shampoo itself a pleasing viscosity or body, adjust the pH, chelate (Section 17.13) the metal ions of hard water that might degrade the surfactant's action, and add color and fragrance. The acidity of the shampoo has a lot to do with its ability to produce a good luster and resilient hair. Other things being equal, the strand of hair is strongest under slightly acidic conditions, at a pH of about 4 to 6. Moreover, the scales of the cuticle tend to swell up and fluff out under basic conditions. This condition causes reflected light to scatter, making the hair look dull. A tight, slightly acidic cuticle reflects light more coherently, giving the hair a pleasant luster (Fig. 21.7). The ingredients of a typical clear shampoo appear in Table 21.1.

A **follicle** is a microscopic sac, under the surface of the skin, that holds the root of a strand of hair.

The **cortex** is the central core of a strand of hair. The cortex forms the bulk of the strand and contains its pigments. The **cuticle** is the scaly sheath that covers the cortex. **Sebaceous glands** are glands lying in the skin, near the follicle, which secrete **sebum**, an oily substance that lubricates the cuticle and give it a gloss.


Hair shampoo, a blend of detergents, conditioners, stabilizers, fragrances, and other ingredients that clean your hair and present it in its best light.

TABLE 21.1 Ingredients of a Typical Clear Liquid Shampoo

Ingredient	Weight (%)	Function
Purified water, H_2O	60	Solvent and filler
Triethanolammonium lauryl sulfate, $(HO{-}CH_2{-}CH_2)_3N^+H\,^-O_3SO{-}CH_2{-}(CH_2)_{10}{-}CH_3$	32	Surfactant
Myristic acid, $CH_3{-}(CH_2)_{12}{-}CO_2H$	4	pH adjustment
Oleyl alcohol,  $CH_3{-}(CH_2)_7{-}\underset{H}{\underset{\vert}{C}}{=}\underset{H}{\underset{\vert}{C}}{-}(CH_2)_7{-}CH_2{-}OH$	2	Conditioning agent
Fragrance	1	Perfume
Formaldehyde,  $H{-}\overset{O}{\overset{\Vert}{C}}{-}H$	0.5	Preservative
Other additives	0.5	Sequestrants and colorants

QUESTION

The sulfur–sulfur bonds (—S—S—) of a single cystine molecule can be broken by the addition of a molecule of hydrogen to produce a new amino acid, containing an —SH group. What is the name of the amino acid produced by addition of hydrogen to cystine? (See Table 15.1.) ____________________

21.6 Hair: Coloring the Cortex

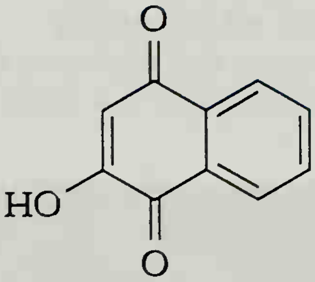


Figure 21.8
Lawsone, the coloring agent of henna.

As we saw in Section 21.1, the use of deeply colored vegetable extracts and of powdered metals to color hair goes back to the earliest records of human history. Some of these dyes, the henna of Section 21.1 for example, are still used. *Lawsone* (Fig 21.8), the active component of henna, gives hair a red-orange tint.

While powdered metals themselves are no longer used as commercial hair colorings, some contemporary products darken hair through the action of metal atoms incorporated into organic molecules. One of these is the *lead acetate*, $Pb(O_2C{-}CH_3)_2$, of products such as Grecian Formula. The lead reacts slowly with the cystine of keratin, converting the amino acid's sulfur into dark lead sulfide, PbS. The process take place slowly, requiring repeated applications over several days, and results in a gradual darkening of the hair.

While the vegetable dyes of antiquity are still used occasionally, changing the color of hair today is more likely to be accomplished through the reactions of complex synthetic organic and organometallic chemicals devised only within the last hundred years or so.

Hair itself contains two natural pigments: **melanin**, the dark brown pigment of the skin, and **phaeomelanin**, a red-brown or yellow-brown pigment

Melanin is the dark brown pigment of the skin and hair; **phaeomelanin** is a red-brown or yellow-brown pigment chemically similar to melanin.

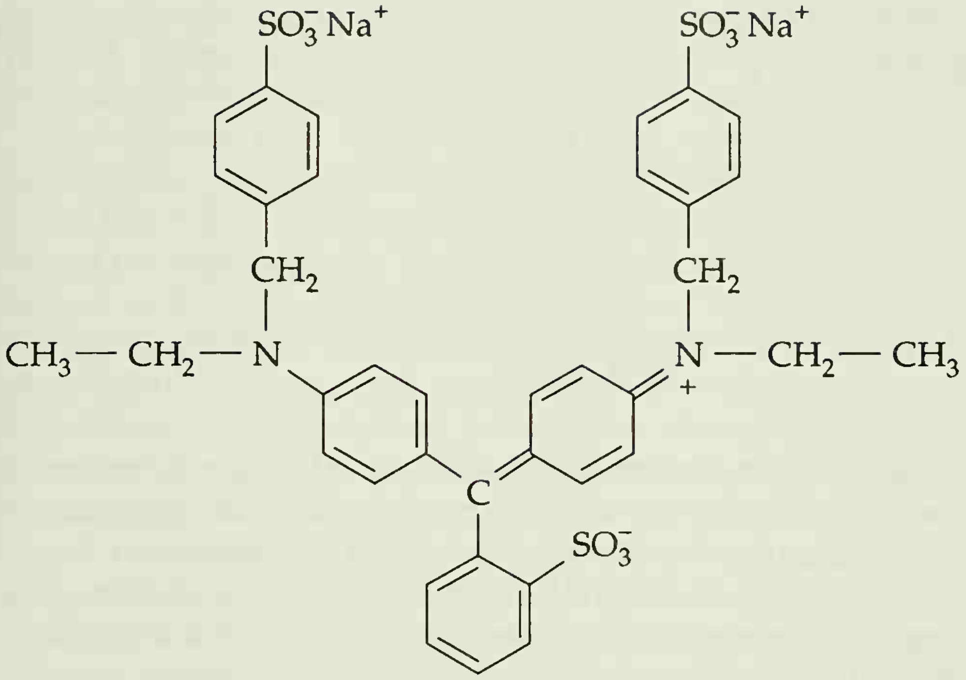


Figure 21.9

FD&C Blue No. 1, a temporary hair dye. It washes out with a single shampooing.

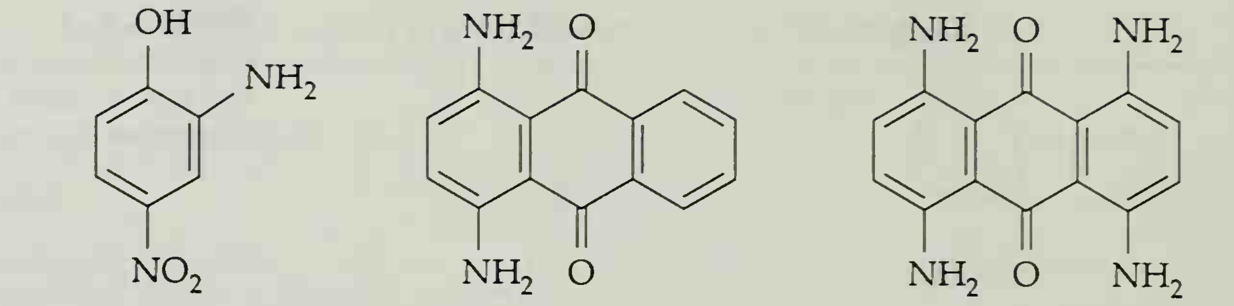
chemically similar to melanin. The color of hair depends on the amounts and physical conditions of these two pigments within the strand. Their absence produces white or gray hair. Converting dark hair to a lighter shade requires bleaching these natural pigments, usually with a solution of hydrogen peroxide, H_2O_2, and replacing them with a synthetic dye. Adding dyes without bleach darkens the color.

The variety of synthetic dyes now available gives us some flexibility in choosing the permanence of any color change. Temporary dyes and rinses color the hair with chemicals that wash out easily with a single shampooing. The most popular of these contain the salts of large, acidic molecules, such as FD&C Blue No. 1 shown in Figure 21.9. The multiple sulfonate groups, $—SO_3^-$, on the molecule add to its solubility in water, yet because of its large size the colorant doesn't penetrate easily into the cortex. Instead it coats the surface of the cuticle and leaves with the next rinse.

[The *FD&C* of the dye's identification number indicates that the Food and Drug Administration has approved its use in *f*ood, *d*rugs, and *c*osmetics, as specified in the Food, Drug and Cosmetic Act (Section 17.8). In an actual commercial formulation the blue dye wouldn't be used alone as the sole coloring agent. It would be blended with others to produce a pleasing shade or tint.]

Smaller molecules, which can penetrate more readily through the cuticle and move into the cortex, make up formulations designed to produce semipermanent dyes, those that last through half a dozen or so washings. Naturally, since the dye molecule is mobile enough to penetrate into the cortex, it can diffuse out, too, during the repeated shampoos. The colors simply last a bit longer than the temporary tints. Typical dyes of this kind appear in Figure 21.10.

Permanent dyes, those that last as long as the strand of hair itself, are made up of molecules with little ability to migrate out of the cortex, either because of their size or because of some structural feature that tends to immobilize them within the keratin. Once inside the cortex they stay there for the life of the strand. But if the molecules won't migrate *out*, we might wonder how they travel *into* the cortex in the first place.



2-amino-4-nitrophenol (yellow)

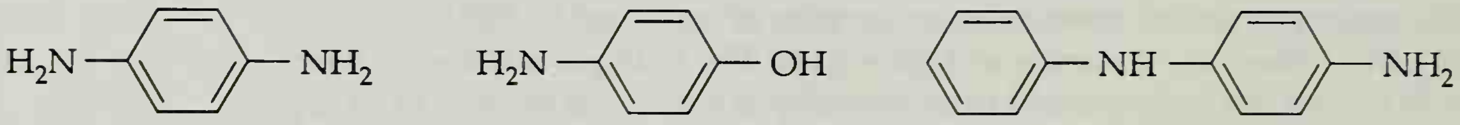
1,4-diaminoanthraquinone (violet)

1,4,5,8-tetraaminoanthraquinone (blue)

Figure 21.10 Representative semipermanent hair colorants. These last through about half a dozen shampooings.

Actually, they don't. The molecules of the permanent dyes don't even exist until they are formed well inside the cortex through a chemical combination of smaller, more mobile molecules that penetrate from the outside. A three-component system consisting of an oxidizing agent, such as hydrogen peroxide, and two organic intermediates—a *primary intermediate* and a *secondary intermediate* or *coupler* (Fig. 21.11)—does the job by an ingenious bit of chemistry. The small and highly mobile molecules of the intermediates, usually colorless themselves, move into the keratin much like those of the semipermanent dyes. As these relatively small organic molecules travel into the cortex, the one representing the primary intermediate is oxidized by the hydrogen peroxide. The product of this reaction combines with the other component, the secondary intermediate or coupler, to form the immobile, permanent coloring. Shades darker than the natural color of the hair are

Typical primary intermediates

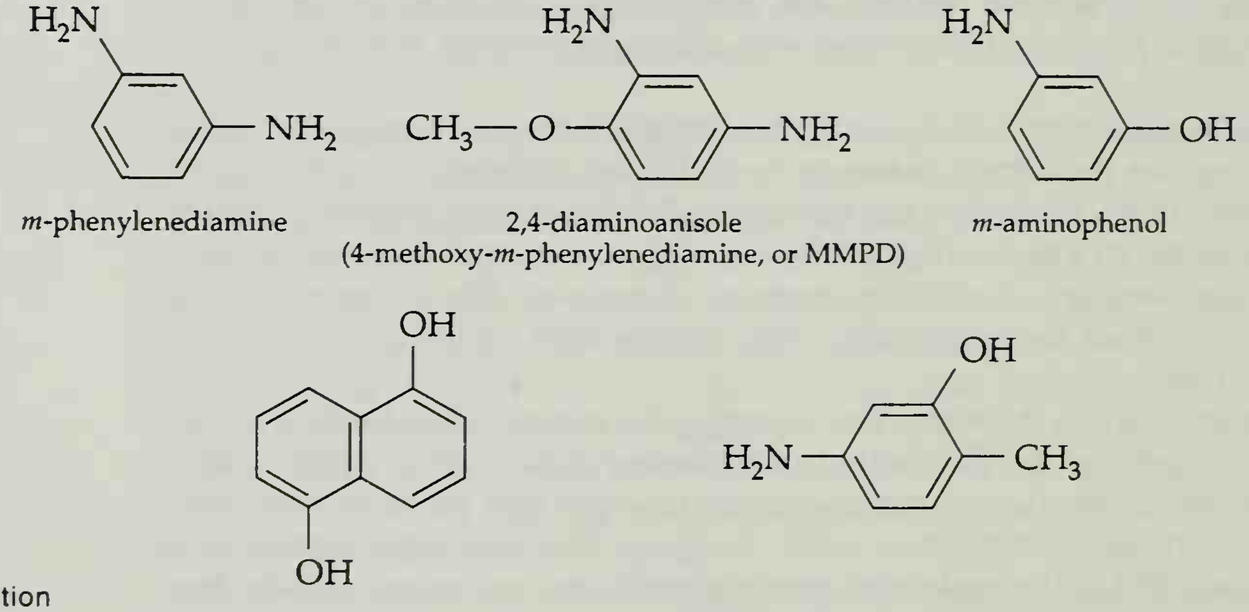


p-phenylenediamine

p-aminophenol

p-aminodiphenylamine

Typical secondary intermediates, or couplers



m-phenylenediamine

2,4-diaminoanisole (4-methoxy-*m*-phenylenediamine, or MMPD)

m-aminophenol

1,5-dihydroxynaphthalene

4-amino-2-hydroxytoluene

Figure 21.11 Intermediates in the formation of permanent hair dyes.

produced as the newly introduced dye adds to the color of the melanin already present. Lighter shades result as larger amounts of the oxidizing agent bleach the melanin even as they induce formation of the dye.

Dyeing hair with these systems may carry some risks. Many contain ingredients that can produce allergic reactions in sensitive individuals and, if used on eyebrows or eyelashes, could cause blindness in extreme cases. A few of the intermediates, such as the 2,4-diaminoanisole of Figure 21.11 (also known as MMPD, a shortened form of an alternative name, 4-*m*ethoxy-*m*-*p*henylene*d*iamine), have been shown to produce cancer in laboratory animals. MMPD itself has been removed from most commercial hair dyes. Those that still contain it must carry a cautionary statement on the label: "Warning—Contains an ingredient that can penetrate your skin and has been determined to cause cancer in laboratory animals." Still other ingredients give positive Ames tests (Section 18.14) and are suspect as mutagens or carcinogens. Nevertheless, no authentic connection between these dyes and human cancer or birth defects has been established. As for the question of whether hair dyes are actually safe, the discussion of risks, hazards, and safety in Chapter 18 applies to these ingredients as well as to food and its additives. As before, safety is largely a matter of the acceptability of known risks.

QUESTION

What does hydrogen peroxide react with as it lightens the color of hair? What does lead acetate react with as it darkens hair and what is the product of the reaction?

21.7 A Note on Names

Notice that Figure 21.11 uses two different systems to name the organic molecules of the intermediates. In one, numbers indicate the positions of groups bonded directly to the rings. The benzene ring of *4-amino-2-hydroxytoluene*, for example, holds an amino group on its No. 4 carbon and a hydroxyl group on position 2, as shown in Figures 21.11 and 21.12. (The methyl group of toluene always occupies the No. 1 position.)

An alternative system (Fig. 21.12) uses the underlined or italicized letters *o*, *m*, and *p*, (for *ortho*, *meta*, and *para*) to define the positions of *two* substituents *relative to each other*. Those located on adjacent ring carbons, such as the two chlorines of *o*-dichlorobenzene, are **ortho** to each other.

Two substituents separated by one ring carbon are **meta** to each other, as in the *m*-phenylenediamine of Figure 21.11 and the *m*-dichlorobenzene of Figure 21.12. (The *meta* substituents are separated by three ring carbons if we trace around the ring in the other direction.) **Para** substituents, indicated by the letter *p*, lie directly across the ring from each other, as in the *p*-phenylenediamine and *p*-dichlorobenzene of the two figures.

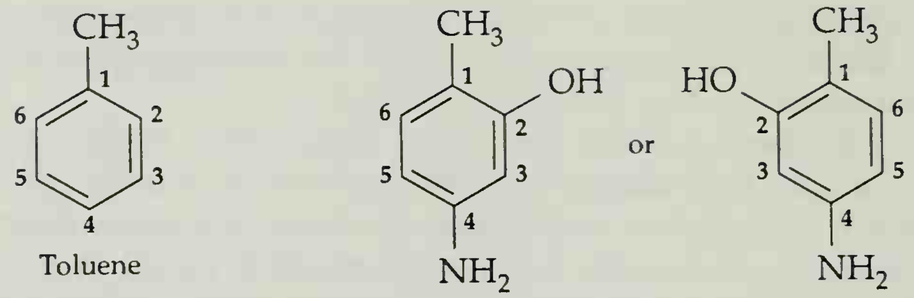
Substituents on a benzene ring are **ortho** to each other when they are located on adjacent carbons of the benzene ring.

Substituents on a benzene ring are **meta** to each other when they are located on carbons of a benzene ring that are separated from each other by a single ring carbon. **Para** substituents are located on ring carbons that lie directly across from each other.

QUESTION

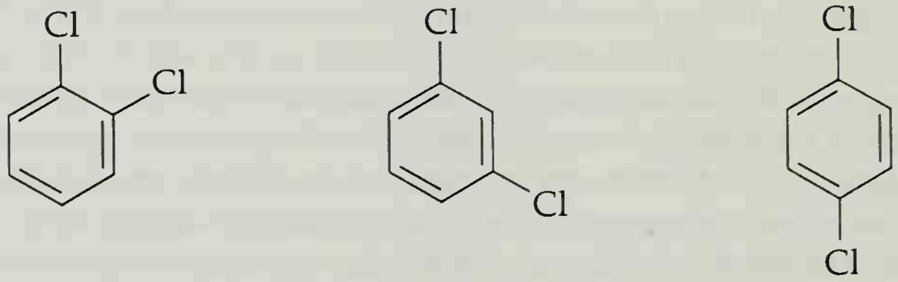
Give an alternative name for each of the following: (a) 1,3-dinitrobenzene, (b) *p*-chlorotoluene, (c) 2-iodotoluene.

Figure 21.12
Naming substituted benzenes.



Toluene

4-amino-2-hydroxytoluene



o-dichlorobenzene
(*ortho*-dichlorobenzene)
1,2-dichlorobenzene

m-dichlorobenzene
(*meta*-dichlorobenzene)
1,3-dichlorobenzene

p-dichlorobenzene
(*para*-dichlorobenzene)
1,3-dichlorobenzene

21.8 Hair: Curling the Keratin

Several forces combine to keep a strand of hair straight or in loose waves or tight curls. The most important of these forces are:

- Disulfide links, the sulfur–sulfur covalent bonds of the keratin's cystine
- Salt bridges, the ionic bonds that form between the acidic group of one amino acid and a basic (amino) group of another amino acid located somewhere else on the same or an adjacent protein molecule
- Hydrogen bonds

We discussed the *disulfide links* of cystine groups in the keratin earlier, (Section 21.5). The salt bridges form as the proton of a carboxyl group (—CO_2H) on an amino acid, such as aspartic acid or glutamic acid, transfers to a nearby amino acid containing a free amine group (—NH_2), such as the lysine or proline of another chain (see Table 15.1). This acid–base reaction produces the ionic bonding of a carboxylate anion (—CO_2^-) and an ammonium ion (—NH_3^+) that holds portions of adjacent keratin chains near each other just as ionic bonds cement a crystal of sodium chloride.

Hydrogen bonds, which we first encountered in Section 15.10, are weak electrical attractions between the hydrogen of an NH group or an OH group, on the one hand, and any one of a few other atoms, including oxygen and nitrogen (but not carbon), on the other. Hydrogen bonds are plentiful in water and in the polymeric proteins, where the hydrogen on a nitrogen of one amide link bonds (weakly) to the carbonyl oxygen of another. Figure 21.13 sums up these interactions in the keratin of hair and in water.

While individual hydrogen bonds are weaker than any of the ionic or covalent bonds, their sheer numbers give dry hair most of its strength. In wet

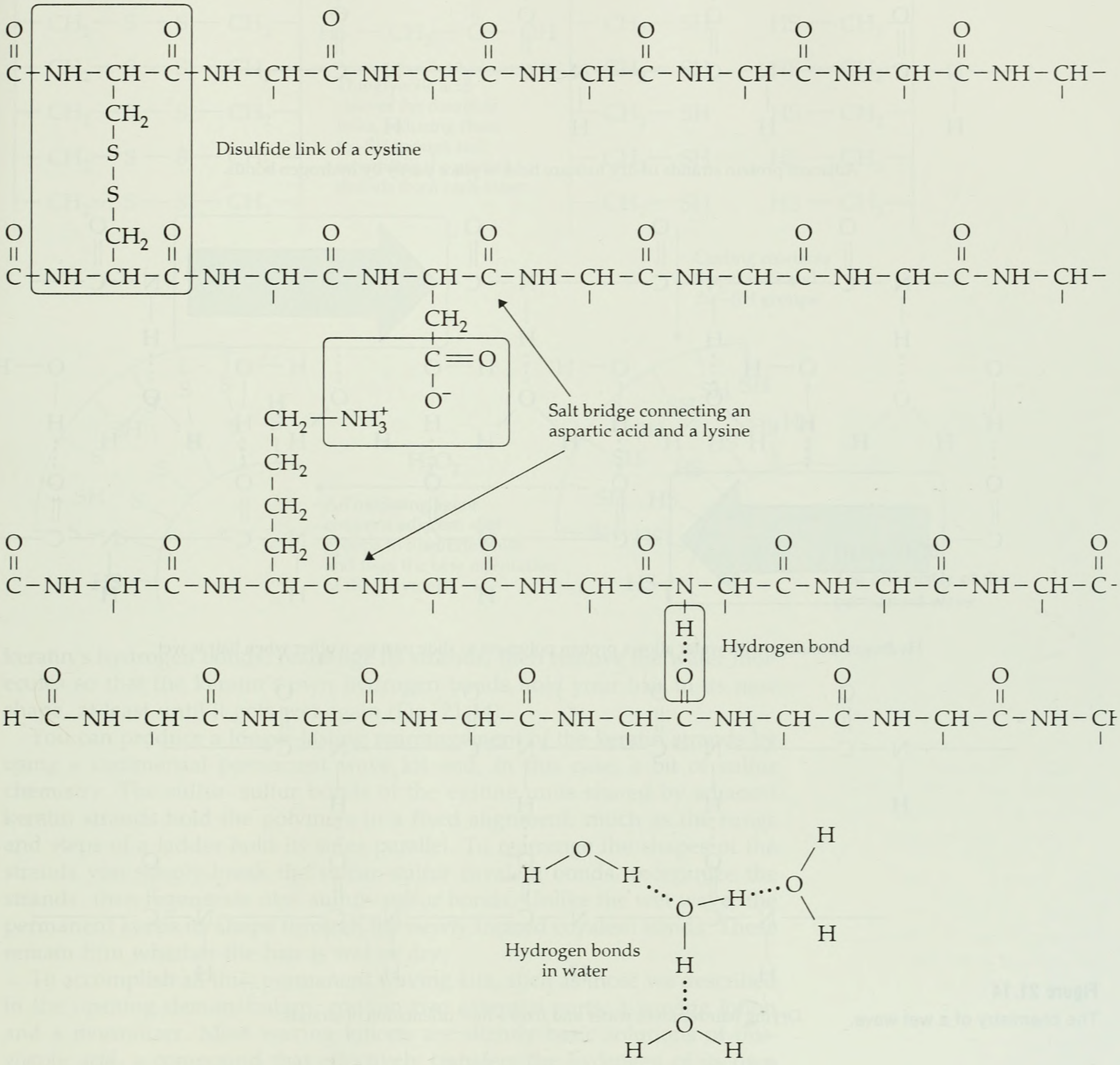
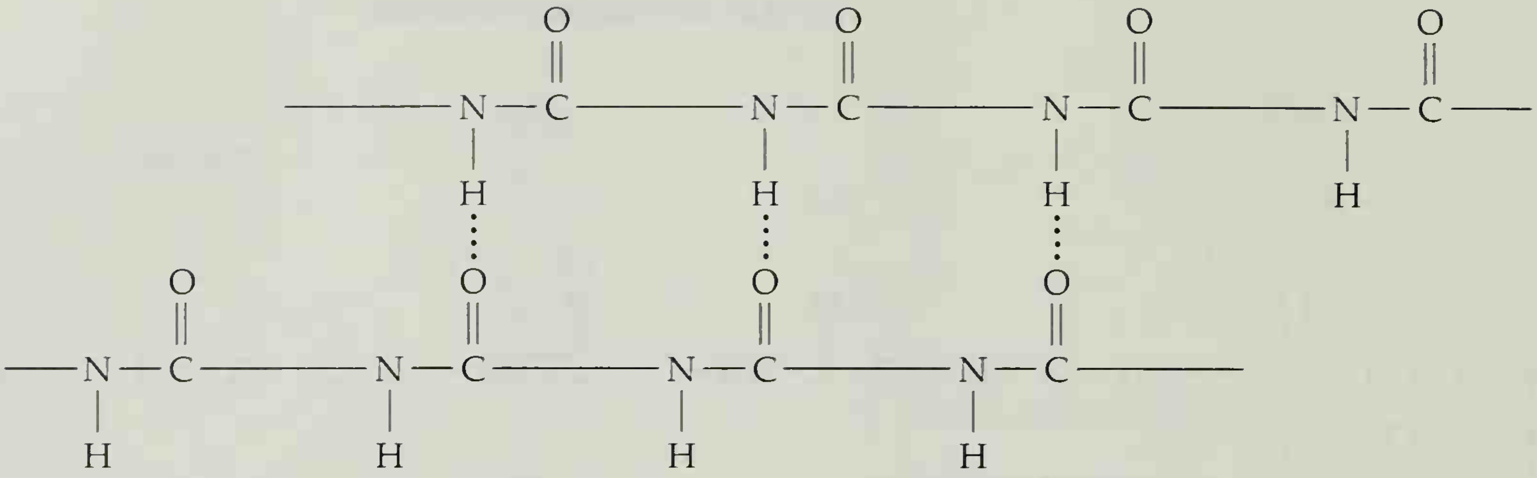
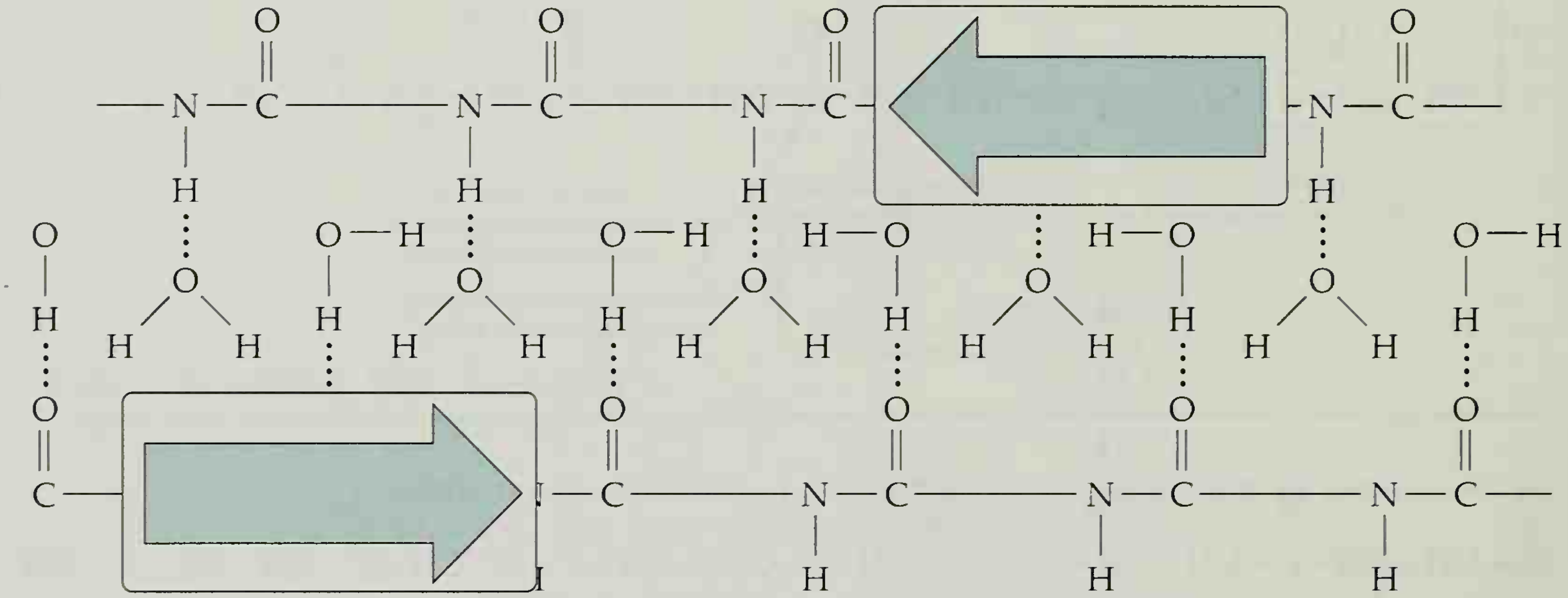


Figure 21.13
Bonding in proteins and in water.



Adjacent protein strands of dry hair are held in place partly by hydrogen bonds.



Hydrogen bonding with water allows protein polymers to slide past each other when hair is wet

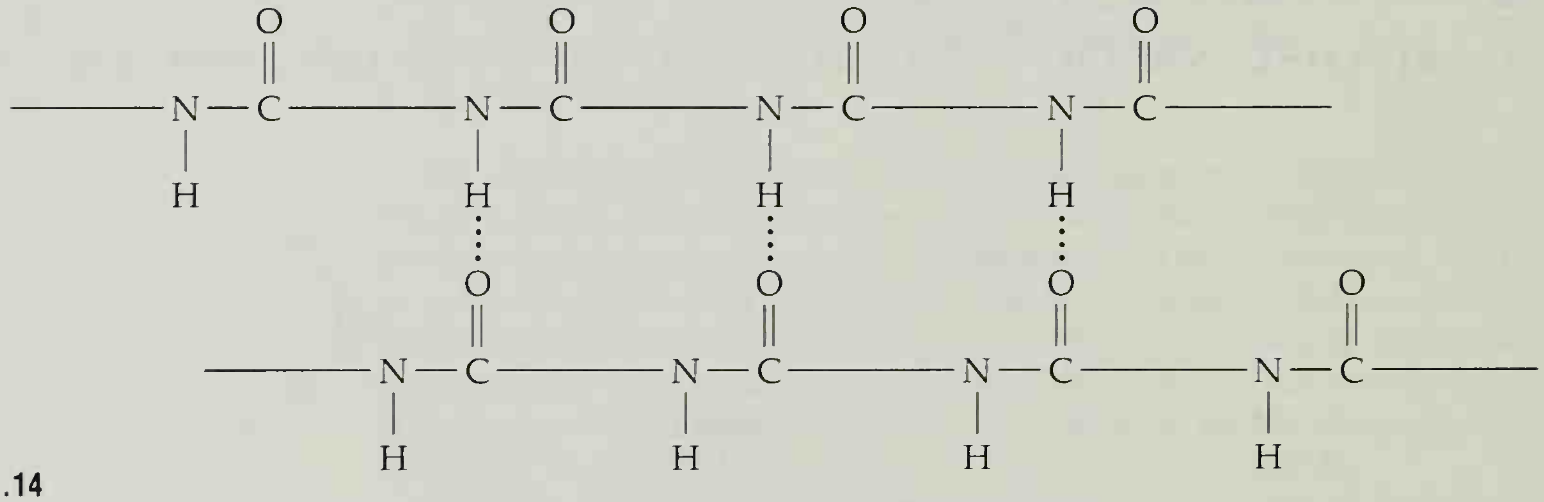
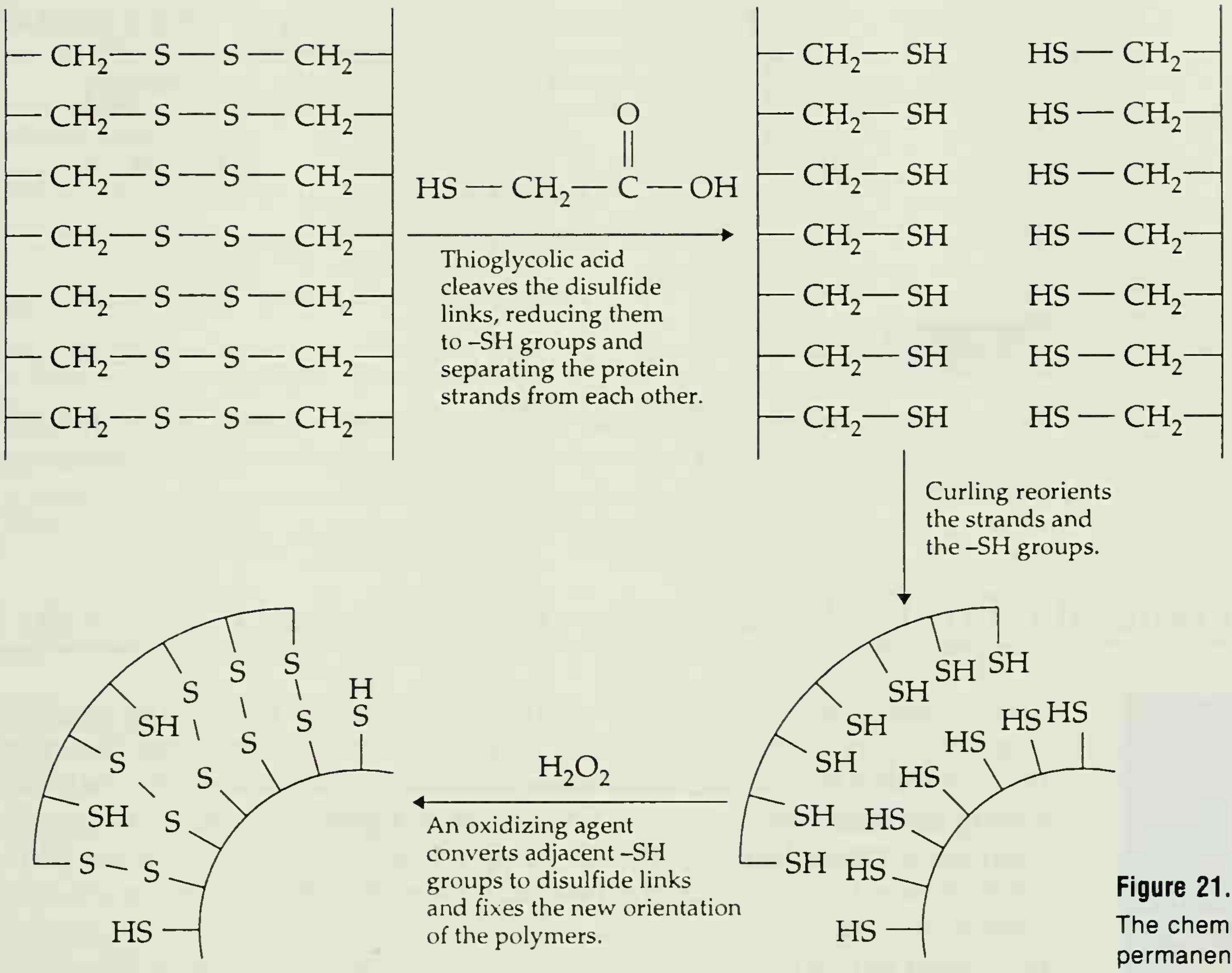


Figure 21.14
The chemistry of a wet wave.

Drying hair removes water and fixes a new orientation of strands.

hair, though, water molecules intrude between the keratin strands, disrupt the hydrogen bonds that keep them aligned with each other, and allow them to shift a bit. As hair dries, the water molecules leave and the hair retains its new shape, held intact by the combined force of large numbers of hydrogen bonds in the newly realigned polymeric chains. Every time you wash your hair, set it, and then blow-dry it, you use a bit of chemistry to disrupt the



Thioglycolic acid cleaves the disulfide links, reducing them to –SH groups and separating the protein strands from each other.

Curling reorients the strands and the –SH groups.

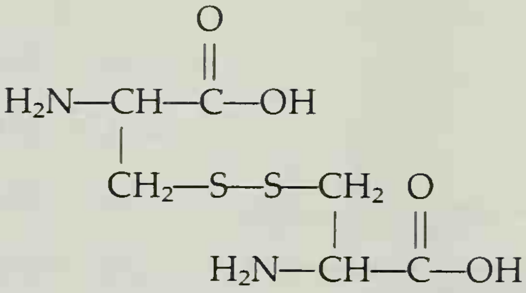
An oxidizing agent converts adjacent –SH groups to disulfide links and fixes the new orientation of the polymers.

Figure 21.15
The chemistry of the permanent wave.

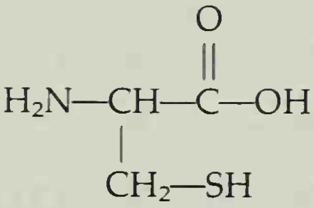
keratin's hydrogen bonds, rearrange its strands, then remove the water molecules so that the keratin's own hydrogen bonds hold your hair in its new shape, at least until it gets wet again (Fig. 21.14).

You can produce a longer-lasting rearrangement of the keratin strands by using a commercial permanent wave kit and, in this case, a bit of sulfur chemistry. The sulfur–sulfur bonds of the cystine units shared by adjacent keratin strands hold the polymers in a fixed alignment, much as the rungs and steps of a ladder hold its sides parallel. To rearrange the shapes of the strands you simply break the sulfur–sulfur covalent bonds, reorganize the strands, then regenerate new sulfur–sulfur bonds. Unlike the wet wave, the permanent keeps its shape through the newly formed covalent bonds. These remain firm whether the hair is wet or dry.

To accomplish all this, permanent waving kits, such as those we described in the opening demonstration, contain two essential parts: a waving lotion and a neutralizer. Most waving lotions are slightly basic solutions of *thioglycolic acid*, a compound that effectively transfers the hydrogen of its own sulfur to the cystine units and cleaves them to cysteines. The result resembles what we'd get if we sawed straight down the middle of the steps and rungs of the ladder. With this accomplished, straight keratin strands can curl, or curled strands can be straightened. Now the neutralizing part of the kit, usually a dilute solution of hydrogen peroxide, converts the cysteines back to cystine and the new shape takes hold (Fig. 21.15).



cystine



$H_2N{-}CH(CH_2{-}SH){-}C({=}O){-}OH$

cysteine

QUESTION

Considering the nature of the transformation of cystine to cysteine that is produced by thioglycolic acid, suggest a possible fate of the thioglycolic acid in the chemistry of permanent waving. ______________________________

21.9 Toothpaste, the Fresh Abrasive

Toothpaste, a combination of abrasives, detergents, flavorings, and, in many cases, fluorides and other ingredients that protect against decay.

Clean teeth are healthy teeth. But while cleaning teeth is the primary function of a toothpaste, and while we see a rich foam as the clearest indication that the toothpaste is working, those same surfactants that produce the foam are among the least important cleansing agents of a good dentifrice. They aren't what keep teeth clean and healthy, and a few powdered dentifrices don't even contain them. In fact, the Food and Drug Administration doesn't consider a surfactant to be an active ingredient of a toothpaste. What's needed for a good dentifrice is an effective abrasive. To understand why takes a bit of dental chemistry.

A healthy tooth is covered by a layer of enamel that serves both to grind food and to protect the interior regions of the tooth itself. As in bone, calcium makes up most of this extremely hard surface, which is composed largely of the mineral *hydroxyapatite*, $Ca_{10}(PO_4)_6(OH)_2$. Despite its toughness, the enamel is susceptible to acids that come from a thin, adhesive, polysaccharide film called **plaque**.

Plaque is a thin layer of a polysaccharide that sticks to the surface of teeth and harbors bacteria.

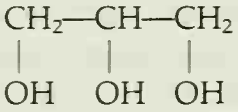
Bacteria of the mouth continuously convert some of the sugars of our food into this plaque, which attaches to the enamel and serves as a home to still other bacteria. These other bacteria, in turn, convert the plaque into an acid that erodes the calcium and the phosphate from the hydroxyapatite that protects the tooth. When enough erosion has occurred microorganisms can pass through the weakened barrier to begin their work on the interior. The result is *dental caries*, better known as tooth decay or cavities.

The key to keeping teeth free of cavities lies in removing the accumulated plaque, and that depends more on grinding it away with a good dental abrasive than on the detergent action of a surfactant. With daily removal of the plaque, the calcium and phosphate normally present in saliva replace any that might have been removed by mouth acids. As long as no bacteria have entered the body of the tooth itself, this reconstitution process, known as *remineralization*, returns the enamel to its original strength. To be useful as a dental abrasive the grinding agent must be harsh enough to remove accumulated plaque, yet not grind away the enamel itself. Table 21.2 presents some of the chemicals used as abrasives in commercial dentifrices.

TABLE 21.2 Typical Dentifrice Abrasives

Abrasive	Formula
Calcium carbonate	$CaCO_3$
Calcium pyrophosphate	$Ca_2P_2O_7$
Dibasic calcium phosphate	$CaHPO_4$
Hydrated aluminum oxide	$Al(OH)_3$
Magnesium carbonate	$MgCO_3$
Talc	$Mg_3(Si_2O_5)_2(OH)_2$
Titanium dioxide	TiO_2
Tricalcium phosphate	$Ca_3(PO_4)_2$

TABLE 21.3 Composition of a Typical Dentifrice

Ingredient	Formula	Weight (%)	Function
Water	H_2O	37	Solvent and filler
Glycerol	 $\begin{array}{ccc} CH_2 — & CH — & CH_2 \\ \mid & \mid & \mid \\ OH & OH & OH \end{array}$	32	Humectant, retains moisture
Dibasic calcium phosphate	$CaHPO_4$	27	Abrasive
Sodium *N*-lauroyl sarcosinate	(See Fig. 21.4)	2	Surfactant and inhibitor of enzymes that produce decay
Carrageenan	A carbohydrate of seaweed	1	Thickening agent and stabilizer
Fluorides and other additives		1	Enamel hardener; sweeteners and preservatives

Fluoride ions also help maintain the strength of the enamel. Fluorides are present in toothpastes largely in the form of stannous fluoride (SnF_2, Fluoristan), sodium monofluorophosphate (Na_2PO_3F), and sodium fluoride (NaF). The fluoride seems to act in two ways: (1) it replaces some of the hydroxy groups in the enamel's hydroxyapatite, converting it to a harder mineral, *fluoroapatite*, which is more resistant to erosion by acids; and (2) it suppresses the bacteria's ability to generate acids.

While not our principal protection against tooth decay, the surfactants of toothpaste formulations do effectively remove loose debris from the mouth and also give us the sense of cleanliness. Almost all dentifrices contain a bit of saccharin and some flavoring or fragrance to leave us with a sense of sweetness and freshness after brushing. The components of a typical toothpaste appear in Table 21.3.

QUESTION

Brushing with ordinary baking soda ($NaHCO_3$) has been recommended as an alternative if toothpaste is unavailable. While it doesn't contain either an abrasive or a detergent (or a pleasant flavor or fragrance), baking soda does provide one benefit as a dentifrice. What is the benefit? ____________________

21.10 To Make Our Skin Moist, Soft, and . . .

On average, about a quarter of every dollar we spend for cosmetics goes toward the care of our skin with moisturizers and emollients (softeners), with hand, face, and body soaps, and with deodorants and antiperspirants. We've already examined the chemistry of soaps and detergents in Chapter 11; here we'll take up the means by which we keep our skin—the organ that envelops our bodies—moist, soft, and inoffensive. (In the next section we'll discuss deodorants and antiperspirants.)

If an organ is a group of tissues that perform one or more specific functions, as the heart pumps blood or the kidneys filter it, then our skin is indeed an organ, the largest one of the entire body. Its functions range from the obvious covering of our bodies and protection from damage by foreign matter and microorganisms, to the more subtle tasks of regulating body temperature, sensing the stimuli provided by the outside world, and even synthesizing compounds such as vitamin D (Section 16.8).

The **dermis** is the portion of the skin that contains nerves, blood vessels, sweat glands, and the active portion of the hair follicles, and also supports the upper layer, the **epidermis**.

The skin itself is made up of two major layers, the underlying **dermis**, which contains nerves, blood vessels, sweat glands, and the active portion of the hair follicles, and which also supports the upper layer, the **epidermis** (Fig. 21.6). The epidermis consists of several tiers of cells. At its bottom, resting on top of the dermis, is a single sheet of cells that divide continuously, always pushing upward. As they move toward the outside of the skin, driven along by new cells coming up from beneath, they lose their ability to divide and eventually die. By the time they become the lifeless, outermost layer of the skin, the *stratum corneum*, they have been transformed into keratin, the same protein that forms the hair.

The **stratum corneum** is the outermost layer of skin, a protective shield consisting of 25 to 30 layers of dead cells.

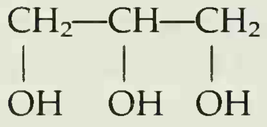
The **stratum corneum** itself is a layer of 25 to 30 tiers of these dead cells whose sole function is to protect us against the outside world, including the world of our cosmetics and toiletries. The condition of this layer depends mostly on its water content. Too much moisture nourishes the growth of fungi and other microorganisms; too little dries it out, producing flaking and cracking. A water content of 10% is just about right for the stratum corneum.

The body supplies protection to the skin with the sebum secreted by the sebaceous glands of hair follicles. This oily substance coats the adjacent skin (Section 21.5), lubricating and softening its dead keratin (as well as the hair's), and lowering the rate at which water evaporates from its surface. These sebaceous glands occur only at the hair follicles themselves. No sebum coats the skin of the hairless regions of the body, such as the palms of the hands and the soles of the feet.

Commercial cosmetic lotions and creams are emulsions, or colloidal dispersions (Section 11.7) of two or more liquids that are insoluble in each other (usually an oil and water). These personal care products act in much the same way as sebum. A contemporary form of *cold cream*, one of the oldest and most common of the skin moisturizers, consists of an emulsion of about 55% mineral oil, 19% rose water, 13% spermaceti (a wax obtained from the sperm whale), 12% beeswax, and about 1% borax. A typical *vanishing cream*, which fills in wrinkles and appears to make them vanish, incorporates about 70% water, 20% *stearic acid* (partly as its sodium salt), and 10% *glycerol* (also known as *glycerin*), with traces of potassium hydroxide, preservatives, and perfumes. In the more freely flowing hand and body lotions, water and oils replace some of the waxes of the creams. Since the function of these lotions and creams is to keep the outer layer of skin moist, they are most effective when applied after a bath or shower, while the skin is still damp.

$CH_3—(CH_2)_{16}—CO_2H$

stearic acid



$$\begin{array}{ccccc} CH_2 & — & CH & — & CH_2 \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

glycerol
or glycerin

QUESTION

We have seen repeatedly that a particular chemical can have more than one use and that sometimes these uses are very different from each other. Name two uses for mineral oil that involve the human body. (See Section 7.3 for one of them.) With your answer in mind, if you skin is dry and cracked and you have no lotions or creams at hand, what other consumer product could you use in an emergency? ______

21.11 . . . Inoffensive

We control our body's temperature by perspiring (from Latin words meaning "to breathe through") or sweating (an Anglo Saxon word that means just what it says). When you're warm or in a tense situation, your sweat glands begin their work of cooling you off. One set of these glands, the *eccrine* glands (sometimes called the "true" sweat glands), covers most of the skin. They're especially dense on the forehead, face, palms, soles, and armpits, and they secrete a slightly acidic, very dilute solution of inorganic ions (largely sodium, potassium and chloride), lactic acid ($CH_3—CHOH—CO_2H$), some urea ($H_2N—CO—NH_2$; Section 7.1), and a little glucose. The cooling effect of sweating comes from the evaporation of the water from this secretion, which ordinarily has no odor.

Another set, the *apocrine* glands, releases a different kind of substance, one that can easily become disagreeable. Like the sebaceous glands, these apocrine glands secrete their fluids into the hair follicles. But unlike the sebaceous glands, which occur wherever hair grows, these apocrine glands lie almost exclusively under the arms, in the groin, and in a few other smaller regions of the body. While their secretions produce little or no odors in themselves, bacteria that accumulate in the nearby strands of hair can degrade the contents of the apocrine fluids into foul-smelling products.

Antiperspirants inhibit sweating and keep the body relatively dry. **Deodorants** directly attack odors themselves.

To control the wetness of perspiration and any of its associated odors we have available two personal care products, **antiperspirants** and **deodorants**. The antiperspirants inhibit sweating and keep the body relatively dry. Deodorants, on the other hand, directly attack odors themselves. The most widely used of the antiperspirants are the *aluminum chlorohydrates,* $Al_2(OH)_4Cl_2$ and $Al_2(OH)_5Cl$. These release aluminum cations, which seem to reduce wetness by physically closing the ducts of the eccrine glands for as long as several weeks. They also reduce the odor associated with the apocrine glands, probably by killing the bacteria that decompose the organic portion of the fluid.

Deodorants mask odors with fragrant ingredients that cover the offending aroma and also with antibiotics that eliminate the bacteria. In addition to the aluminum salts, these antibacterial agents include various salts of zinc as well as the broad spectrum antibiotic *neomycin*. Since the odor itself comes from the action of bacteria on the accumulated residue of perspiration, daily washing alone often solves many of the problems.

QUESTION

How do the aluminum chlorohydrates act to reduce perspiration? How do antibiotics act to reduce body odors? ______________________________

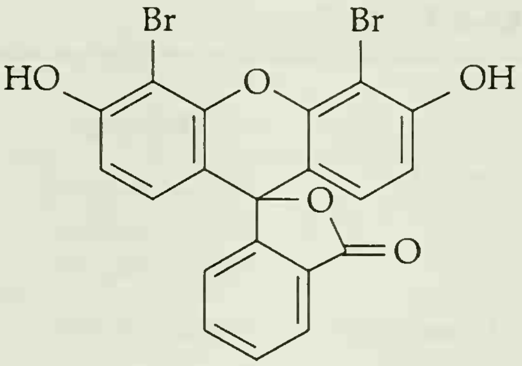
21.12 Putting a Little Color on Your Skin

The oils, waxes, polymers, and dyes of lipstick protect, soften, and brighten the lips.

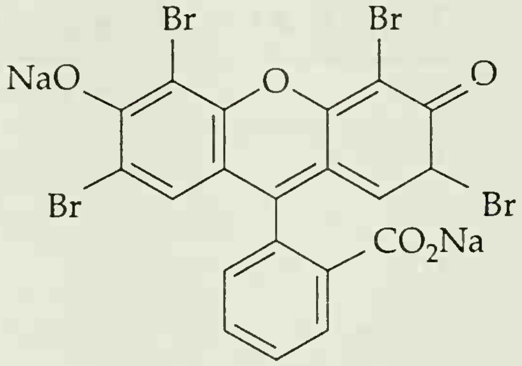
With our hair, teeth, and skin clean and in good shape, we'll focus now on lipsticks, eye colorings, nail polish, and face powder. Lipstick provides a softening and protecting film for the lips, as well as colors ranging from soft and unobtrusive to dazzling. About half the weight of a tube of modern lipstick is highly purified castor oil (a mixture of triglycerides obtained from plant seeds). This oil serves to dissolve the dyes and, more importantly, to give the stick the ability to remain a waxy solid in its container yet flow smoothly as it touches the warmer lips. Most of the remainder of the stick is a mixture of oils, waxes, hydrocarbons, esters, *lanolin* (the waxy sebum of sheep), and polymers, all formulated to produce a desirable texture, melting point, ingredient mix, and film flow. In addition, the castor oil and other oils and waxes help keep the skin of the lips moist and soft. The remaining ingredients, dyes, perfumes, and preservatives, make up a very small percentage of the weight.

Major dyes of modern lipsticks include D&C Orange No. 5, known chemically as a *dibromofluorescein,* and D&C Red No. 22, a *tetrabromofluorescein* (Fig. 21.16). The D&C here indicates that the Food and Drug Administration has approved these dyes for use in *d*rugs and *c*osmetics (Section 21.6).

Eye shadows use intensely colored, largely inorganic dyes incorporated into mixtures of beeswax, lanolin, and hydrocarbons. The colorings include *ultramarine blue* (an inorganic polymer consisting of the elements aluminum, oxygen, silicon, sodium, and sulfur), iron oxides of various shades, *carbon*



D & C Orange No. 5
4',5'-dibromofluorescein



D & C Red No. 22
2',4',5',7'-tetrabromofluorescein

Figure 21.16 Lipstick dyes.

black (a very finely divided form of carbon resembling powdered charcoal), and *titanium dioxide*, TiO_2. This last ingredient, a white powder, is quite opaque and is useful in hiding or muting the natural color of the skin as the other dyes show through.

Because eyelashes turn pale near their ends, they tend to get lost against a lighter background of the skin and eyes. Mascaras give the lashes a longer look by darkening the ends for more contrast. Despite the term *lengthening mascara*, these cosmetics don't actually lengthen the eyelashes. They just make them seem longer by making their ends more visible against a lighter facial background. To protect the eyes against any potential for allergic reactions to synthetic dyes, the FDA requires that only natural dyes, inorganic pigments, and carbon black be used as mascara colorants. Otherwise, mascaras are prepared in much the same way as other cosmetics.

Nail polish is simply a highly specialized, flexible lacquer that can bend with the nail rather than crack and flake. Its pigments include ultramarine blue, carbon black, organic dyes, and various oxides of iron, chromium, and other metals. These, together with nitrocellulose, plasticizers, and a resin, are all dissolved in a mixture of hydrocarbons and esters, including *n*-butyl acetate and ethyl acetate. As the volatile solvents evaporate they leave the dyes embedded in a polymeric film that grips the nail. Most commercial nail polish removers contain ordinary organic solvents, primarily ethyl acetate (a common solvent for the polish itself) and acetone. Since these remove the natural oils of the nail along with the hardened polish, the removers also contain castor oil, lanolin, or other emollients to keep fingernails and the surrounding skin soft.

Face powders are a bit different from the other cosmetics of this section. Unlike lipsticks, eye shadows, and nail polishes, these powders aren't designed to replace a natural shade with a deep or striking color. Instead, they dull the glossy shine of sebum and perspiration while at the same time adding a pleasant tint, texture, and odor of their own, all without calling attention to their own presence. The composition of a typical cake of face powder appears in Table 21.4.

QUESTION

What function does titanium dioxide, TiO_2, serve in a cosmetic? ______________

TABLE 21.4 Composition of a Caked Face Powder

Ingredient	Weight (%)	Formula	Function
Talc	65	$Mg_3(Si_2O_5)_2(OH)_2$	Forms cosmetic bulk, provides desired texture
Kaolin	10	Al_2SiO_5, hydrated	Absorbs water
Zinc oxide	10	ZnO	Provides hiding power
Magnesium stearate	5	$Mg(O_2C{-}C_{16}H_{32}{-}CH_3)_2$	Provides texture
Zinc stearate	5	$Zn(O_2C{-}C_{16}H_{32}{-}CH_3)_2$	Provides texture
Mineral oil	2	(Hydrocarbons)	Emollient
Cetyl alcohol	1	$CH_3{-}(CH_2)_{14}{-}CH_2OH$	Binding agent
Lanolin and other additives	2		Softening and coloring agents, perfumes

21.13 A Few Notes on Perfume

Despite the variety of personal care products we've encountered in this chapter, all share a single characteristic: a pleasant odor or flavor. (Our sense of *taste* is limited to sweet, sour, bitter, and salt. *Flavors* are combinations of these four tastes with the sense of smell. Odors affect our perception of flavor.)

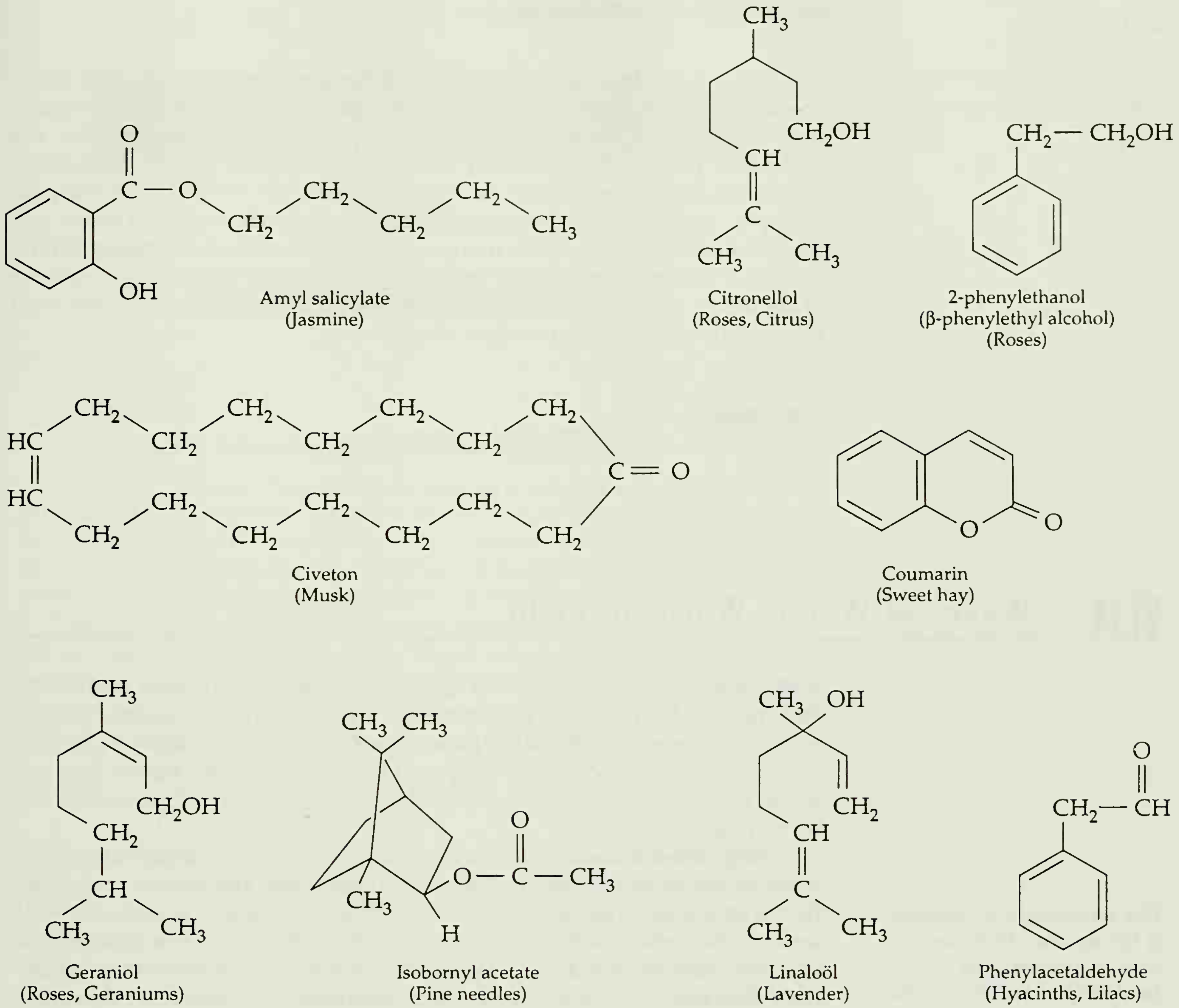
Perfumes are blends of various synthetic chemicals, animal oils, and extracts of fragrant plants, all dissolved as 10% to 25% solutions in alcohol.

Our perfumes, colognes, and lotions, like the products we use to color our hair and bodies, have their origins in antiquity. The word **perfume** itself comes from the Latin *per* ("through") and *fumus* ("smoke"), and may have applied originally to scents carried by the smoke of incense and odorous plants used in sacred ceremonies. Today's perfumes are the products of a long history of changes in the popularity of different sorts of odors and of the methods of blending them. Modern perfumes are blends of various synthetic chemicals, animal oils, and extracts of fragrant plants, all dissolved as 10% to 25% solutions in alcohol.

Colognes are much more dilute and much less expensive versions of perfumes.

Cologne, a shortened form of *eau de Cologne* (from the French for "water of Cologne"), is a much more dilute and much less expensive version of a perfume, with concentrations of the fragrant oils running about a tenth those used in the perfume. The term itself refers to the city of Cologne, Germany, where an Italian, Giovanni Maria Farina, settled in 1709 and began manufacturing a lotion based on citrus fruit. The product became a very popular toiletry, providing fame to the city and wealth to Farina and his heirs.

For devising the odors of today's cosmetics and toiletries the modern perfumer has available a set of some 4000 aromatic plant and animal substances and another 2000 synthetic organic chemicals. The blended fragrance itself reaches the nose in three phases.



Amyl salicylate
(Jasmine)

Citronellol
(Roses, Citrus)

2-phenylethanol
(β-phenylethyl alcohol)
(Roses)

Civeton
(Musk)

Coumarin
(Sweet hay)

Geraniol
(Roses, Geraniums)

Isobornyl acetate
(Pine needles)

Linaloöl
(Lavender)

Phenylacetaldehyde
(Hyacinths, Lilacs)

Figure 21.17
Organic fragrances.

1. The first impact, the *top note*, comes from components that vaporize easily and move to our nose quickly. A typical example is *phenylacetaldehyde*, which brings the odor of hyacinths and lilacs. The top note is the fragrance of the perfume that makes the first impression.
2. The fundamental odor, the *middle note*, is produced by compounds such as *2-phenylethanol* (also known as β-*phenylethyl alcohol*) with its aroma of roses.
3. The *end note* is a residual, longer lasting scent carried by substances like *civetone*, a cyclic organic compound with a musklike odor. The end note of a perfume is the fragrance that lingers.

Civetone is the odorous component of the secretions of the Ethiopian civet cat and was originally obtained by prodding and scraping the glands of the caged animals. Today a more humane preparation comes from syntheses carried out in chemical laboratories.

Examples of the organic compounds used in blending fragrances appear in Figure 21.17. The choice of specific ingredients depends on the nature of the application, the chemical behavior of the available materials, and safety considerations. A nicely scented substance that oxidizes easily to a foul smelling product could hardly be used in a face powder, which is exposed to the air for long periods. In addition to these technical factors, though, consumers' perceptions and expectations come into play as well. A deodorant soap, for example, might carry a strong smell suggesting the clean air of a forest, yet the scent of a lipstick must be more subtle and too weak to interfere with the taste of food and drink. These matters of perception, both our perceptions of chemicals and the effects of chemicals on our perceptions, are topics we'll examine more closely in our final chapter.

QUESTION

What's the difference between a perfume and a cologne?

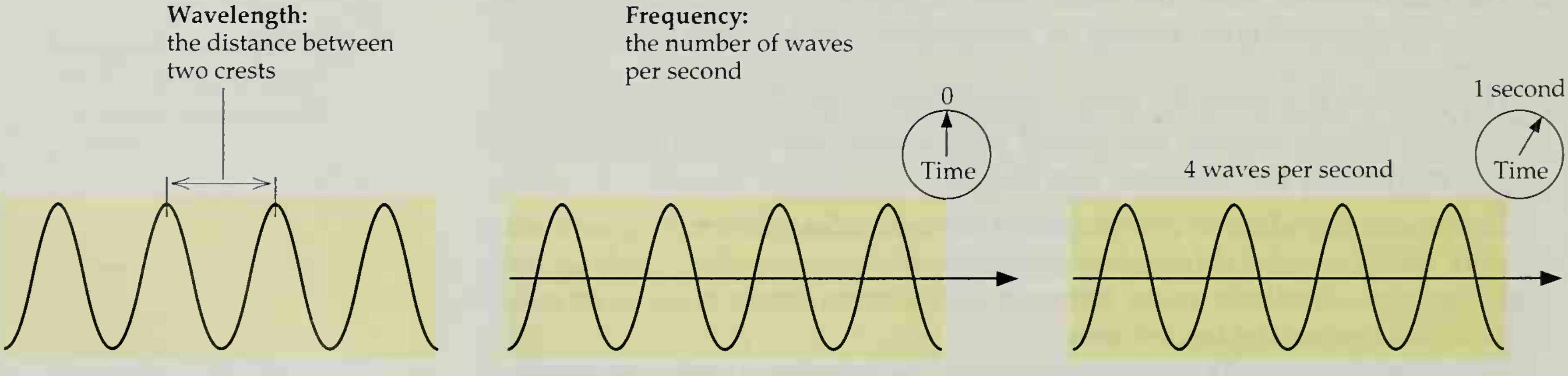
21.14 Waves of Water, Waves of Light

We'll close with a survey of still another way you can decorate your body, this time without the use of commercial dyes, detergents, lotions, creams, perfumes, metals, or any other kind of chemical. Yet this mode of changing the appearance of the human body could pose a far greater hazard than any of the synthetic or natural chemicals that go into our modern cosmetics. It's by getting a suntan.

To understand how our bodies respond to the sun's radiation, why we get a tan by sitting in the sun, and how tanning creams and lotions work, we'll first take a closer look at the sun's rays. The sun's energy reaches the earth as *electromagnetic radiation,* the same sort of phenomenon that carries radio and television signals, radar, microwaves, X rays, the ultraviolet rays of Sections 16.8 and 19.11, and the very light and colors that stimulate the retinas of our eyes. The simplest way to discuss this form of energy follows from its resemblance to the waves of water. Both water and electromagnetic radiation move along at a measurable speed with alternating crests and troughs. As with the waves of water, we can characterize electromagnetic radiation through its **wavelength**, which is simply the distance from one crest to an-

The **wavelength** of radiation is the distance from one crest to another. The **frequency** of radiation is the number of waves that pass a fixed point in a specific period.

Figure 21.18
Wavelength and frequency.



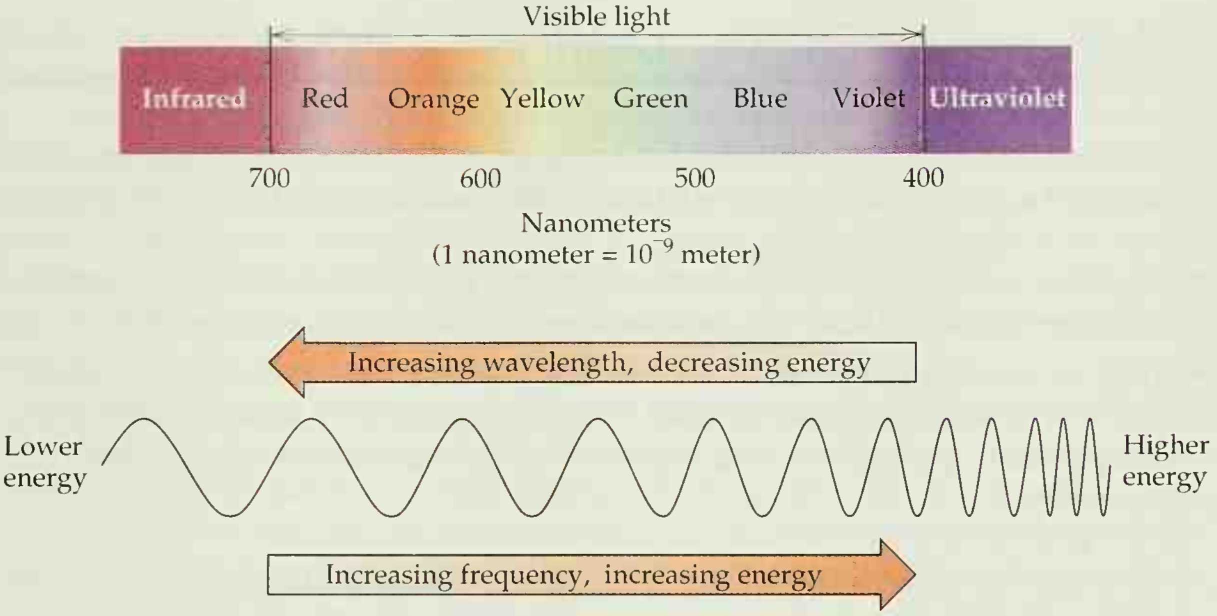


Figure 21.19
Wavelength, frequency, and energy.

other. What's more, since all forms of electromagnetic radiation travel at a fixed velocity (almost exactly 3.0×10^{10} cm/sec as long as they're moving through a vacuum) we can describe them in terms of their **frequency**, which is the number of waves that pass a fixed point in a specific period (Fig. 21.18).

These two characteristics of any wave motion, wavelength and frequency, are mutually reciprocal. That is, the larger (or smaller) the wavelength, the smaller (or larger) the frequency. The shorter the distance between two wave crests, for example, the more waves will pass a fixed point over any particular period, as long as they're moving along at a uniform rate.

$$\frac{\text{wave speed}}{\text{wavelength}} = \text{frequency}$$

Here radiation takes on its own set of characteristics and our analogy to water loses its value. The energy of electromagnetic radiation, for example, depends *directly* and *only* on its frequency. The greater its frequency (or the shorter its wavelength), the higher its energy. For that matter, frequency is the only characteristic that differentiates one form of electromagnetic radiation from another. X rays, for example, travel with a shorter wavelength and a higher frequency (and therefore a higher energy as well) than radio or television waves. It's this difference alone that makes them behave as they do.

With one *nanometer* (*nm*) equal to 10^{-9} meter (m), visible light comes to us in a range of wavelengths from about 400 to 700 nm. Red light lies at the longer end of the spectrum, while invisible, heat-bearing infrared radiation lies beyond, at wavelengths a bit longer than 700 nm. At the shorter end of the spectrum visible light carries a blue-violet color. Still shorter wavelengths, running from about 290 to 400 nm, form the portion of the sun's ultraviolet (UV) radiation that penetrates the ozone layer and reaches the earth's surface and our exposed skin (Fig. 21.19; also see Section 19.11).

QUESTION

Which carries greater energy: (a) X rays or television transmissions; (b) red or blue light; (c) ultraviolet or infrared radiation? ______________________

PERSPECTIVE: Making Choices—Health Vs. Beauty

The effects of the sun's ultraviolet radiation on our skin provide us with additional examples of themes we have developed in our study of chemistry:

- That the substances and phenomena of our everyday world aren't intrinsically beneficial or harmful, but become so only in the ways we use them
- That in our everyday activities we are continuously faced with choices, many of which are easier to make if they are backed by a knowledge of the composition, properties, and behavior of the substances and phenomena we meet

Beginning to burn from too much exposure to the sun's ultraviolet radiation.

In a specific illustration of the first theme, sunlight striking the skin can generate the vitamin D that promotes the formation of healthy bones and teeth, as we saw in Section 16.8. On the other hand, excessive exposure to the intense UV radiation coming from the sun can cause damage to the skin ranging from mild burns to cancer. Sunlight, like so many other substances and effects, provides benefit or harm in proportion to our exposure and use.

As for the second theme, in many regions of the world a well-tanned skin is considered attractive and a mark of someone who has the leisure to lie for many hours in the sun. Desiring this cosmetic effect, yet knowing that UV radiation can damage the skin, many of us choose to expose ourselves to the sun's radiation for long periods, relying on the protection afforded by the chemicals of commercial suntan and sunscreen lotions. An understanding of the effects of sunlight on our skin and how chemicals can help moderate these effects can help us in our choices.

A suntan is simply the visible evidence of the body's attempt to protect itself from harm. Any bare skin exposed to the sun is bathed in relatively high-energy, potentially damaging ultraviolet radiation. In fact, the very absorption of this radiation stimulates the body to take protective measures. As one means of shielding itself from harm, the skin begins producing substantial amounts of the dark pigment melanin (Section 21.6). This newly generated melanin screens out part of the radiation and helps minimize the damage. An attractive tan, then, is the visible evidence of the generation of protective melanin in response to potential harm.

The possibility of damage comes from two adjoining segments of the sun's UV radiation, its UV-A and UV-B regions, which affect the skin in slightly different ways. UV-B radiation, the more powerful of the two, occupies the shorter wavelength region, from 290 to 320 nm. (Recall that the entire UV region extends over the range of about 290 to 400 nm.) It does part of its damage quickly, with the remainder coming more slowly, over a longer term. The acute injury lies in the tissue destruction of sunburns. The results, redness, blistered and peeling skin, and pain, are the same as for burns produced by ionizing radiation (Section 5.9) and by intense heat. Repeated exposure to the UV-B region over a longer period produces skin cancers, especially among fairhaired, light-skinned people. One beneficial effect of the absorption of small amounts of UV-B radiation is the generation of vitamin D.

The less energetic zone, the UV-A of longer wavelengths (320 to 400 nm), isn't as effective at tissue destruction. Instead of burning, it tends to produce a slow tan. It's not quite innocuous, though, since it adds to UV-B's ability to generate cancer and it also damages connective tissue, eventually producing the wrinkles and sag of prematurely aged skin.

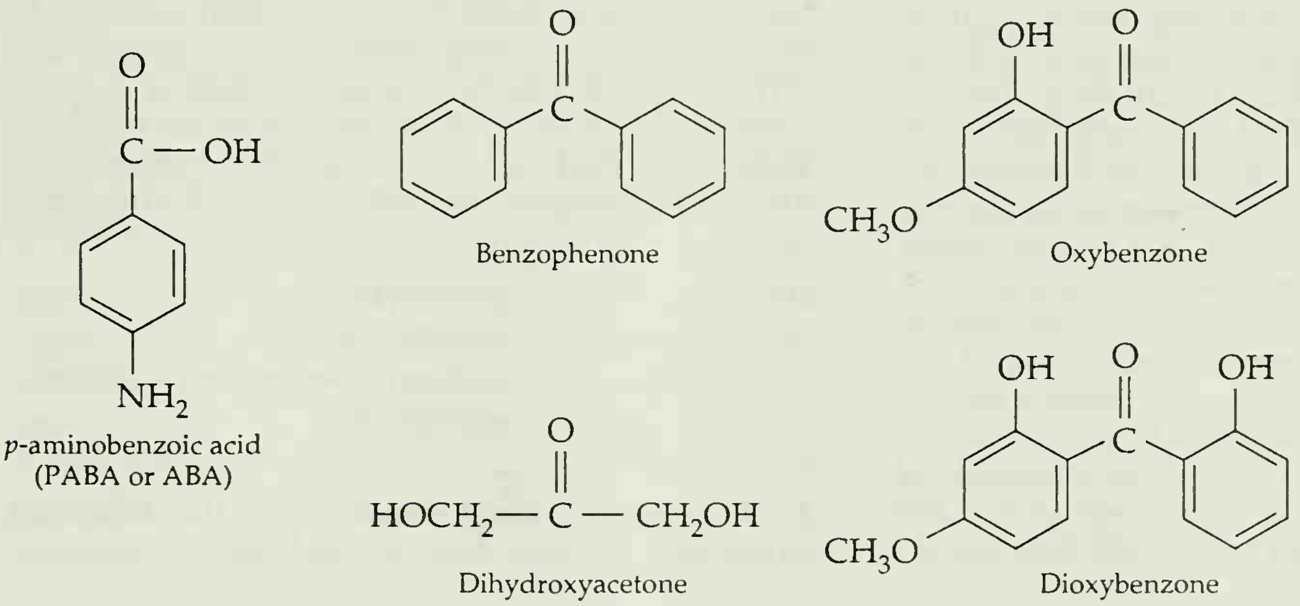
Commercial suntan and sunscreen products act either by blocking the UV-B selectively, letting the UV-A produce its slow tan, or by blocking out both regions, shielding us from the entire solar UV spectrum. The most effective shields are creams containing opaque inorganic oxides, especially zinc oxide and titanium dioxide. These scatter all the radiation, letting none through to the skin. They are usually applied to the nose and the tops of the ears, areas that receive the most direct exposure.

Among the more widely used selective agents are *p-aminobenzoic acid* (PABA or ABA) and its many structural modifications. PABA does a good job of absorbing UV-B radiation while letting UV-A radiation pass through to produce a tan. For this reason lotions containing PABA and similar compounds are considered tanning lotions rather than sunscreens. Other UV absorbing compounds, such as *benzophenone, oxybenzone,* and *dioxybenzone,* absorb throughout the UV spectrum and, sometimes in combination with PABA, provide a wider range of protection. The structures of these absorbers appear in Figure 21.20.

Whatever specific ingredients it may contain, the lotion's **sunscreen protection factor (SPF)**, which appears on its container, serves as a measure of its protecting power. A product with an SPF of 6, for example, reduces the amount of UV radiation reaching the skin by a factor of 6. With it you would receive only a sixth of the radiation reaching you without any protection at all. This means that after 6 hours in the sun, protected by a sunscreen lotion with SPF 6, you would have received the same amount of UV radiation as someone who spent only 1 hour in the sun with no UV protection at all. An SPF of 15 or higher effectively blocks out all the UV radiation at sea level in most regions of the United States. Although SPFs much higher than 15 are available, it's doubtful whether they provide any additional, significant protection to the average person at sea level.

The **sunscreen protection factor (SPF)** of a suntan or sunscreen lotion reveals the fraction of ultraviolet radiation it allows to pass through to the skin.

Some chemicals, such as *dihydroxyacetone* (DHA, Fig. 21.20), react with the amino acids of the skin to produce a brown pigment. Dihydroxyacetone and compounds that produce the same effect are components of products sold to produce a tan-like color of the skin without exposure to the sun, a "sunless


p-aminobenzoic acid (PABA or ABA)

Benzophenone

Oxybenzone

Dihydroxyacetone

Dioxybenzone

Figure 21.20
Tanning compounds.

tan." While dihydroxyacetone alone isn't an effective sunscreen, its combination with the lawsone of henna (Section 21.6) forms a sunscreen the Food and Drug Administration considers to be safe and effective.

Like so many other activities, choosing to lie in the sun for a tan involves balancing a risk, skin damage, against a benefit, the cosmetic effect of a tan. To minimize the risk and enhance the benefit we have a range of degrees of chemical protection available to us, marked by the sunscreen protection factors of lotions and creams. The best way to use them depends, of course, on your own genetic preparation. Many authorities recommend that a person with a particularly light skin start slowly, well protected by an SPF of 10 or 15. Only after developing a light, protective tan (through melanin production) is it safe to drop to lower SPFs for a deeper shade of bronze. Because the best protection comes from sunscreen chemicals that have been absorbed into the outer layer of skin, it's best to apply the lotion about half an hour before going out into the sun. As a rough guide, it takes about one ounce of lotion to cover the body of an adult.

EXERCISES

FOR REVIEW:

1. Complete this statement with the following words and phrases. Each is used once.

Hair care products include shampoos, colorants, and curling or straightening agents. Many of the more popular shampoos contain ______ such as sodium and ammonium ______ , as well as other agents to stabilize the shampoo, color it, adjust the ______ , and ______ the metal ions of hard water. Among the hair colorants are rinses and temporary dyes, which often contain acidic molecules that adhere to the outside of the hair, but are too large to penetrate into the ______ and are washed out easily. Many of the permanent dyes operate through a three-component system consisting of two small organic molecules and an oxidizing agent such as ______ . The small organic molecules penetrate easily into the hair's cortex where one of them, the primary intermediate, is oxidized and reacts chemically with the second, which is known as a secondary intermediate or ______ . The product is an organic molecule too large to migrate out of the cortex easily. Most ______ lotions consist of solutions of ______ , which effectively converts the cystine units that unite adjacent protein molecules of the hair into ______ . With this conversion accomplished, individual protein strands are separated from each other and the hair can be straightened or curled. The neutralizing agent regenerates the ______ connections, which help fix the new shape.

chelate
cortex
coupler
cysteine
cystine
hydrogen peroxide
lauryl sulfonates
pH
surfactants
thioglycolic acid
waving

2. Complete this statement with the following words and phrases. Each is used once.

The active ingredient of a toothpaste is its ______ , rather than the foaming ______ , since the prevention of dental cavities, or ______ , requires the grinding away of plaque, a thin film of ______ that adheres to the surface of teeth. The caries form as bacteria, which thrive in the plaque, erode the hard surface of the teeth. This hard surface consists of the mineral ______ , which contains the element ______ along with ______ groups and OH groups. While the abrasive action of a toothpaste is the primary defense against caries, some surfactants, such as ______ , also help prevent cavities by inactivating bacterial ______ that produce decay.

abrasive
calcium
caries
enzymes
hydroxyapatite
phosphate
polysaccharides
sodium *N*-lauroyl sarcosinate
surfactant

3. Complete this statement with the following words and phrases. Each is used once.

Skin care products include lotions and creams, which are ______ of water and oily substances that soften the ______ of the skin in much the same way as the ______ secreted by glands of the skin itself. Other skin care products, the deodorants and antiperspirants, keep the skin free of perspiration and pleasant smelling. While much of the fluid of perspiration comes from secretions of the ______ , or the "true" sweat glands, offensive odors are the products of the action of skin bacteria on the secretions of the ______ glands. The effective ingredients of antiperspirants are ______ , which physically close the ducts of the eccrine glands, thereby eliminating their secretions. While frequent bathing removes both the residues of perspiration and the bacteria that convert them into offensive substances, deodorants also help by providing fragrances that mask undesirable odors and antibacterial agents such as ______ salts and ______ , which help prevent odors by eliminating the bacteria that cause them.

aluminum chlorohydrates
apocrine
eccrine
emulsions
neomycin
sebum
stratum corneum
zinc

4. Complete this statement with the following words and phrases. Each is used once.

Lipsticks, eye colorings, nail polish, and face powder add color to the face and nails. A highly purified form of ______ , which is a plant ______ , forms the major ingredient of most modern lipsticks. In addition to this oil, lipstick also contains other lubricants including ______ , the waxy ______ secreted by sheep. Among the dyes added to lipstick are the red ______ and the orange ______ . Coloring agents used in eye shadows include the inorganic polymer ______ , blackening agents such as ______ , and whiteners such as ______ . Nail polish is simply a mixture of a ______ , such as ______ , dyes, plasticizers, and other substances, all dissolved in organic solvents including ______ and esters such as ______ . As the solvents evaporate they leave the ingredients embedded in the polymer, which adheres to the nail.

carbon black
castor oil
dibromofluorescein
ethyl acetate
hydrocarbons
lanolin
nitrocellulose
polymer
sebum
tetrabromofluorescein
titanium dioxide, TiO_2
triglyceride
ultramarine blue

5. Complete this statement with the following words and phrases. Each is used once.

A suntan is the body's defense against the damaging effects of ______ . The sun's ultraviolet radiation consists of two segments, the shorter-wavelength and more powerful ______ region, and the longer-wavelength and less powerful ______ region. While the UV-B radiation is responsible for the tissue destruction of sunburn, it also produces the beneficial effect of generating ______ within the skin. The skin's absorption of UV-A, on the other hand, produces a slow tan by stimulating production of the dark pigment ______ , which tends to block the absorption of the entire range of ultraviolet radiation. This UV-A can also damage the skin's connective tissue, leading to aging of the skin. Both UV-A and UV-B can generate ______ on prolonged exposure. Among the UV-absorbing agents of commercial suntan and sunscreen products are ______ , which selectively blocks absorption of the UV-B, allowing the UV-A to produce a tan, and ______ , which absorbs throughout the ultraviolet spectrum, thereby providing a wider range of protection against the harmful radiation. Some commercial products promise a "sunless tan" through the action of ______ , which produces a brown pigment through its reaction with the ______ of the skin.

amino acids
benzophenone
dihydroxyacetone
melanin
p-aminobenzoic acid, or PABA
skin cancer
ultraviolet radiation
UV-A
UV-B
vitamin D

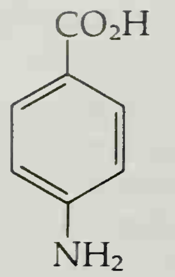
6. Define, explain, or identify each of the following.

a. civetone
b. cologne
c. dermis
d. epidermis
e. frequency (of radiation)
f. hydrogen bond
g. keratin
h. nanometer
i. sunscreen protection factor
j. wavelength

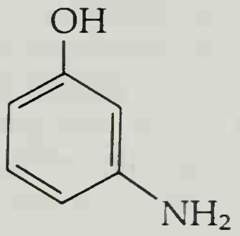
7. Name each of the following compounds and describe its function in personal care products.

a. H_2O_2
b. ZnO
c. $HS—CH_2—CO_2H$
d. $Al_2(OH)_4Cl_2$
e. Na_2PO_3F
f. $Pb(O_2C—CH_3)_2$
g. TiO_2
h. $Ca_2P_2O_7$

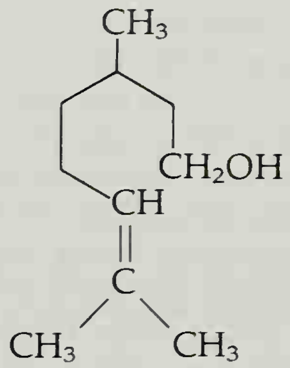
i.



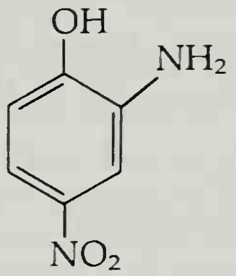
j.



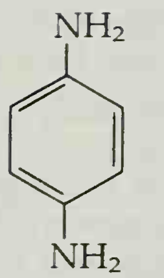
k.



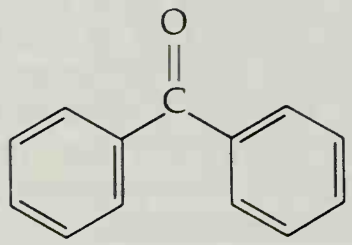
l.



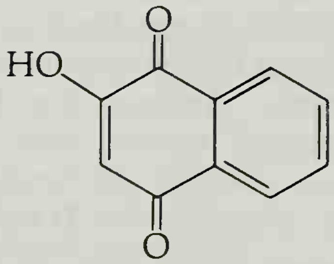
m.



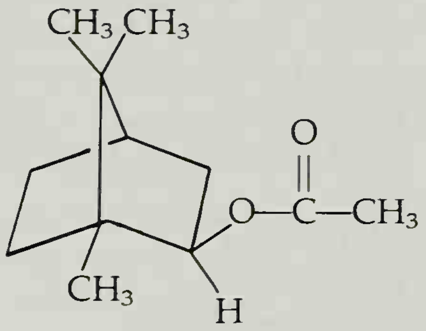
n.



o.



p.



8. Gram for gram, what are the most expensive ingredients of cosmetic and personal care products?

9. Describe the chemistry, applications, and effects of each of the following as products related to tans or exposure to the Sun: (a) zinc oxide; (b) *p*-aminobenzoic acid; (c) a combination of *p*-aminobenzoic acid and dioxybenzone; (d) dihydroxyacetone.

10. Why is either ammonium lauryl sulfate or triethanolammonium lauryl sulfate better suited than sodium lauryl sulfate for use as a detergent in a hair shampoo?

11. In addition to its action as a detergent, the sodium salt of *N*-lauroyl sarcosinate has another property that makes it useful as a toothpaste ingredient. What is that property?

12. What is the difference between the cortex and the cuticle of a strand of hair?

13. Name three chemical forces that give the hair strength and explain how each works.

14. What kinds of chemical bonds are broken and then reformed in (a) a wet wave; (b) a permanent wave?

15. What is the difference between UV-A and UV-B radiation?

16. What kind of skin damage results from overexposure to (a) UV-A radiation? (b) UV-B radiation?

17. What do the terms *ortho*, *meta*, and *para* signify in the names of organic compounds?

18. In what way(s) are light waves and water waves similar?

19. In what way(s) are light waves and water waves different?

20. Describe the function of the following chemicals.

a. thioglycolic acid in home permanent kits
b. hydrogen peroxide in home permanent kits
c. hydrogen peroxide in permanent hair dyes
d. triethanolammonium sulfate in hair shampoo
e. titanium dioxide in a dentifrice
f. zinc oxide in a face powder
g. castor oil or lanolin in nail polish remover

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

21. Suppose that on your first day of vacation you planned to spend no more than 20 minutes in the sun, without any sunscreen protection. Now you decide you want to spend much more time outside in the sun, on your first day, yet you still want no more than the equivalent of 20 minutes of UV radiation. How much time could you spend in the sun, still getting only the equivalent of 20 minutes of UV radiation, if you use a sunscreen lotion with an SPF of (a) 6? (b) 10? (c) 15? (d) 30?

22. Light with a wavelength of 400 nm lies near the border between ultraviolet light and visible, violet light. If we increase the wavelength by 50%, to 600 nm, (a) do we increase or decrease the energy of the light? (b) What color light to we obtain?

THINK, SPECULATE, REFLECT, AND PONDER

23. In what ways are the characteristics of a hair shampoo and a toothpaste similar? In what ways are they different?

24. While an SPF of 15 is generally regarded as sufficient at sea level, a person living at a high altitude or on a mountain-climbing expedition might want to use a much higher SPF. Why?

25. How does mascara "lengthen" eyelashes?

26. Describe the role of dental plaque in tooth decay.

27. Describe the chemical differences between a wet wave of the hair and a permanent wave.

28. Hydrogen peroxide takes part in chemical reactions that make the hair lighter in color and also in reactions that make hair darker. Explain how the hydrogen peroxide acts in each of these systems.

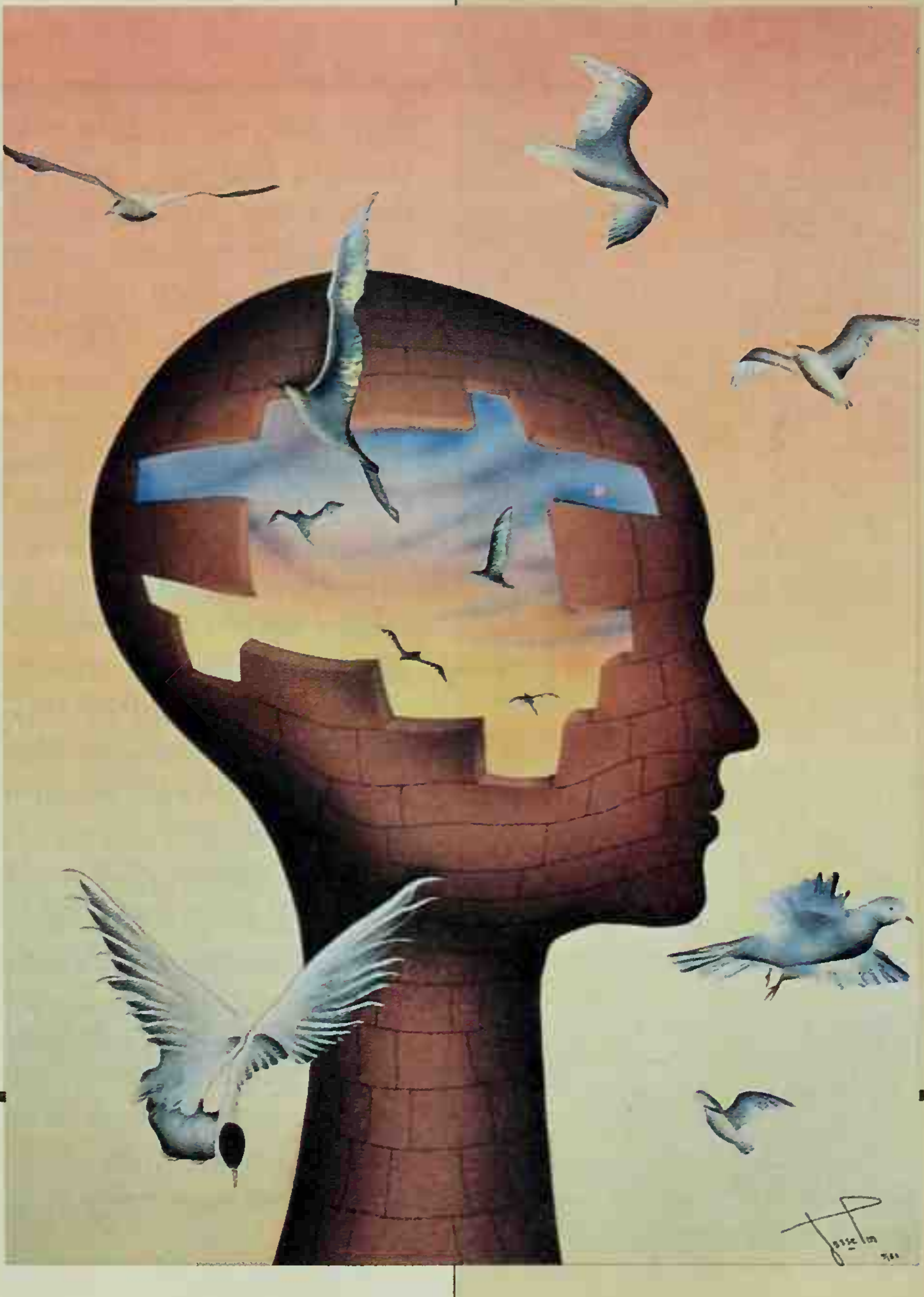
29. Describe the chemical differences among the dyes of hair rinses, temporary dyes, and permanent dyes. Explain how these differences affect the ease with which the dye is washed out of the hair.

30. Explain why the pH of the hair is important to its appearance.

Chemicals and the Mind

22

CHEMICALS OF PERCEPTION AND THE PERCEPTION OF CHEMICALS



Chemicals and the mind: chemically altered states of perception.

Faces or a vase?

Perception, Reality, and Chemicals

The world as we see it isn't necessarily the world as it exists. In Figure 22.1 you see two horizontal lines, each ending in diagonal lines slanting one way or another. Most people see the horizontal line ending with the outward slanting lines (right) as longer than the one ending with the inward slanting lines (left). Measure them, though, and you'll find that the two horizontal lines are of equal length. Then there's the stovepipe hat (Fig. 22.2). Most people see the height of the hat as greater than the width of the brim. Again, measure the height and the width and you'll find that they are the same.

Misperceptions like these can be corrected easily by tests of the physical world, such as we use in applications of the scientific method. Here we can test reality with a ruler and learn whether our perceptions about the length of lines are true. The opening photo on this page presents a trickier case, one that can cause problems. When you look at it, do you see an oddly shaped vase or the silhouettes of two people facing each other? Some people see one, some see the other. Maybe you can see both. There's no objective test of reality here. One person can call it a vase, another can call it a pair of silhouettes, and both can be right.

As the illusion of the opening photo brings home to us, two different viewers can perceive the same reality in different ways. Each might agree that someone else could interpret things differently. Then again, they might not. Differences in perceptions of this sort can be troublesome. It can be hard for people to work out their differences on issues they disagree on when they see the same thing differently and neither can view it from the other's perspective. What we call "reality" sometimes depends on just how we view the world we all live in, on what our perceptions are. Living in a society like ours can present problems when our own perceptions of reality don't match those of others.

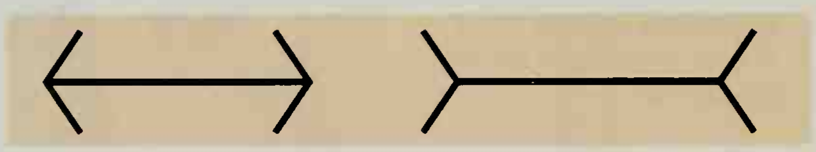


Figure 22.1
Which line is longer?

Our perceptions of the world and their effects on our actions are important to a discussion of chemistry. Chemicals, including those we classify as medicines and drugs, can affect our views of reality and our actions. The effects can be beneficial, as when we use chemicals to ease pain so that we can carry on with our work and our lives, or they can carry a potential for disaster, as when they produce hallucinations or remove us from contact with reality in other ways. In this chapter we'll examine some of the chemicals that affect the mind and the ways they change our perceptions of reality. We'll also examine a phenomenon called the *placebo effect*, in which our own belief about how a specific chemical might affect us can actually influence the way our bodies respond to that chemical. As a result of the placebo effect, chemicals as innocuous as table sugar sometimes produce or relieve symptoms dramatically, but only because we are led to think that they will. We'll also examine a technique called the *double blind* experiment that allows us to learn whether the action of any particular medication results from a direct chemical influence on the way our bodies operate, regardless of our expectations, or from the action of the placebo effect, through nothing more than our faith in the substance's effectiveness. We'll start our examination of the connection between chemicals and perceptions with agents of mercy, the *analgesics* or painkillers.

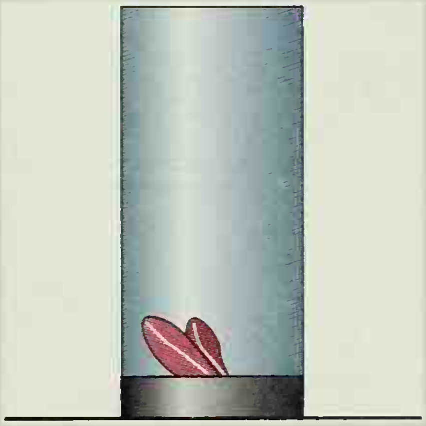


Figure 22.2
Is the hat taller than the brim is wide, or is it the other way around?

22.1 Aspirin

Today's leading commercial pain reliever is common *aspirin*. Since its initial synthesis in 1853 and its acceptance into medical practice at the turn of the century, aspirin has become the most widely used of all drugs for the treatment of illness or injury. More aspirin has been taken over the years by more people throughout the world than any other single medication of any kind.

In this examination of the extraordinary chemistry of our ordinary chemicals, aspirin must be recognized as one of the most extraordinary of all, with the power to act as an **analgesic** (to relieve pain), as an **antipyretic** (to lower fever), and as an **anti-inflammatory agent** (to reduce inflammation). It's the drug of choice for the treatment of rheumatoid arthritis. It's also effective in preventing specific kinds of strokes and heart attacks, those resulting from the accumulation of platelets in the blood vessels. Yet it's also one of the most common of all medications, inexpensive, and available to virtually everyone, almost everywhere.

Aspirin itself, **acetylsalicylic acid**, is prepared easily through the reaction of *acetic anhydride* with *salicylic acid* (Fig. 22.3). (Acetic anhydride results from the dehydration of acetic acid through the removal of one water molecule from two molecules of the acid. The product is a good *acetylating agent*, which means that it's useful for adding the *acetyl* group, to another molecule, as it does in the synthesis of aspirin.)

An analgesic is a substance that reduces or eliminates pain. An **antipyretic** is a substance that lowers or eliminates fever. An **anti-inflammatory agent** is a substance that reduces or eliminates inflammation.

Aspirin is the common name or trade name of **acetylsalicylic acid**, an analgesic, antipyretic and anti-inflammatory medication.

$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{OH\ \ H}-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

Dehydration of acetic acid .. . . . produces . . . . . . acetic anhydride

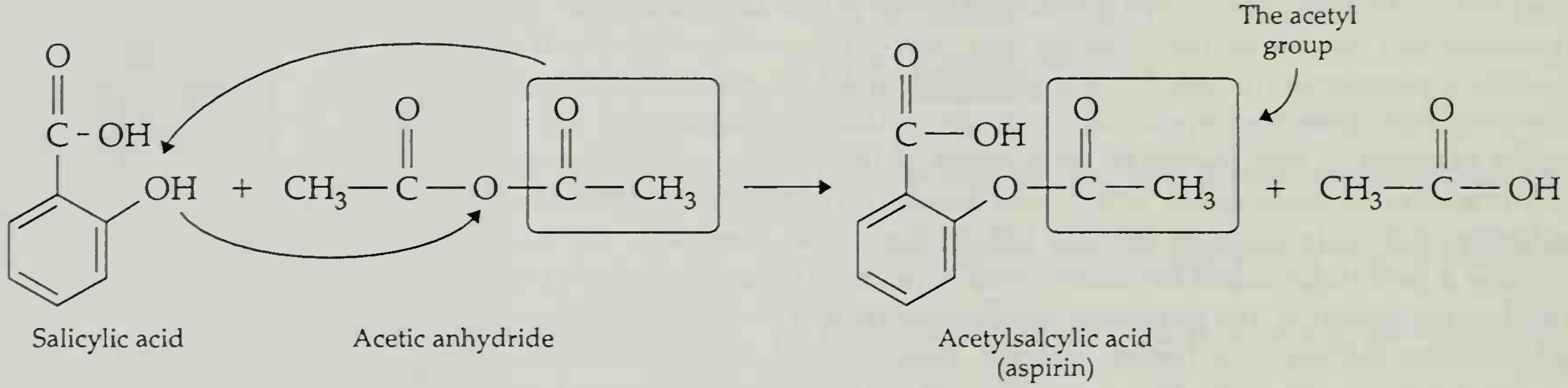
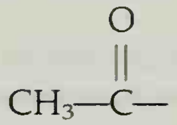


Figure 22.3
Aspirin from the acetylation of salicylic acid.



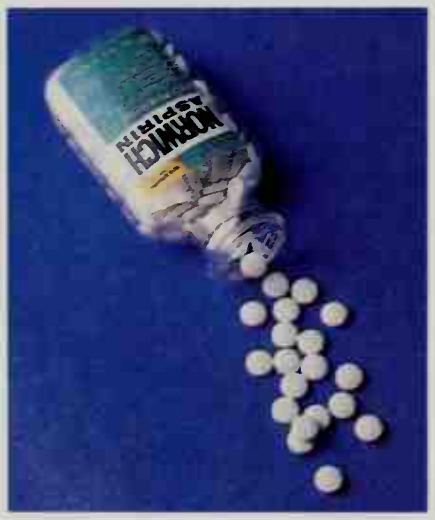
$$CH_3-\overset{\overset{O}{\|}}{C}-$$

the acetyl group

QUESTION

What three symptoms of illness or injury does aspirin relieve? ________________

22.2 How Aspirin Got Its Name



Aspirin is the most widely used of all drugs for the relief of symptoms of illness and injury.

Although neither salicylic acid (the molecule being acetylated) nor acetylsalicylic acid (the product itself) occurs in nature, several closely related compounds do. Physicians as far back as Hippocrates, the ancient Greek healer known as the Father of Medicine, knew of the curative powers of the bark of the willow tree and closely related plants, and especially their antipyretic or fever-reducing properties.

In 1827 willow bark yielded its active agent, *salicin*, to chemists of the era. A few years later this salicin was hydrolyzed to glucose and *salicyl alcohol*, which was in turn oxidized to salicylic acid (Fig 22.4). The Latin term for willows, *salix*, gives us the name of an entire family of compounds, the *salicylates*, whose molecules resemble those of both the alcohol and the acid. It's also the term for the botanical genus of the tree itself, *Salix*.

At about the same time, salicylic acid was also obtained from the reaction of salicylaldehyde with strong base (Fig. 22.5). This fragrant aldehyde (Section 14.4) was itself isolated from meadowsweet flowers, which belong to the genus *Spiraea*. Many years later, with the commercial production of acetylated salicylic acid, the term *aspirin* was coined by adding an *a* (for "acetylated")

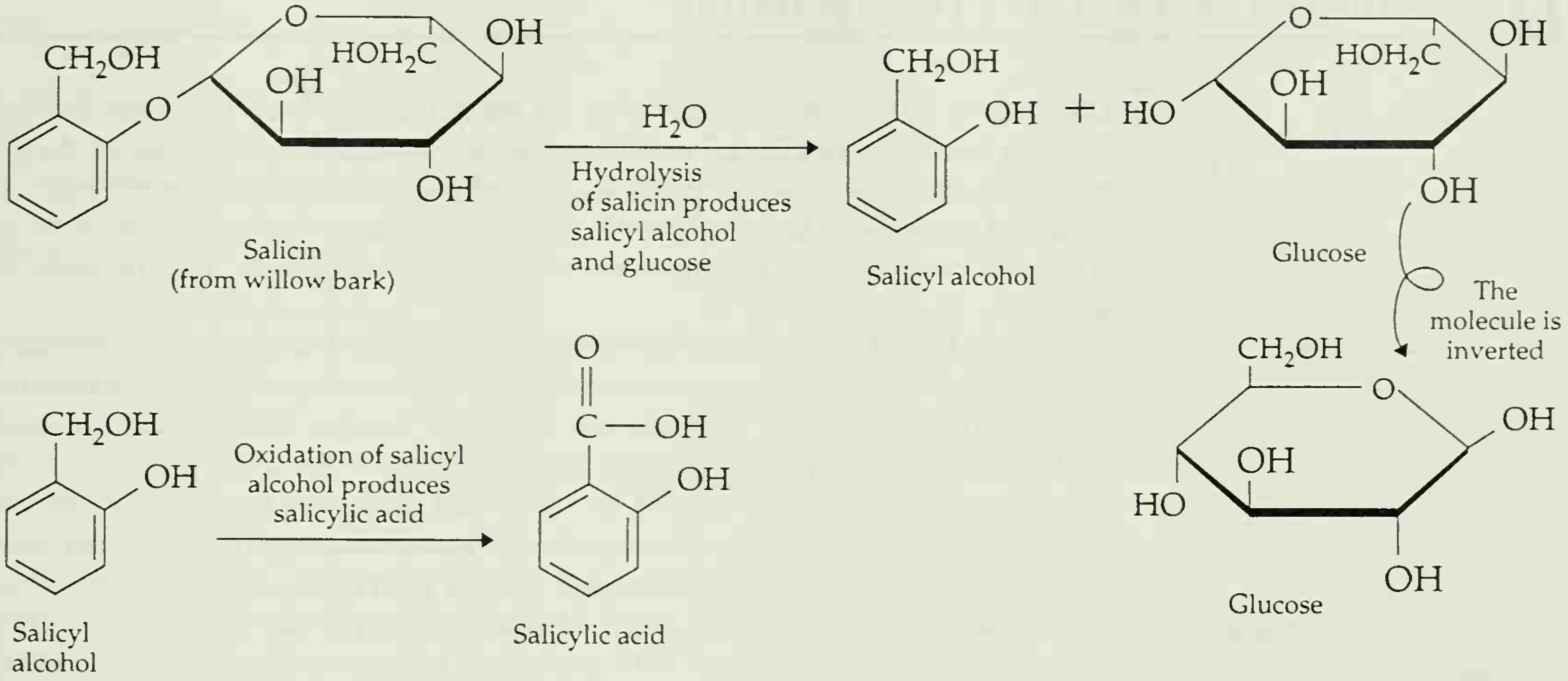
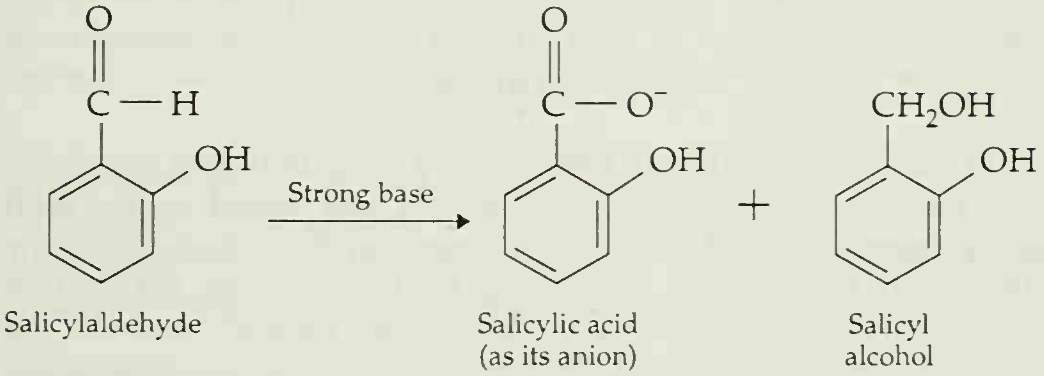


Figure 22.4
Salicylic acid from the bark of the willow tree.



The (unbalanced) reaction of salicylaldehyde with strong base to produce salicylic acid (and salicyl alcohol).

Figure 22.5
Salicylic acid from salicylaldehyde.

to a portion of an older name of the acid, "*spir*aeic acid," which was derived from the botanical genus of the meadowsweet.

Another one of the salicylates, *methyl salicylate,* is the fragrant methyl ester of salicylic acid, known more commonly as *oil of wintergreen* (Fig. 22.6). In addition to its use in perfumery and (in very small amounts because of its toxicity) as a flavoring for candy, chewing gum, and medicines, methyl salicylate is also the active ingredient of liniments for relieving the pain of aching muscles and joints. As it's rubbed into the skin, the ester's irritant action acts as a counter-irritant to deeper aches and eases the discomfort they produce. The irritant action of the methyl salicylate also stimulates blood flow into the deeper regions, adding to its analgesic effect.

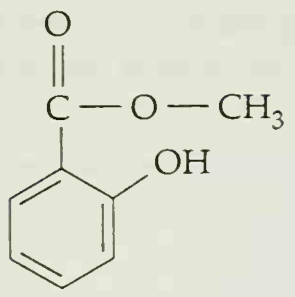


Figure 22.6
Methyl salicylate, oil of wintergreen. This ester of salicylic acid is used in making perfumes, in flavoring candy, chewing gum, and medicines, and in liniments used for the relief of muscular pain.

QUESTION

Draw the portion of their molecular structures that is common to all the salicylates.

22.3 Salicylates Vs. the Prostaglandins

Like many of the other salicylates, at least those whose toxicities are low enough that they can be taken internally in amounts large enough to do any good, salicylic acid relieves pain, fever, and inflammation. But while both the acid and its sodium salt are effective against all three, the acid itself is far too corrosive to tissues to be taken internally by most people, and its salts are generally unpalatable.

In 1893 Felix Hofmann, a chemist working for the Baeyer firm in Germany, found a way around these problems. To provide relief for his father's rheumatoid arthritis, Hofmann turned from salicin, a weaker but popular analgesic of the time, and from salicylic acid, whose corrosive character produces stomach discomfort, to the acetylated acid that had been prepared 40 years earlier. He started aspirin on its road to success by demonstrating that in its acetylated form the salicylate is easily tolerated and by providing convincing evidence of its potent analgesic effect. Baeyer began selling powdered aspirin in envelopes and capsules in 1899; in 1915 the tablets were introduced. Today's tablets ordinarily contain between 309 and 341 mg of acetylsalicylic acid, held in shape by a binder. ("Extra strength" aspirin contains about 500 mg of acetylsalicylic acid per tablet. The "extra strength" comes simply from the larger amount of the active ingredient in each tablet. The additional strength can be obtained equally well and usually at lower cost by taking two of the ordinary tablets.)

"**Buffered" aspirin** is a combination of acetylsalicylic acid and one or more bases. The combination accelerates the disintegration of the tablet.

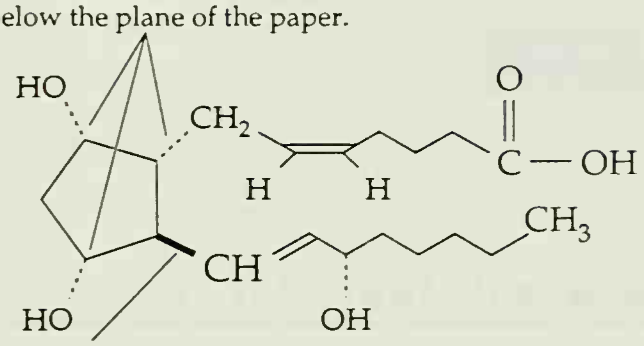
As we might expect, aspirin doesn't begin to do its work until it enters the bloodstream. The time it takes for the acetylsalicylic acid bound up in a solid aspirin tablet to enter the blood is governed largely by the rate at which the tablet disintegrates in the stomach. This rate, in turn, depends on pH (Section 10.10). The higher the pH, the faster the tablet breaks up and the faster the acetylsalicylic acid gets into the blood. To accelerate the disintegration of the tablet and the solution of the aspirin itself, some companies produce a "buffered" aspirin. Despite the term, these tablets aren't truly buffered. A buffer, as you'll recall from Section 10.17, is a combination of an acid or a base and one of its salts. By reacting with both acids and bases, this combination is able to keep pH within a narrow range. Rather than a combination of acetylsalicylic acid and one of its salts, which would constitute a true buffer, the "buffered" aspirins consist of a combination of aspirin and one or more bases. The widely available Bufferin, for example, contains magnesium carbonate, $MgCO_3$, and aluminum glycinate, the aluminum salt of the amino acid glycine (Section 15.2), along with aspirin. Magnesium hydroxide, $Mg(OH)_2$, and aluminum hydroxide, $Al(OH)_3$, are also widely used in "buffered" aspirin. Although the addition of these bases to the tablet does increase rates of disintegration and absorption, rigorous clinical studies have failed to produce any evidence of faster or greater pain relief from "buffered" aspirin than from the "nonbuffered" variety. In clinical tests, a simple aspirin tablet of the ordinary variety works as well as the buffered types.

The beneficial effects of aspirin and other salicylates come from their ability to prevent the formation of *prostaglandins* within the body (Fig. 22.7). These compounds, named for the seminal fluid and prostate tissue in which they were discovered, occur in virtually every tissue and fluid of the body and they participate, in one way or another, in almost every bodily function. They

Prostaglandin E_1

Prostaglandin E_2
(the most abundant and most active
of the prostaglandins)

Dotted bonds indicate the substituent lies below the plane of the paper.



Heavy bond indicates the substituent lies above the plane of the paper.

Prostaglandin $F_{2\alpha}$

Figure 22.7

Typical prostaglandins. Important in many bodily functions, they play a major role in the sensation of pain. Aspirin relieves pain, fever, and inflammation by inhibiting the synthesis of prostaglandins.

play particularly important roles in the sensation of pain and its transmission along the nervous system, in the generation of fevers, and in the swelling of inflammations. By interfering with the formation of the prostaglandins, salicylates relieve each of these conditions.

QUESTION

What is the source of the extra strength in "extra strength" aspirin tablets?

22.4 Aspirin: Risks along with Rewards

While less destructive to body tissues than salicylic acid itself, aspirin can nonetheless produce some nasty side effects, including upset stomach, gastrointestinal bleeding, and various allergic reactions. It's estimated that 2% to 10% of all those who take aspirin suffer occasionally from some form of stomach distress or nausea.

More serious is *Reye's syndrome*, a rare and sometimes fatal reaction to aspirin experienced by children and adolescents recovering from chicken pox or the flu. For an unknown reason aspirin seems to trigger this syndrome, which is accompanied by confusion, irritability, nausea, lethargy, and other symptoms. Aspirin labels in the United States now carry warnings that a physician should be consulted before giving the drug to children or adolescents with either of these diseases.

In addition to producing these relatively rare reactions, aspirin is more toxic than we may realize. With an LD_{50} of 1.5 g/kg (orally in mice and rats; Table 18.1), there's a 50% chance that 15 g—about 45 tablets—would be enough to kill a 10 kg child. These, of course, are no more than impersonal statistics. Yet they take on a more human dimension when we recognize that no one is perfectly average and that some of us are more susceptible than others to the lethal effects of aspirin or any other potentially toxic substance. Before enactment of the Poison Prevention Packaging Act of 1970, for example, more than 40 children under the age of five in the United States were dying each year from accidental aspirin poisoning. With the introduction of childproof caps on aspirin containers, the rate dropped sharply to about 25 per year (Section 18.2).

QUESTION

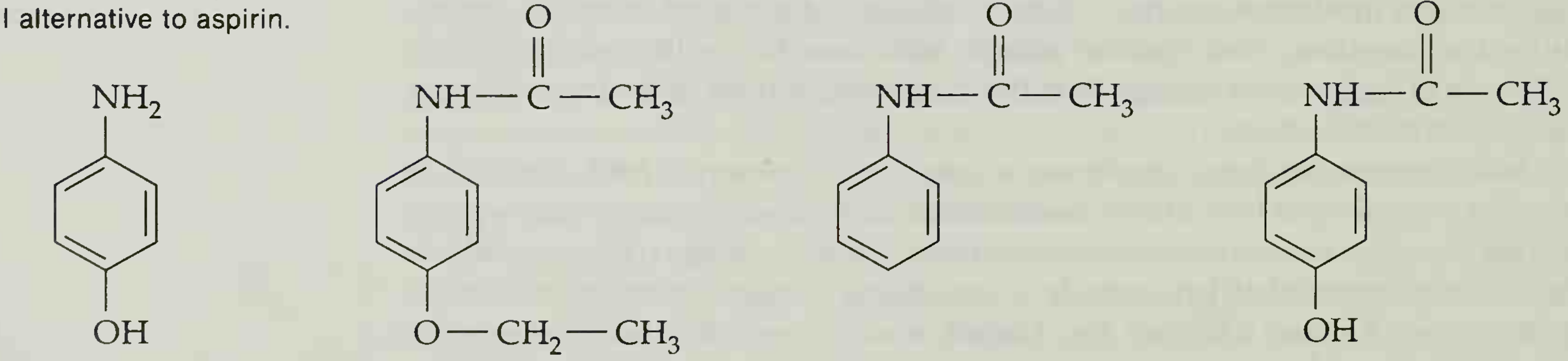
What benefits does aspirin provide? What are the risks in using it?

22.5 Acetaminophen, a Substitute for Aspirin

For those of us who may be allergic to aspirin or who find that it produces stomach disorders, there's an alternative in *acetaminophen*, the active ingredient of Tylenol and Datril. Acetaminophen is the least toxic member of a class of analgesic and antipyretic (but *not* anti-inflammatory) medicines known as the *p-aminophenols* (Fig 22.8). Compounds of this sort trace back to *acetanilide*, which isn't actually a *p*-aminophenol since its ring doesn't bear nitrogen and oxygen atoms on its No. 1 and No. 4 carbons (Section 21.7). Acetanilide was used to alleviate fever as early as 1886, but it proved too toxic for general use. Yet it offered promise. Investigations of similar compounds led to trials of *p*-aminophenol (which also proved too toxic) and of compounds related to it.

In the following year, 1887, *phenacetin* (also called *acetophenetidin*) and, in 1893, acetaminophen (Tylenol, Datril) were introduced. In 1983, almost a century after phenacetin was first used as an analgesic, the U.S. Food and Drug Administration banned it from both prescription and nonprescription medications because of its tendency to damage the kidneys and to produce disorders of the blood when used excessively.

Figure 22.8
p-Aminophenol and related compounds. Acetaminophen is a useful alternative to aspirin.



p-aminophenol

Phenacetin (acetophenetidin)

Acetanilide

Acetaminophen

A year later, in 1984, the FDA approved the sale of *ibuprofen* as an over-the-counter drug for the relief of pain, inflammation, and fever. Before the FDA's action, ibuprofen had been available in the United States only as a prescription drug. It's currently available without a prescription in medications such as Advil and Motrin. Ibuprofen appears to act much like aspirin in interfering with formation of the body's prostaglandins. What's more, ibuprofen *does* control inflammation (unlike acetaminophen) and is *not* a *p*-aminophenol (again, unlike acetaminophen; Fig. 22.9). While the occasional use of any of these painkillers by a healthy person who has no allergic reaction to them doesn't seem to result in harmful effects, there is evidence that *daily* use of acetaminophen over a long period can produce a risk of kidney damage.

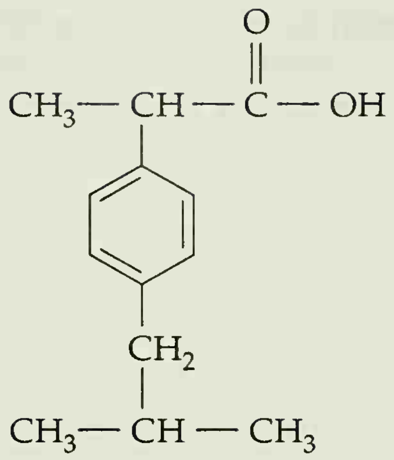


Figure 22.9
Ibuprofen, an alternative to aspirin for the relief of pain, fever, and inflammation.

As we move to other chemicals that can change our perceptions of pain and of the world about us we'll begin with a short look at a few of the analgesics with the longest histories of use, thousands of years in some cases. Since several of these seem to stand at a borderline between what we would now call a medicine and what we might consider to be a drug, we'll first examine some differences between the two categories.

QUESTION

What symptoms are alleviated by (a) aspirin, ibuprofen, *and* acetaminophen? (b) aspirin and ibuprofen, but *not* acetaminophen? __________________

22.6 Chemicals, Medicines and Drugs

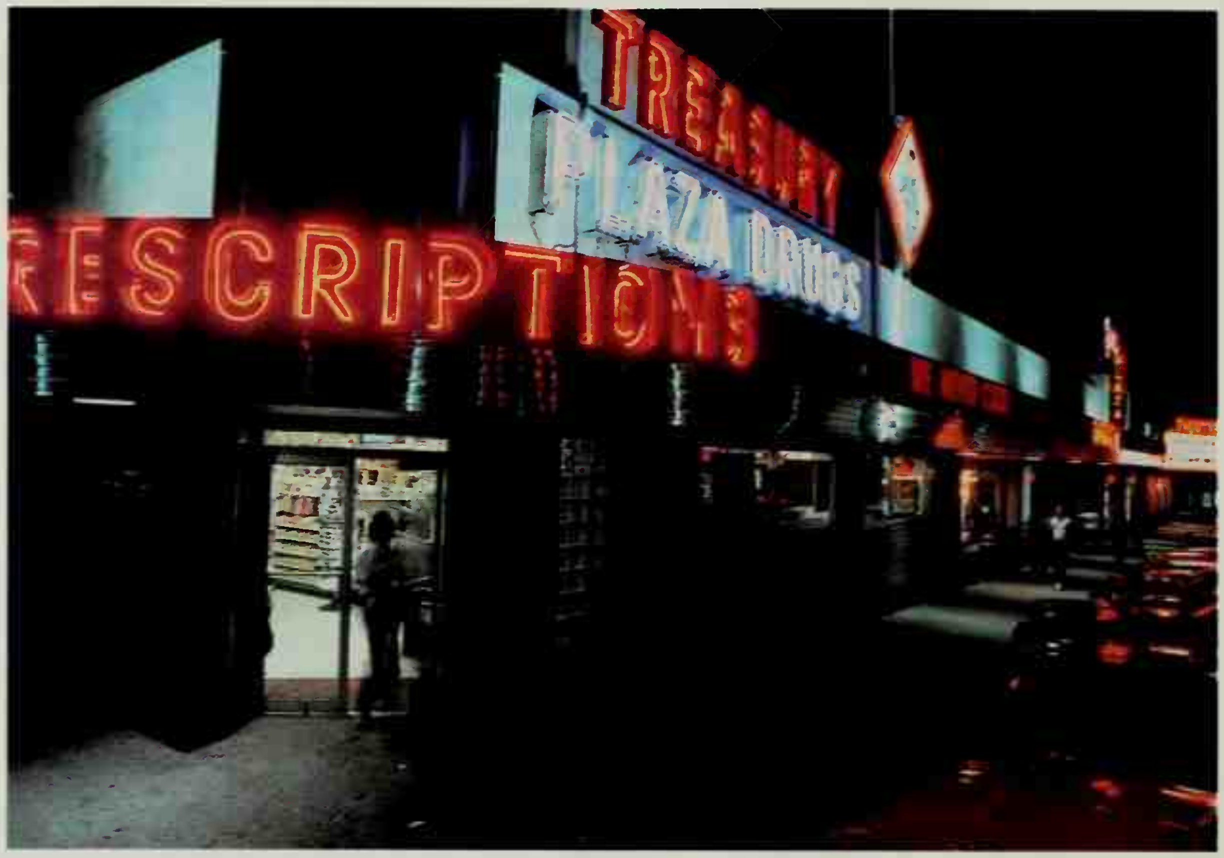
As we've seen in earlier chapters, the cry "There are *chemicals* in our foods!" acts to generate suspicion, if not actual fear, in the hearts of some consumers. Something similar may be happening to the language of medicinal chemicals. To say, for example, that someone is "on drugs" could one day cast a shadow on what we might legitimately buy in a "drugstore."

Drugs and **medicines** are chemicals used medically for treating diseases and injuries. **Drugs** carry the added connotation of narcotics and addiction.

In one sense **drugs** and **medicines** are virtually indistinguishable from each other as chemicals used medically for treating diseases and injuries. Yet the term *drugs*, unlike *medicines*, carries with it the connotation of narcotics, addiction, and crime. All this works to elevate the term *medicines*, despite the valid use of narcotics in the practice of medicine and the possibility of addiction to some of our more readily available, entirely legitimate medications.

We've seen sporadically, in our examination of the chemistry of ordinary things, the subtle connections between the way we use a chemical and the history of its name or of terms connected with it. Something of this sort also works to separate *drugs* from *medicines*. The word *medicine* came into the English language through French, from the Latin *medicina* meaning, according to its context, either a medication, the practice of the physician, or the place where the physician works.

The less reputable *drugs* bears an uncertain ancestry. It entered into several European languages, in one form or another, by obscure routes and with various implications. As with the substances themselves, the word *medicine* seems to have a clearer ancestry, a purer pedigree than does *drug*. It's a bit more respectable.



Drugs for sale, legitimately.

22.7 Narcotics and Alkaloids: The Opium Alkaloids

A **narcotic** is a substance that produces a stupefying, dulling effect and that induces sleep.

Opium is the dried sap of the poppy. It contains several narcotic compounds.

At any rate, the essence of a **narcotic** is clear. From the Greek *narkotikos*, meaning "numbing" or "stupefying", a narcotic is a chemical that dulls the mind, induces sleep, and generally numbs the senses. As the origin of the word in the classic Greek language suggests, the use of narcotics is an ancient activity. The Sumerians, one of the earliest of civilizations, were probably familiar with the narcotic effects of **opium**, the dried sap of the poppy, some 6000 years ago. (The Sumerian term for the flower can be translated as "joy plant.") The first clear reference to the sap of the poppy appeared in Greek writings of about 300 B.C. Later, Arabian healers used its medical powers, as did those of the Orient. Thomas Sydenham, the 17th-century English physician known as "the English Hippocrates," wrote of the substance's powers to ease pain:

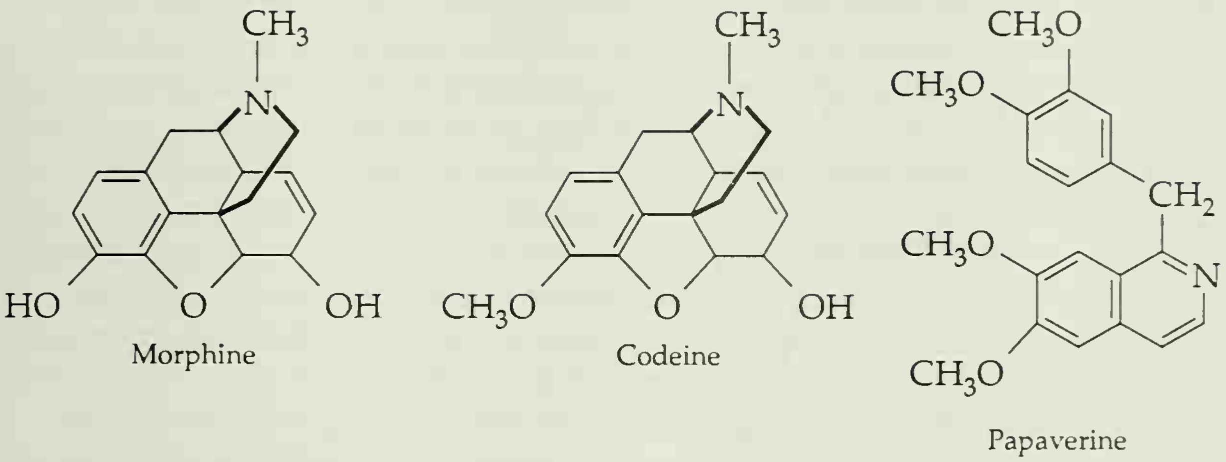
> Among the remedies which it has pleased Almighty God to give to man to relieve his sufferings, none is so universal and so efficacious as opium.

Alkaloids are basic, bitter-tasting, nitrogen-containing compounds that are found in plants and that produce physiological reactions of various kinds and intensity.

Morphine is the major alkaloid of opium.

Opium's power arises from several of its narcotic compounds, all members of a major category of plant substances known as **alkaloids** for their *alkalinity*, their basic behavior toward acids. At the molecular level the alkaloids all owe their basicity to one or more amine nitrogens in their molecular structures; most taste bitter and produce physiological reactions of various kinds and intensity.

In the dried opium itself, alkaloids of all sorts make up about a quarter of the total weight. **Morphine**, the first alkaloid of any kind ever to be isolated, leads the list at about 10%. In 1803 Friedrich Sertürner, a German pharmacist,



Morphine

Codeine

Papaverine

Figure 22.10

Alkaloids of opium. These occur in the sap of the poppy.

obtained it in pure form, described it, and named it for Morpheus, a Roman god of dreams. Morphine is a powerful narcotic, long a valuable tool in the physician's bag. It's a potent analgesic as well as a cough suppressant. Morphine produces a variety of psychological responses, including apathy and euphoria. It's also highly addictive.

Another one of the opium alkaloids is *codeine*, isolated in 1832 by a French pharmacist, Pierre-Jean Robiquet. Codeine is a less potent analgesic than morphine, and yet it's one of the most powerful cough suppressants known. *Papaverine*, discovered in 1848, is also present. It's useful for relaxing the smooth muscles (such as those of the blood vessels, the stomach, the intestines, the bladder, and the uterus) and for dilating or enlarging blood vessels, especially within the brain.

While they differ in their specific actions on the body and in their potency, these and the other opium alkaloids share two important characteristics. They are all addicting and they are all among the most powerful constipating agents known, with substantial value in controlling diarrhea. Figure 22.10 presents their molecular structures.

QUESTION

In what way does the molecular structure of codeine differ from the molecular structure of morphine? ______________________________

22.8 A Good Idea Gone Very, Very Bad

The medical value of morphine in vanquishing pain is counterbalanced by its very great capacity to produce addiction. Just as the search for better, less toxic analgesia through molecular modifications of acetanilide led to the *p*-aminophenols (Section 22.5), a search for nonaddictive molecular modifications of morphine soon produced a promising synthetic substance. In 1898 the diacetylation of morphine in the chemical laboratories of a German dye manufacturer led to *diacetylmorphine* through a chemical transformation very much like the acetylation of salicylic acid to aspirin (Section 22.1). Immediately on its introduction into medicine at the turn of the century, this diacetylated molecule proved to be a much more powerful narcotic and cough suppressant than morphine itself. It was so powerful, in fact, and the size of its effective doses were so low that it gave promise, at first, of being nonaddictive.

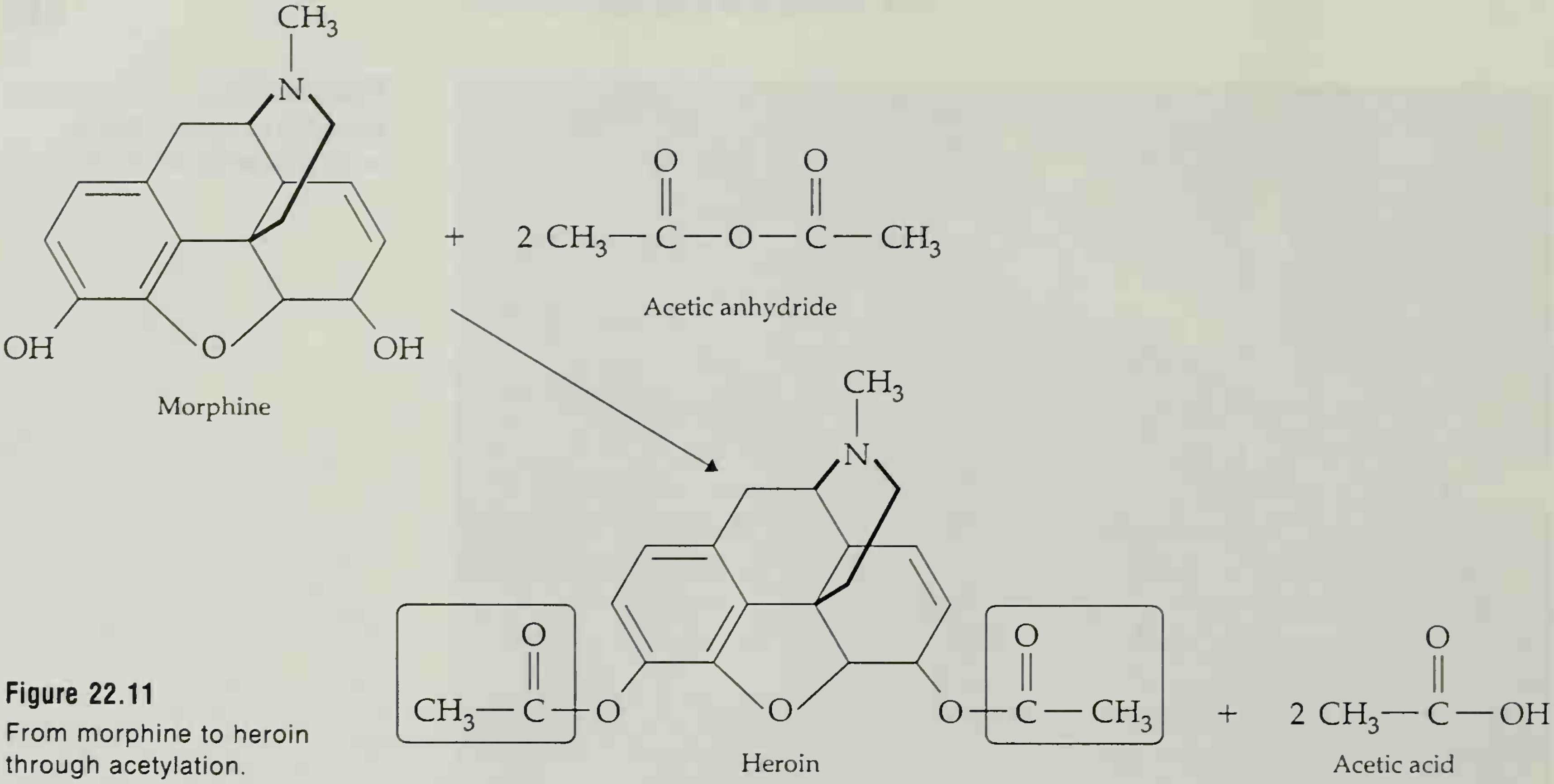


Figure 22.11
From morphine to heroin through acetylation.

Heroin is diacetylmorphine, morphine in which two —OH functional groups have been converted to ester functional groups.

The promise fell through, badly. Diacetylmorphine proved to be one of the most addictive drugs known, so powerfully addictive that its use, possession, manufacture, and importation into the United States and several other countries have been banned by law. It's known more commonly by an early trade name dating from the time of its medical trials, **heroin** (Fig. 22.11).

(A bit of practical chemistry comes into play in enforcing the ban on its manufacture. Farmhouses in rural France were occasionally used as secret factories to manufacture heroin for international distribution. One of the byproducts of the acetylation with acetic anhydride, shown in Figure 22.11, is acetic acid, the major organic component of vinegar. To locate the heroin factories French police trained dogs to sniff out the vinegar-like odor and to lead them straight to its source.)

QUESTION

Why is diacetylmorphine a particularly dangerous chemical? ____________

22.9 Sigmund Freud, Medieval Poisoners, and Beautiful Women: Cocaine and Related Alkaloids

Still another plant, the South American coca bush, produces the alkaloid *cocaine*, used medically as a topical or local anesthetic. Cocaine resembles morphine in its medical value, in this case as a local anesthetic, and also in its ability to produce a fast and powerful addiction. Beyond its therapeutic uses, cocaine produces euphoria, a great sense of well-being, and delusions of immense power—all followed by a depression that leads the user to crave another jolt of euphoria, which is followed by the same cycle of euphoria, depression, and a craving for more. Morphine and heroin produce a truly physical addiction in that physiological symptoms—watery eyes and nose, yawning, sweating, goose flesh, and dilated pupils, for example—occur during withdrawal. Cocaine's addiction seems to be purely psychological, without physical symptoms on withdrawal, but its psychological addiction is nonetheless as real and as powerful as any physical addiction.

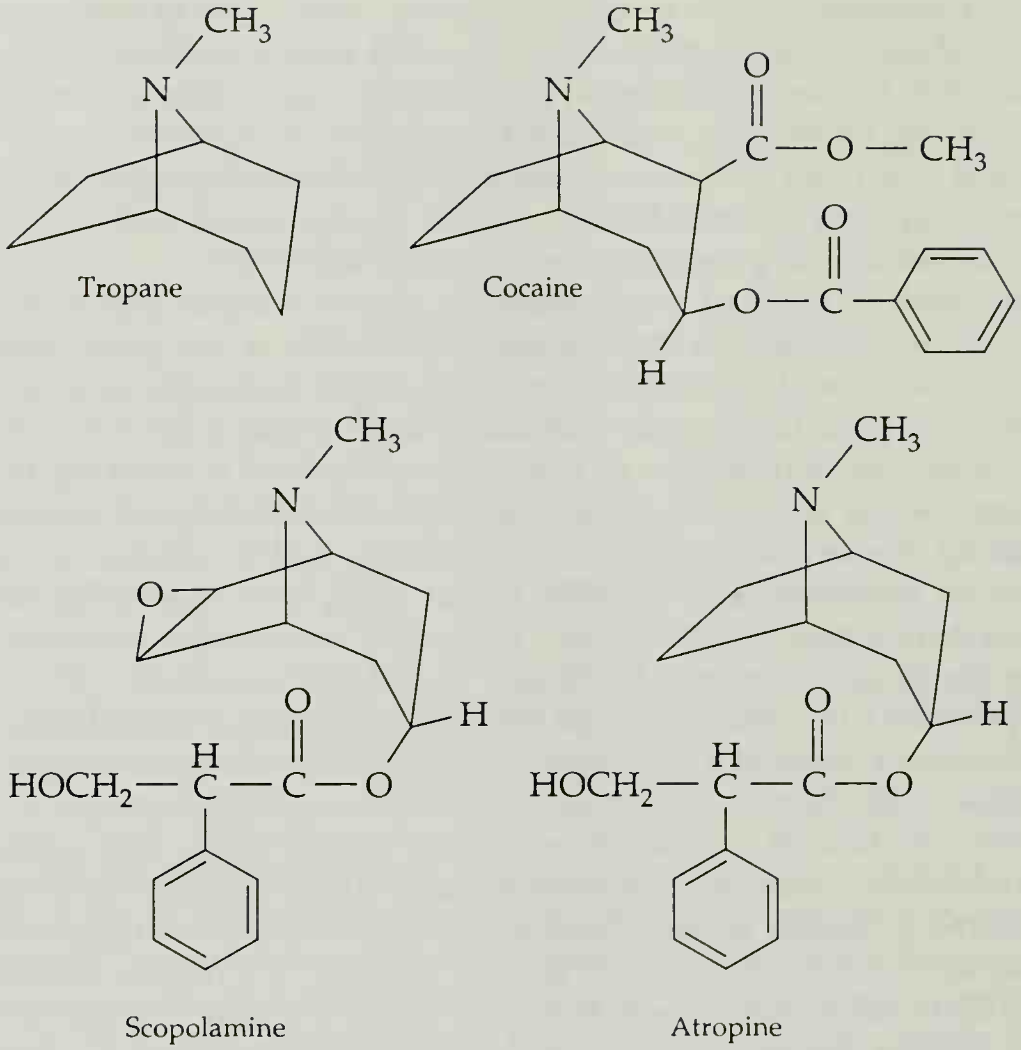
Sigmund Freud, founder of psychoanalysis, played a major role in the discovery of cocaine's addictive and anesthetic potential. A few years after the compound's isolation from coca leaves, Freud began studying it as an aid to his treatment of patients. He soon persuaded a fellow physician who was addicted to morphine, Karl Koller, to use cocaine as an aid in breaking his morphine habit. Koller succeeded, at the cost of becoming addicted to cocaine instead. During his experimentation with cocaine, Koller recognized its properties as an anesthetic and, in 1884, began using it to anesthetize his patients' eyes during medical procedures. Within the year another physician began using the drug in dentistry as the first local dental anesthetic.

Cocaine provides a fine example of the connection between chemical properties and the use or abuse of a substance. Chemically, cocaine is a nitrogen-containing base, with *chemical* properties similar to those of other amines we have examined (Section 15.2). Like other amines, cocaine reacts with acids, including hydrochloric acid, to form salts. Cocaine hydrochloride, the form in which cocaine is usually isolated from coca leaves, is a salt with physical properties similar to those of common sodium chloride. It's readily soluble in water and fairly stable toward heat. It doesn't vaporize readily. On reaction with a base, cocaine hydrochloride is converted to the pure cocaine, often called the "free base," which has far different physical properties. During this chemical conversion of cocaine hydrochloride (the salt) to cocaine (the base), the generated base forms as a white solid sheet that cracks into large lumps or "rocks." This formation of "rocks" as the solid cracks into individual lumps gives the product the name *crack cocaine* or simply *crack*. Unlike the crystalline salt, the free base readily vaporizes. Inhaling cocaine vapors quickly produces a sharper, more intense sensation than the one produced by the hydrochloride salt. The fall into depression that follows is also steeper.

Chemically, cocaine belongs to the *tropane* alkaloids, all of which are molecular variations of the parent, tropane (Fig. 22.12). Other members of the family include *atropine* and *scopolamine*, both of which affect the nervous system in one way or another and occur in plants of the nightshade family, a group that encompasses many poisonous species as well as potatoes, tomatoes, red peppers, and eggplants. One of the more toxic of the nightshade plants, *belladonna*, was a favorite poison in the intrigues of the Middle Ages. Atropine, the major alkaloid of the plant, is the active ingredient in tincture of belladonna, a liquid once popular for its ability to increase the size of the pupils and (presumably) make the eyes more attractive. The name of the plant itself, *belladonna*, comes from the combination of the Italian words *bella donna*, "beautiful lady."

Scopolamine, which also dilates pupils, is a powerful sedative. In combination with morphine it was once used to induce "twilight sleep" to ease childbirth. (The combination has been replaced by safer drugs.) Currently, it is an ingredient in some over-the-counter sedatives and motion-sickness preparations.

Figure 22.12
Cocaine and the tropane alkaloids.



QUESTION

Chemically, cocaine contains two different functional groups, one of which is an amine. What is the other functional group? (Notice that this other functional group occurs twice in the molecule.) ______________________

22.10 Caffeine and Nicotine

Caffeine is an alkaloid that occurs in coffee beans and in tea leaves. It stimulates the central nervous system and heightens a sense of awareness.

Probably the most widely used of all the alkaloids are the *caffeine* of the coffee bean and tea leaves and the *nicotine* of the tobacco plant (Fig 22.14). **Caffeine** stimulates the central nervous system and the heart, and heightens a sense of awareness. It's added to cola drinks at a concentration of about 35 to 55 mg per 12-oz bottle and it occurs naturally in tea and coffee. The amount of caffeine in a cup of coffee depends on the strength of the brew, but the alkaloid is generally present at a concentration of about 100 to 150 mg per cup. (Decaffeinated coffee, of course, contains virtually none.) The lethal dose for an adult is estimated at about 10 g, taken orally. That amounts to 70 to 100 cups of brewed coffee at one sitting, a quantity that would generate plenty of discomfort long before the fatal dose is approached.

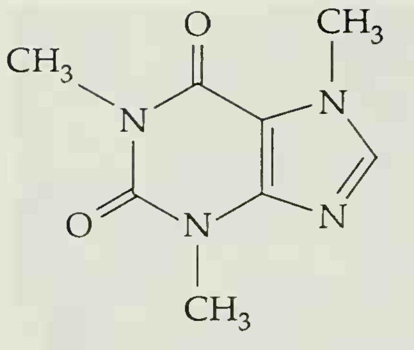
Nicotine is a highly poisonous alkaloid that occurs in tobacco leaves

Nicotine, on the other hand, is a lethal substance that's used as a powerful agricultural insecticide. Absorbing less than 50 mg of nicotine can kill an adult in a few minutes. If it weren't for the oxidation of most of this alkaloid to less toxic products by the high temperatures and the rapidly moving air stream that accompany smoking, no cigarette smoker could possibly last long enough to develop smoking into a habit.

The toxicity of nicotine provides a fine example of the connection between the effects of a poison and the means by which it enters the body. As shown in Table 18.1, when nicotine is administered *orally* to mice it's actually slightly less lethal than caffeine. The LD_{50} for nicotine, orally, is 0.23 g/kg; for caffeine it's 0.13 g/kg. But with direct absorption into the bloodstream, through the skin for example, nicotine becomes almost 1000 times as potent as it is with oral ingestion. In cigarette smoking, nicotine is especially hazardous since it's absorbed directly into the bloodstream through the lungs.

Several generations ago, cigarette smoking was generally accepted as "smart" and sophisticated. With growing recognition of the health hazards posed by nicotine and other components of cigarette smoke, not only to smokers themselves but also to nonsmokers who inhale "second-hand" smoke generated by others, smoking in public places is being restricted severely. Seating in many restaurants, for example, is separated into smoking and nonsmoking sections, and smoking is prohibited on all domestic airline flights within the United States.

The lethal effects of smoking aren't due exclusively to nicotine. Cigarette smoke is rich in toxic carbon monoxide (see Perspective in Chapter 8 and Section 9.2), which decreases the blood's ability to carry oxygen. The smoke also contains tarry substances capable of generating cancer. It's estimated that about 170,000 people die each year in the United States from smoking related heart and circulatory diseases. Another 130,000 deaths linked to cigarette smoking result from cancers of the lungs and other major organs. Roughly a third of all deaths from cancer are believed to be smoking related. Smoking during pregnancy is particularly dangerous to the fetus and can lead to spontaneous abortions, low birth weights, birth defects, and infant deaths.


Caffeine

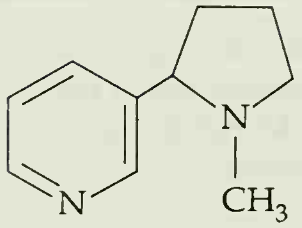

Nicotine

Figure 22.13
Caffeine and nicotine. Caffeine is the major alkaloid of coffee beans. Nicotine is a highly poisonous alkaloid of tobacco.

Tea, coffee, and cola: sources of caffeine.

QUESTION

To what class of basic, bitter-tasting, nitrogen-containing plant substances do both caffeine and nicotine belong? ______

22.11 Natural Vs. Synthetic

Our discussion of nicotine, caffeine, aspirin, acetaminophen, morphine, cocaine, and heroin provides us with another opportunity to examine the (far too common) belief that the products of nature must necessarily be good, or at least far less harmful than what we humans manufacture with our intellects and our skills in laboratories and factories. As in Chapter 18, we find once again that the chemicals of this world, both those we isolate from plants and animals and those of the chemical laboratory, just don't fall neatly into the categories of our simpler notions.

Belladonna comes from *Atropa belladonna*, a plant better known as "deadly nightshade".

The naturally occurring, narcotic alkaloids we've described, for example, are all very useful for the analgesia and other therapeutic effects they provide, but they're also destructive for the addictions they produce. Our laboratories, on the other hand, have produced the wonders of aspirin and acetaminophen, as well as the devastation of heroin. As with the chemicals in our foods, we find again that both benefits and risks come from the fruits of nature as well as from those of the laboratory. To hold that what nature produces is necessarily more benign or less harmful than what humans manufacture is to ignore the difference between acetylsalicylic acid, which does not occur in nature, and cocaine, which does.

QUESTION

Name a compound produced by humans that is useful or beneficial and another that is harmful. Repeat for compounds isolated from plants. Explain your choices.

22.12 Licit Vs. Illicit

There's another difference between aspirin and cocaine. You can buy a bottle of aspirin easily and freely in any drugstore, convenience store, or supermarket. Cocaine, on the other hand, is one of several federally controlled (regulated) substances whose unauthorized manufacture, possession, importation, and use are rigorously prohibited or regulated by law. Aspirin is a licit drug; cocaine is illicit.

Whether a drug is legal and sanctioned by a society or illegal and condemned depends very much on the outlook of that particular society, at that particular time in its history. As with *safety*, any society's tolerance for any particular drug depends (at least partly) on its assessment of the consequences of its use. Today in most Western nations many of the narcotic alkaloids and related synthetic compounds are controlled substances. In the United States this is largely a phenomenon of the 20th century.

Before 1914, habitual opium smoking was both widespread and generally tolerated in the United States. In the first decade of this century, for example, about 150,000 pounds (68,000 kg) of opium were imported *legally* into the United States to support the addiction. The rigorous federal control of addictive substances started with the passage of the Harrison Narcotics Act of 1914. Since that Act and subsequent laws were adopted, the use of narcotics to satisfy an addiction became punishable by law. While we now prohibit by law the nonmedical use of virtually all physiologically active, addictive alkaloids, we still generally tolerate or readily accept a few, especially the caffeine of coffee and the nicotine of tobacco (Fig. 22.14). There's evidence that both these alkaloids can produce addictions.

Our society has had mixed feelings about the nonalkaloid narcotic, *alcohol*, or, more accurately, *ethyl alcohol*, $CH_3—CH_2OH$, which depresses the entire central nervous system and which can produce a powerful psychological addiction. The manufacture, sale, and transportation of alcoholic drinks were

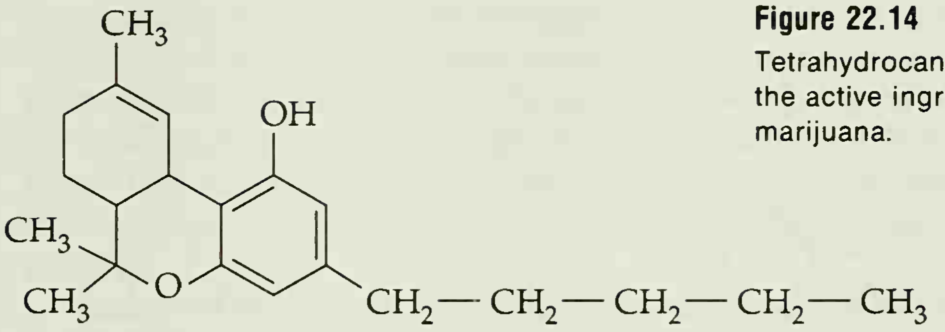


Figure 22.14
Tetrahydrocannabinol, or THC, the active ingredient of marijuana.

prohibited with the force of the 18th Amendment to the U. S. Constitution, which became effective January 16, 1920. Almost exactly 14 years later we changed our societal mind and repealed the prohibition with the 21st Amendment. Thus alcoholic drinks, which had been declared unacceptable to U.S. society with the 18th Amendment, became acceptable once again with the 21st.

Marijuana, whose major, active component is *tetrahydrocannabinol*, or THC (Fig 22.14), has also been the subject of mixed signals. While marijuana seems to have medical value in controlling *glaucoma*, a disease of the eyes in which increasing internal pressure leads to blindness, and in relieving the nausea of chemical treatment of cancers, it's a controlled substance with restrictions similar to those placed on heroin and morphine. Depending on the decade and on the particular region or locality within the nation, the possession and use of small quantities have been subjected to responses ranging from vigorous prosecution to quiet indulgence.

QUESTION

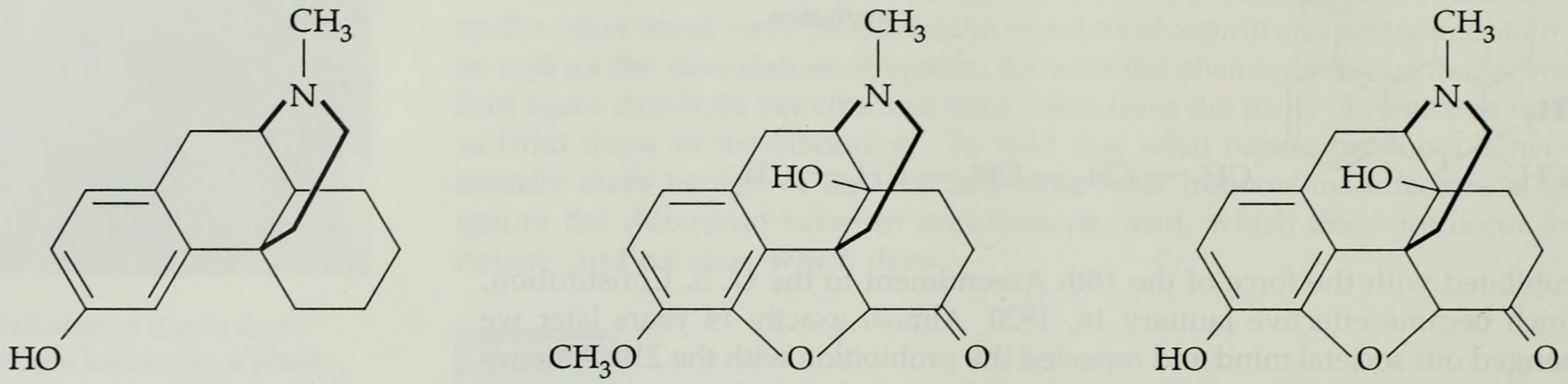
To which one of the following classes of organic compounds does tetrahydrocannabinol belong: (a) hydrocarbon; (b) carboxylic acid; (c) phenol; (d) alkyl halide; (e) aromatic? ____________

22.13 Some Fruits of Imagination and Skill

Long ago, before the full blossoming of chemistry as a science, medicine could ease human suffering only with drugs that were little more than extracts of readily available plants. Some were potent, some were not. A few were addictive poisons.

Today, molecular structures can be assembled and modified to increase drug effectiveness and diminish side effects. Although the ideal drug—immensely powerful, perfectly targeted to a specific illness or symptom, and completely harmless and nonaddictive—hasn't yet been developed (and probably never will be), physicians do now have available a collection of synthetic, well-designed and effective molecules to supplement or replace those that come from plants and animals.

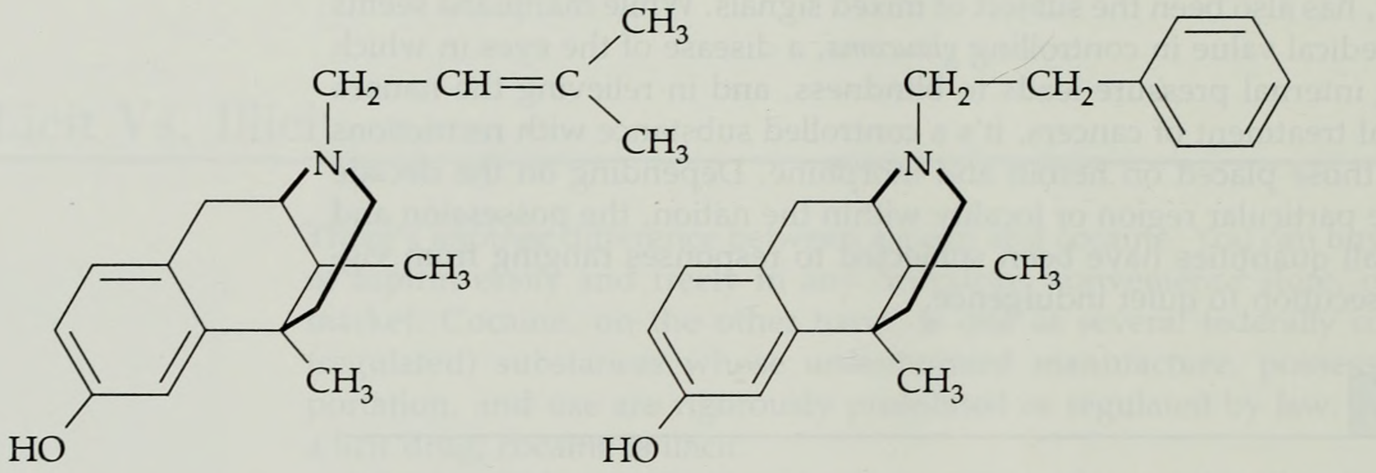
Figure 22.15 presents some of the synthetic narcotics that act much like morphine (and that still present the possibility of addiction). Of all these synthetic compounds, *levorphanol* (Levo-Dromoran) shows the strongest



Levorphanol
(Levo-Dromoran)

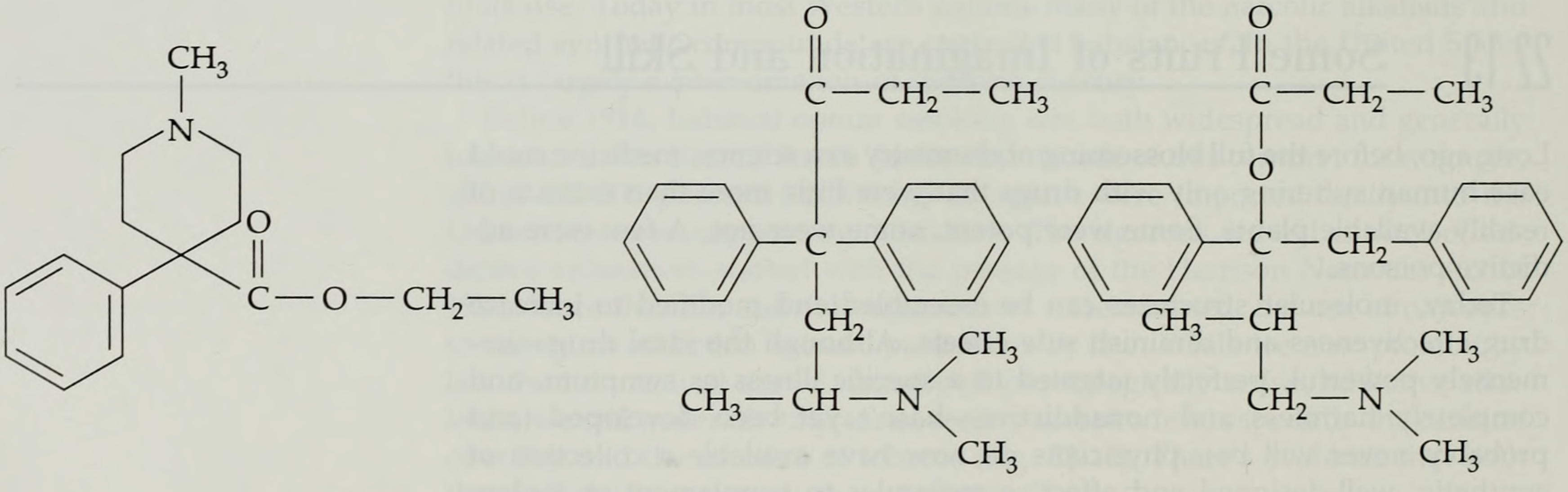
Oxycodone
(Percodan)

Oxymorphone
(Numorphan)



Pentazocine
(Talwin)

Phenazocine
(Prinadol)



Meperidine
(Demerol)

Methadone

Propoxyphene
(Darvon)

Figure 22.15
Synthetic narcotics.

resemblance to morphine in its molecular structure and its actions. *Meperidine* (Demerol) is probably the most widely used synthetic narcotic, while *oxymorphone* (Numorphan) is one of the most powerful, providing about ten times the analgesia as an equal weight of morphine. Some others, such as *propoxyphene* (Darvon) and *oxycodone* (Percodan), are often combined with aspirin for more potent relief than either the narcotic itself or aspirin alone would provide.

Methadone, as its hydrochloride salt (Dolophine Hydrochloride), is both an analgesic in its own right and a useful treatment for heroin addiction. While it is itself addictive, methadone doesn't provide the euphoria or other psychological effects of heroin. Heroin addicts can avoid the crippling effects of withdrawal through a methadone maintenance program that permits them to remain productive members of society.

QUESTION

In what simple way does the molecular structure of oxymorphone (the active ingredient of Numorphan) differ from the molecular structure of oxycodone (the active ingredient of Percodan)? ______

22.14 For a Pain in the Mouth and Other Places

As with morphine, a search for synthetic analogs to cocaine, the oldest of the local anesthetics (Section 22.9), has produced several useful replacements with smaller potential for addiction or other side effects. Like cocaine itself (Fig. 22.11), the synthetic anesthetics in Figure 22.16 consist of three molecular regions: (1) an aromatic ring, usually substituted, at one end of the molecule; (2) a substituted nitrogen at the other; and (3) a section, normally containing an amide or an ester group, connecting the two.

The oldest of these local anesthetics, *procaine*, was synthesized in 1905 and awarded a U.S. patent the following year. As Novocaine it's still used occasionally in dentistry and as a nerve block. Because the body quickly absorbs procaine, it's often injected along with a **vasoconstrictor**, a drug that constricts nearby blood vessels, to keep the anesthetic at the site of the injection as long as possible.

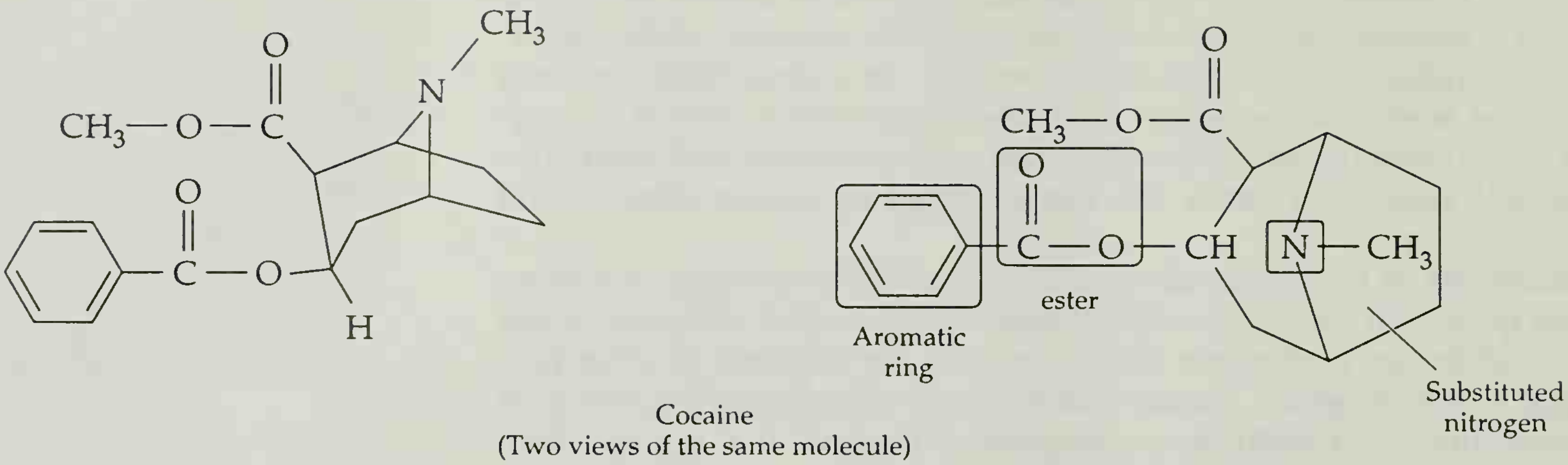
A **vasoconstrictor** is a drug that constricts blood vessels.

Lidocaine, patented in the United States in 1948 and used as Xylocaine, is a much stronger anesthetic than procaine and can be used without a vasoconstrictor. Lidocaine is also effective at returning an irregular heartbeat to its normal rhythm.

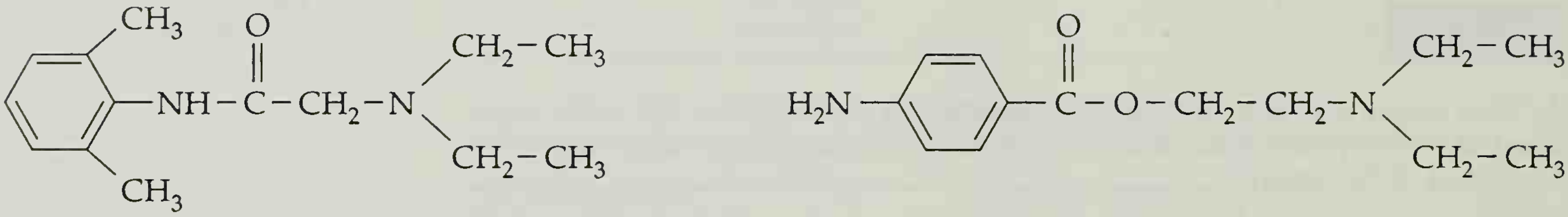
Toxicity or other undesirable properties of an anesthetic can restrict its medical applications. *Naepaine* (Amylsine), for example, is used only on the cornea of the eye, while *dimethisoquin* (Quotane) is most effective on the surface of the skin, especially for the relief of irritations and itchiness, including the discomfort of hemorrhoids.

QUESTION

What structural feature is present in molecules of cocaine, lidocaine, naepaine and procaine, but absent from dimethisoquin? ______

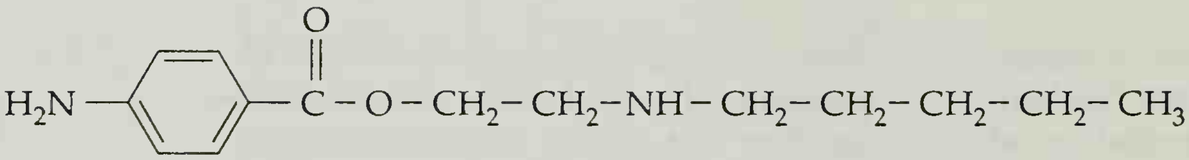


Cocaine
(Two views of the same molecule)

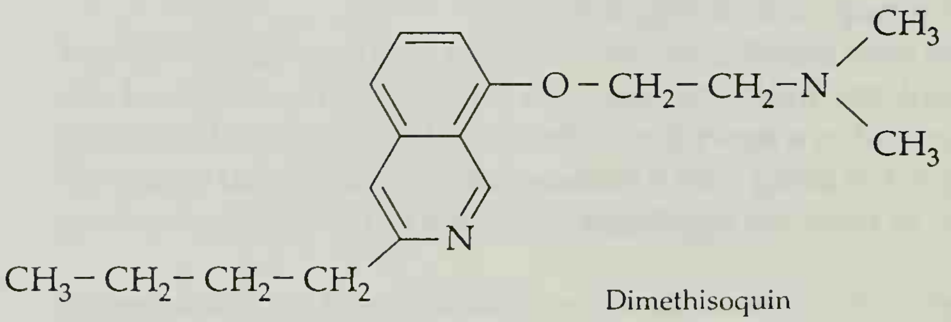


Lidocaine

Procaine



Naepaine



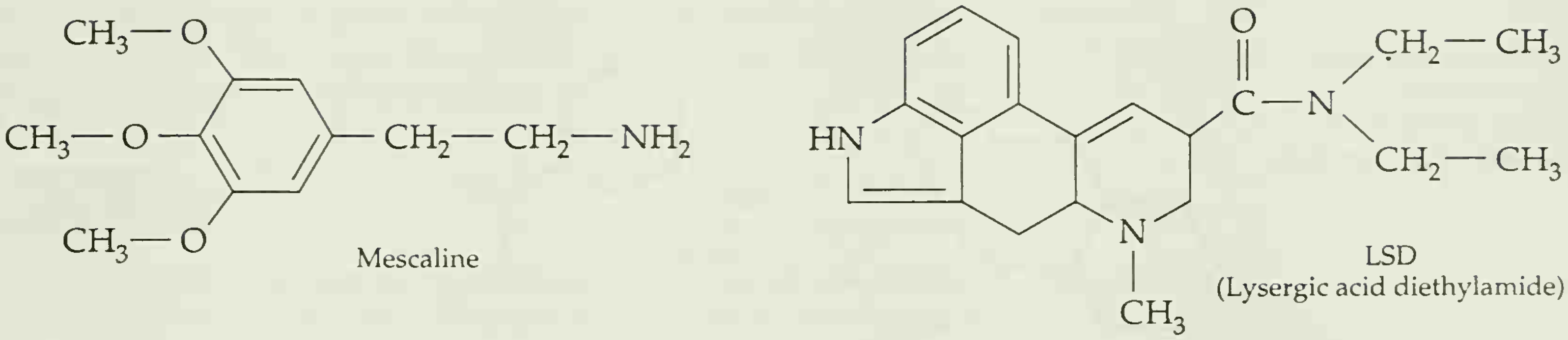
Dimethisoquin

Figure 22.16
Cocaine and related synthetic anesthetics.

22.15 Meditations, Fantasies, and Hallucinations

Drugs can also affect a different sort of perception, other than that of pain. Some substances, with no medical value whatever, can stimulate hallucinations ranging from ecstatic to terrifying and can induce psychological disturbances so powerful that they change the perception of reality itself. Two with particularly interesting histories, *mescaline* and *N,N-diethyllysergamide*, also known as *lysergic acid diethylamide* or *LSD* (from its German name, *lyserg-saure diethylamid*), appear in Figure 22.17.

Mescaline, another of nature's products, forms in the mescal buttons at the top of the peyote cactus. Eating these buttons produces distortions of reality and states of deep meditation that have been part of religious rituals



Mescaline

LSD
(Lysergic acid diethylamide)

Figure 22.17
The hallucinogens mescaline and LSD. Mescaline occurs in the peyote cactus. LSD is a synthetic compound.

of Native Americans of the Western Hemisphere since before the time of Columbus. Today the drug is generally illegal in the United States, although in some regions its use is permitted for religious services of the Native American Church of North America, a church of about a quarter of a million Native Americans of the United States and Canada.

Unlike mescaline, LSD came first from the chemical laboratory, although microorganisms were later observed to produce it as well. The drug was initially prepared in 1938 by Albert Hofmann and a co-worker at Sandoz Laboratories, a Swiss pharmaceutical firm. They set it aside after a few tests indicated that it was a thoroughly uninteresting substance. Five years later, while studying the chemistry of *lysergic acid*, one of the alkaloids of the *ergot* fungus that grows on rye and other cereal grains, Hofmann prepared a bit more of the amide, a few milligrams. Shortly afterward he developed a restlessness and dizziness followed by a fantasy-filled delirium, including what he later called an "intense kaleidoscopic play of colors."

In tracing the source of the disturbance he focused on the diethylamide of lysergic acid that he had prepared the day of the attack. To test his suspicions he swallowed a quarter of a milligram, 0.00025 g, of the substance. The result was more than 6 hours of distortions of vision and of space and time, alternating restlessness and paralysis, dry throat, shouting, babbling, fear of choking, and a sense of existing outside of his body. The worst of the symptoms ended in 6 hours, but the distortions of shapes and colors continued throughout the day. Hofmann recovered completely. Use of LSD has produced far more serious consequences in others, leading some to suicide.

Although neither mescaline nor LSD actually appears to be addictive, each is on the federal list of controlled substances.

QUESTION

Molecules of both mescaline and LSD contain a benzene ring. What other functional group is common to both? What functional group is present in the LSD molecule but not in the mescaline molecule? ____________________

22.16 The Phenylethylamines

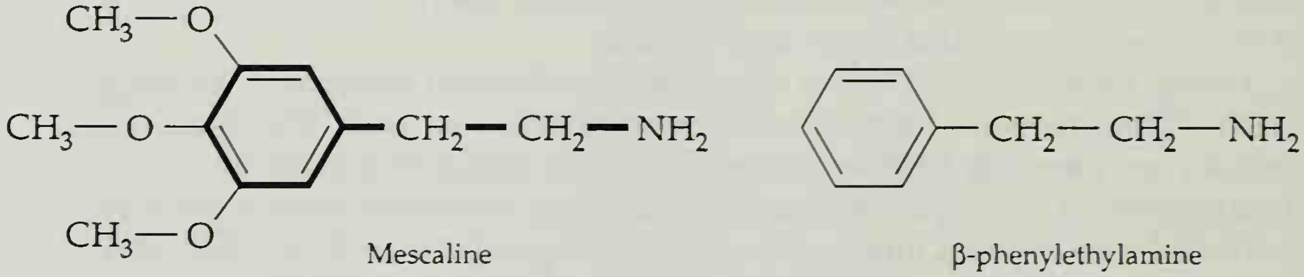
Many of the narcotics and other compounds that alter our perceptions in one way or another, including mescaline, LSD, morphine, heroin, oxycodone (Percodan), oxymorphone, pentazocine, and phenazocine, are composed of molecules with one bit of chemical architecture in common, a β-*phenylethylamine* segment. (See Section 15.3 for a review of the use of Greek letters in

Figure 22.18

Typical β-phenylethylamines. This structure occurs in amphetamines and in many other stimulants and narcotics.

Morphine

LSD
(Lysergic acid diethylamide)



Mescaline

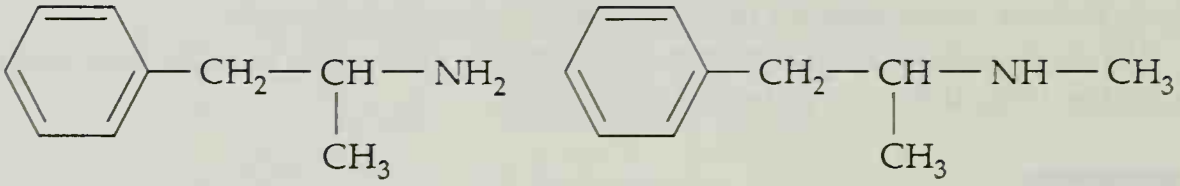
β-phenylethylamine

naming organic compounds.) Molecules containing this structural fragment often affect the way our nerves carry their messages to the brain. Figure 22.18 highlights this structural unit in several of these molecules.

Other substances with this unit include the *amphetamines*, the powerful stimulants in Figure 22.19 that raise the pulse rate and blood pressure, reduce fatigue, and suspend temporarily the desire for sleep. Medically they're useful as decongestants, to control hemorrhaging, to counteract the toxic effects of depressant chemicals, in treating epilepsy, as an aid in weight loss, and for raising blood pressure when it drops to dangerously low levels. They carry

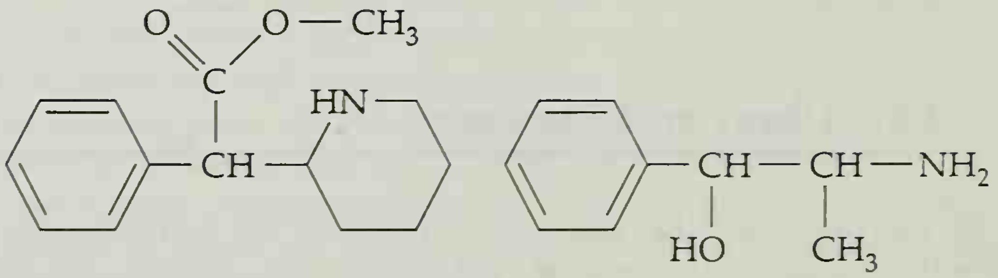
Figure 22.19

Amphetamines. These β-phenylethylamines are powerful stimulants.



Amphetamine
(Benzidrine)

Methamphetamine
(Methedrine)



Methylphenidate
(Ritalin)

Phenylpropanolamine

with them, though, a great potential for abuse, leading even to paranoia and mental illness. Their use, like that of most of the other substances of this chapter, is restricted by federal law.

QUESTION

Using the Greek letter system of nomenclature, designate the carbon of phenylpropanolamine that: (a) bears the methyl group; (b) bears the hydroxyl group.

22.17 For Pain and Suffering of a Different Sort

Beyond the hurts of raw, physical pain, we are also vulnerable to mental and emotional torments, ranging from debilitating anxieties and irrational fears to mental illnesses, psychoses, and disorders of all descriptions and intensities. Mirroring the scope of mental suffering that humans are open to is the complexity of chemical substances that can provide cures, or at least relief. These range from the deceptively simple structure of ionic *lithium carbonate*, Li_2CO_3, to the awesome structure of *reserpine* (Fig. 22.20).

Lithium carbonate provides stability to the mood swings of *manic depression*, a condition that produces the extremes of raging exhilaration and intense, paralyzing depression. It was first used to treat manic patients in 1949, in Australia. Reserpine is the major *rauwolfia* alkaloid produced by climbing rauwolfia shrubs, which are native to India. Ancient Hindus applied extracts of these and similar plants to a variety of illnesses ranging from insomnia to insanity. In modern times reserpine has been used to treat mental illness since 1954, but it's given way recently to more modern drugs. In 1981 the Environmental Protection Agency registered it as a carcinogen.

The kinds of drugs available for the treatment of mental pain (and their effects) are as varied as the symptoms they relieve and their causes. Among the most commonly used are the *tranquilizers* and the *antidepressants*. Physicians write more prescriptions for tranquilizers than for any other class of prescription medicine, with *meprobamate* (Equanil and Miltown) the most popular. This particular tranquilizer belongs to the chemical class of *carbamates*,

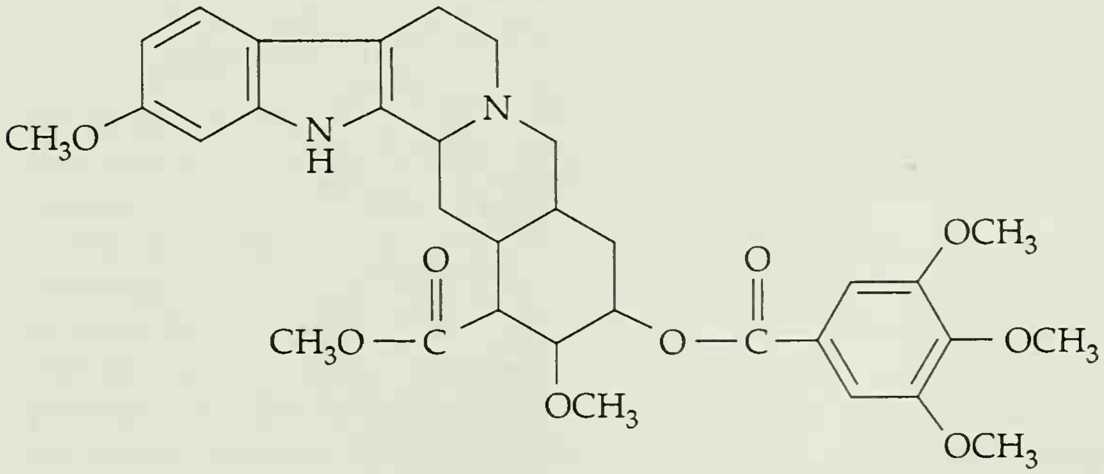
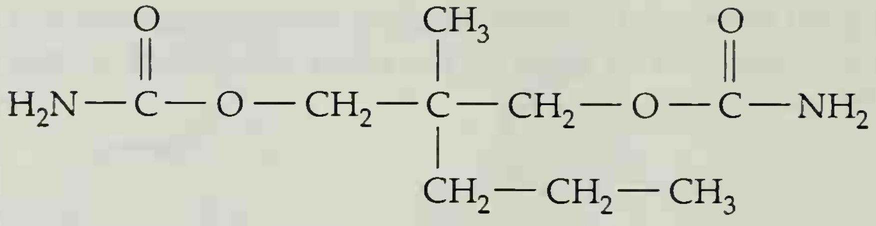


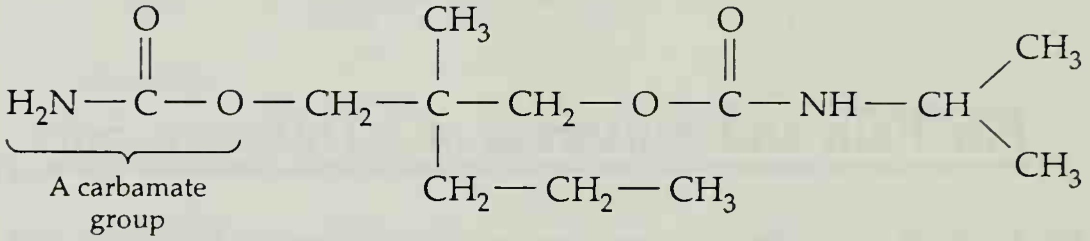
Figure 22.20
Reserpine, an alkaloid of the rauwolfia shrub, has been used to treat various forms of mental and emotional illness.

Figure 22.21
Carbamate tranquilizers.



$$H_2N-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2-CH_2-CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$$

Meprobamate
(Equanil, Miltown)



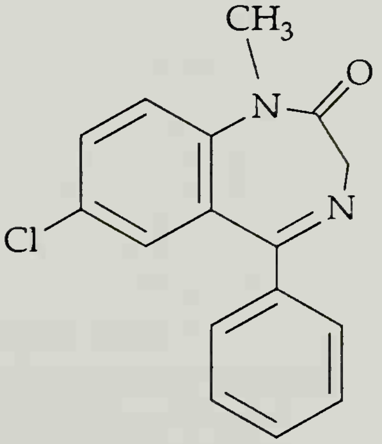
$$\underbrace{H_2N-\overset{\overset{O}{\|}}{C}-O}_{\text{A carbamate group}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2-CH_2-CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH-CH(CH_3)_2$$

Carisoprodol
(Soma)

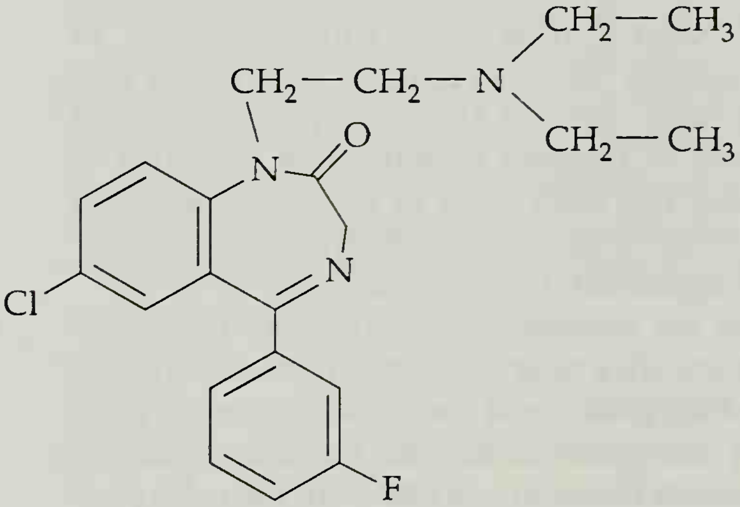
which are esters of *carbamic acid*, $H_2N—CO_2H$ (Fig. 22.21). *Carisoprodol* (Soma), another carbamate, is an effective muscle relaxant.

Diazepam (Valium), *flurazepam* (Dalmane), *oxazepam* (Serax), *clorazepate* (Tranxene), and *chlordiazepoxide* (Librium) are all tranquilizers of a different structural class (Fig. 22.22). First prepared in 1933, they were soon found to

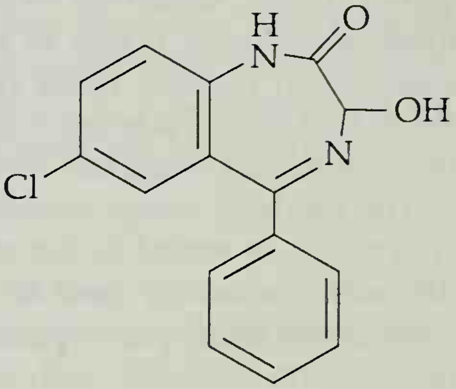
Figure 22.22
Muscle relaxant tranquilizers.



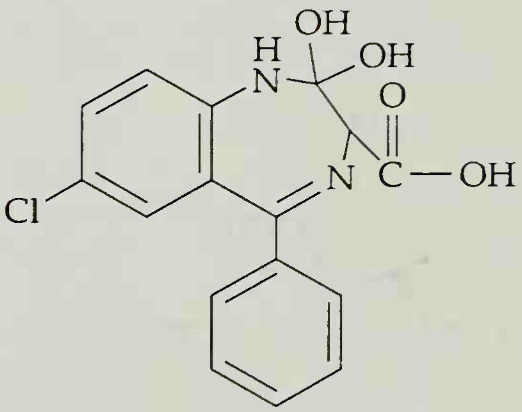
Dlazepam
(Valium)



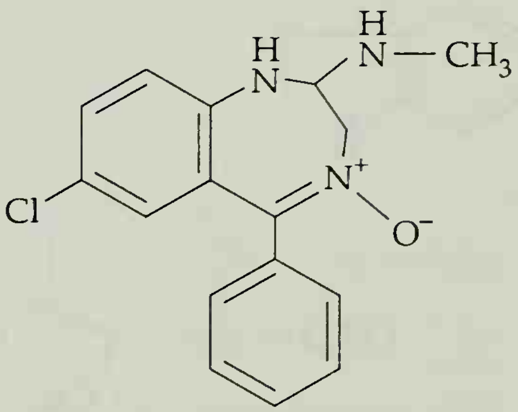
Flurazepam
(Dalmane)



Oxazepam
(Serax)



Clorazepate
(Tranxene)



Chlordiazepoxide
(Librium)

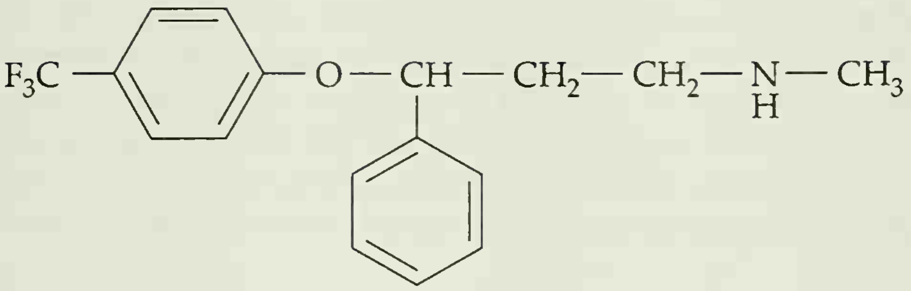


Figure 22.23
Fluoxetine (Prozac), a recently introduced antidepressant.

act as muscle relaxants. It wasn't until a generation later, after they had been used to tame violent monkeys and other animals, that compounds of this structure were first used to treat disorders in humans.

Among the antidepressants, fluoxetine (Prozac, Fig. 22.23), which was introduced in the late 1980s, clearly holds the lead. With about a million prescriptions filled each month, total annual sales amount to almost $700,000,000. Although the drug was subjected to extensive testing before being placed on the market and has been taken by over 2 million people throughout the world with satisfactory results, allegations that it induces violent behavior and suicidal tendencies in some patients have placed it under suspicion. Some authorities claim that patients develop these tendencies as a direct result of the medication, while others point out that the drug is prescribed principally for people who are already depressed or are already suffering from these tendencies, and that no antidepressant is completely effective in curing all patients. Others suggest that these may be real but exceedingly rare examples of a drug making an illness worse rather than alleviating it. Whether these alleged violent and suicidal impulses are independent of the drug (and simply do not respond to the medication) or are caused by the fluoxetine itself is still in dispute. In any event, we see once again that the use of any substance, of whatever kind and for whatever purpose, involves a balance of risks and benefits.

QUESTION

Which one of the muscle relaxant tranquilizers of Figure 22.22 is a carboxylic acid?

22.18 Changing the Brain's Tumblers Provokes a Curious Question

Of all the chemicals that affect our perceptions of pain, a group that could turn out to be the most significant was discovered through a strange connection between human bodies and plants.

The story starts with *naloxone* (Fig. 22.24), a member of a group of morphine-like compounds that have the power to nullify completely the effects of even the most powerful, most addictive narcotics, including heroin. Such compounds are called **opiate antagonists**. Among them are several compounds, including naloxone, that not only reverse the effects of the opiates, but do so without producing any narcotic effects of their own, not even simple analgesia. Moreover, these *pure antagonists* so effectively counteract the op-

Opiate antagonists are compounds that counteract or nullify the effects of opiates, including heroin.

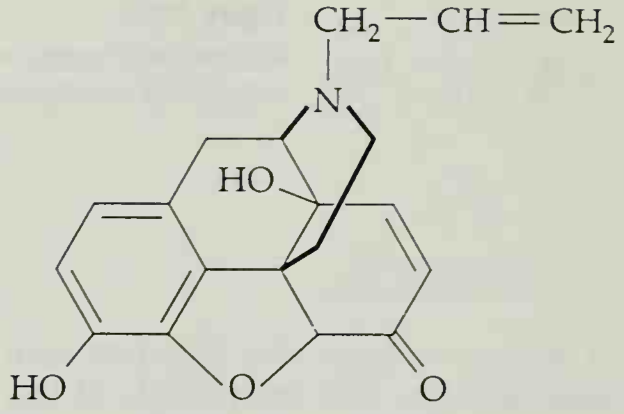


Figure 22.24
Naloxone, a narcotic antagonist, counteracts the effects of narcotics. It is used to treat overdoses of heroin and other narcotics.

iates that they even induce withdrawal symptoms in active addicts. One of their greatest values lies in the emergency medical treatment of narcotic overdoses.

In studying just how the opiates produce their effects on the body and how naloxone and other antagonists are able to counteract these effects, scientists discovered in the 1970s that the nervous system contains gigantic molecules, situated at certain locations within the network, that act as **opiate receptors**. The narcotic molecules fit snugly and precisely into these receptor sites, much like a key in a lock, and interfere with the signals flowing through the network. In one case this interference can result in the merciful blocking of a pain signal. In another case, though, when the narcotic molecule enters the brain and occupies one of the receptor sites within its central network, it can garble fundamental perceptions of reality; warp the sense of space, time, and color; generate hallucinations; and produce extremes of emotional states.

Opiate receptors are extremely large molecules within the nervous system. When narcotic molecules interact with these opiate receptors they block or alter signals flowing through the nervous system.

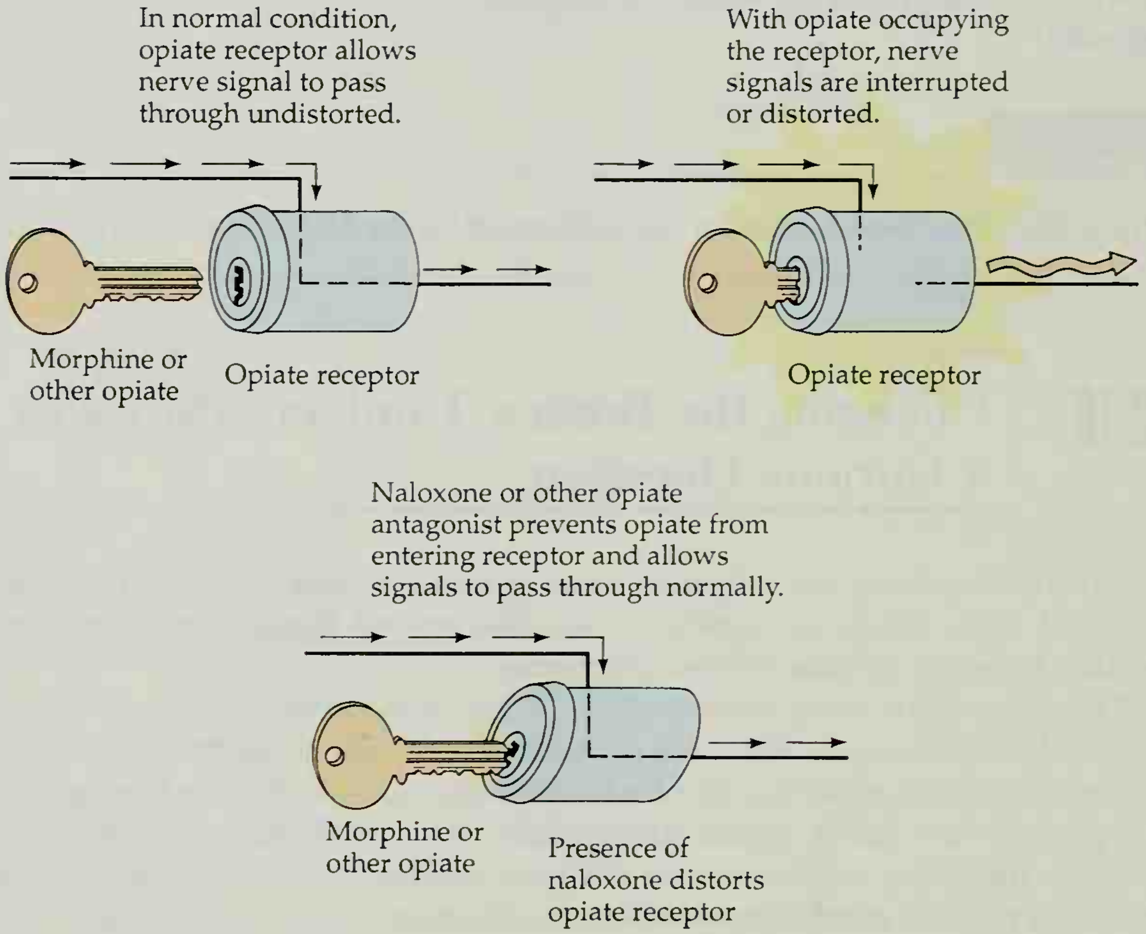


Figure 22.25
The effect of an opiate antagonist.

The antagonists seem to counteract these effects by distorting the opiate receptor site so that the narcotic molecule won't fit. Their action is something like changing the tumblers in the lock, at least for a while, so that the key no longer fits and the signals can no longer be distorted (Fig. 22.25). But the strange question all this provokes is, "Why should *animal* brains have evolved with receptors within them that only molecules produced by *plants* can fit?"

QUESTION

In what way does the molecular structure of naloxone differ from the molecular structure of oxymorphone (Fig. 22.15)? ____________________

22.19 From Antagonists to Enkephalins

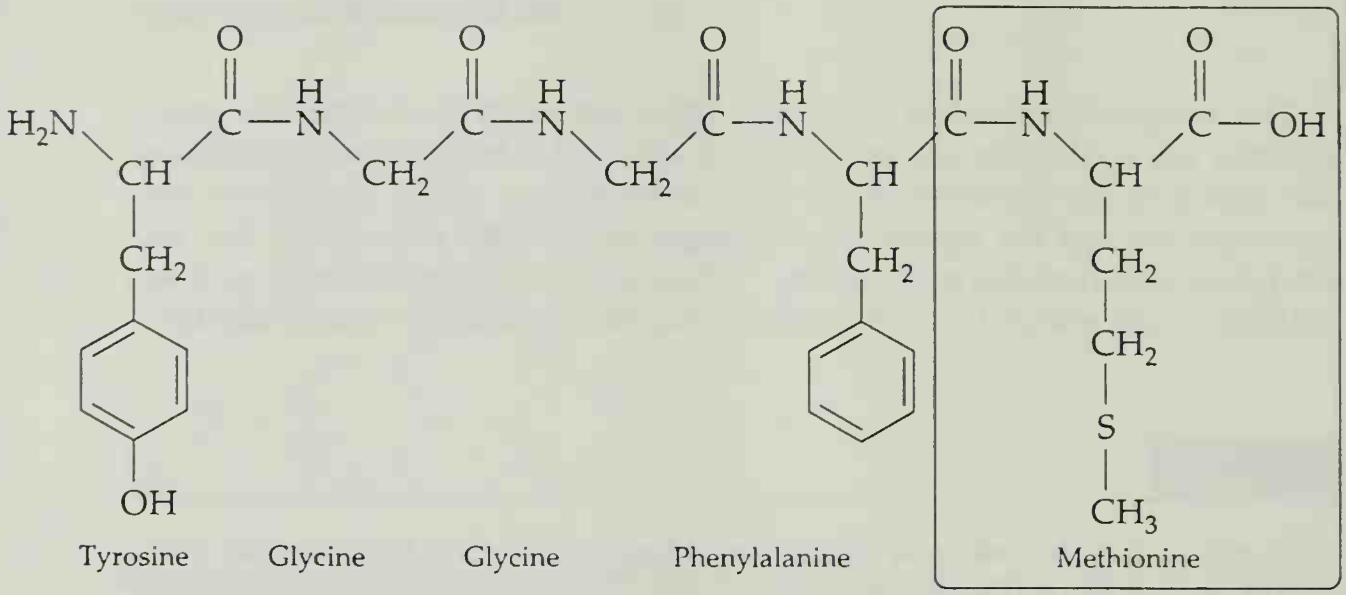
The whole idea that animal brains (more specifically, the brains of vertebrates) might contain within their communications networks certain molecular locks that only special molecular keys, produced by certain plants, could fit seemed so absurd that scientists began searching for molecules produced within the animal itself that would also fit these peculiar receptor sites. Among those looking for these special keys were J. Hughes and H. W. Kosterlitz of the University of Aberdeen (Scotland), L. Terenius of the University of Uppsala (Sweden), E. J. Simon of the New York University School of Medicine, and S. H. Snyder and C. B. Pert of the Johns Hopkins University School of Medicine. They found what they were looking for in substances isolated from the brains of pigs and calves.

These molecular keys of the animal kingdom are pentapeptides (peptide chains of five amino acids; Section 15.7), which their discoverers named *enkephalins* from Greek words meaning "within the head." Figure 22.26 shows the structures of two enkephalins, *methionine enkephalin* and *leucine enkephalin*. Notice that they differ only in the amino acid bearing the free carboxyl group, the amino acid that gives each its unique name.

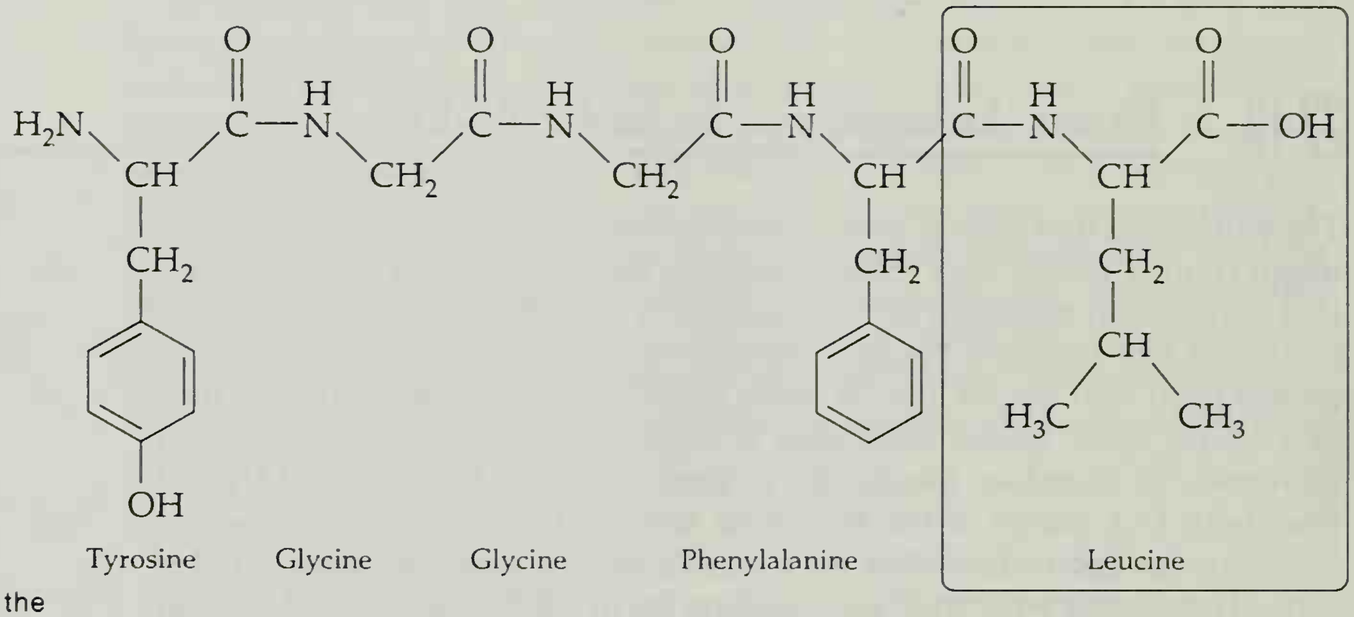
As support for the idea of locks and keys in the network of the nervous system, these enkephalins not only produce analgesia but their effects can be blocked by the same naloxone that works against the plant narcotics. What's more, laboratory rats have become physically addicted to them after repeated injections. (One synthetic enkephalin in which the amino acids of methionine enkephalin have been modified a bit has about 15,000 times the painkilling power of morphine.)

QUESTION

What three amino acids are common to both methionine enkephalin and leucine enkephalin? ____________________



Methionine enkephalin



Leucine enkephalin

Figure 22.26
Enkephalins, narcotic pentapeptides produced in the bodies of animals.

22.20 Endorphins, Our Very Own Opiates

Endorphins are opiates produced within the bodies of animals.

To cover the entire field of opiates produced within the animal body, the enkephalins as well as larger and more complex narcotic molecules, the term **endorphins** was coined as a combination of two words: *endogenous* (meaning "formed within the body") and *morphines* (the kinds of narcotics they mimic). Of these, the major opiate produced by the brain—more exactly by the *pituitary gland*, a small, round gland that hangs down from the base of the brain, roughly at the center of the head—is β-*endorphin*, a polypeptide composed of 31 amino acids. The first five of these are the same as those that form the methionine enkephalin chain (Fig. 22.27).

It appears that endorphins are indeed the body's own opiates, generated as needed to reduce pain and perhaps to produce other effects as well. Sharply elevated levels of β-endorphin occur in the blood of women during childbirth and in their newly born babies, generated perhaps to ease the stress of birth on both the mother and the infant. What's more, endorphins appear to produce the analgesia stimulated by some forms of acupuncture. Since naloxone

Figure 22.27
β-Endorphin, a narcotic produced by the pituitary gland.

Ala = Alanine
Asn = Aspargine
Gln = Glutamine
Glu = Glutamic acid
Gly = Glycine
His = Histidine
Ile = Isoleucine
Leu = Leucine
Lys = Lysine
Met = Methionine
Phe = Phenylalanine
Pro = Proline
Ser = Serine
Thr = Threonine
Tyr = Tyrosine
Val = Valine

can reverse the effect of acupuncture that is accompanied by low-frequency electrical currents, this form of the process must act by stimulating the formation of endorphins.

In addition to relieving pain, endorphins may also play other roles in the body. Their generation after long periods of vigorous exercise suggests that they may be responsible for the "high" long-distance runners and other athletes experience.

QUESTION

What is the name of the amino acid of β-endorphin that bears a free —NH_2 group? What is the name of the one that bears a free —CO_2H group? ________________

22.21 The Power of the Placebo

A **placebo** is a harmless and normally ineffective substance given to someone who complains of a particular ailment, simply to please and pacify the patient.

As we've seen throughout this chapter, chemicals can affect profoundly our perceptions of the outside world and especially our sense of pain. In an odd reversal of roles, our perceptions themselves—our beliefs and expectations—can change the ways in which the chemicals and the physical phenomena of the outside world affect us. It all takes place through the *placebo effect*.

Those who practice medicine have long known of the power of the **placebo,** a harmless and (normally) ineffective substance, often a sugar pill or a starch pill in disguise, given to someone complaining of a particular ailment simply to pacify the person. (*Placebo* comes from the Latin and means "I shall please" or "I shall pacify.")

The idea behind the placebo is that the aches and pains are often imaginary, and that since there is (presumably) nothing really wrong, a simple starch pill (a placebo) will make it appear to the patient that something important is being done and will end the complaints. Callous as this may seem, it often works. But not for the original reasoning. The power of the placebo appears to be real, not imaginary.

Simple placebos have eased pains from a variety of causes and a range of intensity. They have stopped coughs, promoted the healing of wounds, removed warts, lowered blood pressure and pulse rates, and even produced side effects, including dryness of the mouth, headaches, and drowsiness.

It's possible, of course, that chemicals we've long believed to be effective medicines are actually operating through a placebo effect. If a physician says, for example, "This pill will cure you," and if we believe that "This pill will cure me," we may well obtain relief from the placebo effect alone. To examine this possibility, Herbert Benson of the Harvard Medical School has studied the reported effectiveness of medicines used during the past two centuries to treat the chest pains of angina. From an examination of medical reports accumulated over that period, he estimates that newly introduced medicines have been effective in 70% to 90% of the patients receiving them, but that their effectiveness dropped to 30% to 40% after even newer ones were found. Perhaps, he concludes, the physician's faith in the newest medicine is transferred to the patient.

What's the origin of the placebo effect? Can faith alone authentically provide analgesia? To find out whether the opiate effect of endorphins is involved, three physicians of the University of California at San Francisco studied a group of dental patients whose wisdom teeth had just been extracted. As part of the study some were given placebos shortly after the extraction while others were given naloxone, the opiate antagonist described in Section 22.18. (None of the patients knew what any of their pills contained.)

Some of those who responded to the placebo by reporting a drop in the level of the pain (about one person out of three is just such a *placebo responder*) received naloxone as their next treatment. Their pain shot back up to about the level of those who don't respond to placebos at all. (Those who received naloxone as their only drug found no change in their level of discomfort, so the naloxone itself didn't *cause* any of the pain.) The conclusion reached in this study is that since the opiate antagonist naloxone raises the level of pain in the placebo responders, the analgesic effect of placebos appears to come from the release of endorphins by the body, which were subsequently blocked by the antagonist.

QUESTION

What is a "placebo"? ____

PERSPECTIVE: The Scientific Method as a Test of Reality

If a simple starch pill can ease pain (for the third of us who are placebo responders) simply because we believe that it will, is there some way to tell whether aspirin, for example, is any more effective than, say, a teaspoon of starch given to us by someone who speaks with authority, wears a white coat with a stethoscope dangling out of the pocket, and occupies a doctor's office—someone, that is, who inspires us to believe?

There is, through an elegant example of the scientific method at work. The question we ask is: "Can we tell whether pain relief results from a placebo effect or comes from the inherent analgesic action of a compound, independent of a patient's faith or belief in the healing effect of the medicine?" For the answer we use a simple test of reality that operates through a powerful scientific technique called a *double-blind* study. The procedure involves distributing the medication under study to a large number of people who have been divided into two groups by random assignment. One set, the *control group*, receives a placebo. The other, the *test group*, receives the authentic medication, aspirin for example. One of the keys to the study's value lies in separating the preparation of the pills from their distribution so that no one taking the pills can possibly know whether it's the medicine or the placebo, thus nullifying any placebo effect.

To avoid any possibility that those conducting the test might pass along a clue, even unconsciously by a facial expression or a body attitude, the identity of each individual pill is kept hidden from those distributing them. To achieve this level of secrecy the double-blind test requires two sets of examiners. One identifies each pill with a code number that reveals its contents, but is "blind" to the method of distribution. The other set of examiners, "blind" to the significance of the codes, distributes the pills to the members of both groups. With this level of concealment, and with the pills appearing identical in all respects except for their coding, the placebo effect operates equally with everyone involved. Through the operation of the double-blind investigation no one, neither the examiners nor the participants, knows until the end of the test whether any particular participant is in the control group or in the test group.

At the end of the study the effects of the pills are correlated with their coding. If those receiving the authentic medication respond differently from those receiving the placebo, the difference must be due to the real potency of the medicine and not simply to a placebo effect. Here we see the scientific method at work, isolating the narrow question we are asking and removing any possibility that those receiving the pills (placebo or medication) can receive any clues about their contents. With this double blind procedure, we can be certain that belief and expectation play no part in the answer we obtain.

It's a good test of reality; it's scientific evidence of the effectiveness of any chemical that produces a human response. Use of a double-blind study, for example, proves clearly that aspirin is an effective analgesic, producing relief from pain beyond that due to a placebo effect alone. It's important to treat claims not backed by studies like these with a good deal of skepticism. They may not represent a form of reality beyond the simple release of endorphins from someone's pituitary gland. In the double-blind approach we glimpse a chemical reality untainted by our own expectations.

EXERCISES

FOR REVIEW

1. Complete this statement with the words and phrases that follow. Each us used once.

The world's most widely used ______ is ______ , which is known chemically as ______ and is prepared by the reaction of ______ acid with ______ . The biological effects of this medication can be traced to its ability to interfere with the body's synthesis of ______ , which play a major role in the generation of inflammation and fever and in the sensation of pain. While ______ lacks aspirin's ability to reduce inflammation, it can serve as a substitute for those of us who may be allergic to aspirin.

Among naturally occurring substances, several members of a group of compounds found in ______ and known as ______ produce notable physiological effects. The first member of this class to be isolated was ______ , a powerful ______ that is the largest single component of ______ . An attempt to produce a less addictive drug by diacetylating morphine led to the powerfully addictive narcotic, ______ . Another highly addictive alkaloid, ______ , is found in the leaves of the coca bush and was once used medically as a ______ .

______ , a compound whose molecular structure resembles that of morphine, belongs to a class of compounds known as ______ that can counteract the effects of narcotics. Studies involving the action of these compounds have revealed the existence of narcotic ______ that are produced within the human body. These compounds, named ______ to reflect their origins and actions, appear to be responsible for the operation of the ______, which allows a simple starch or sugar pill to relieve pain and produce many other remarkable physiological effects.

acetaminophen
acetic anhydride
acetylsalicylic acid
alkaloids
analgesic
aspirin
cocaine
endorphins and enkephalins
heroin
local anesthetic
morphine
naloxone
narcotic
opiate antagonists
opium
placebo effect
plants
polypeptides
prostaglandins
salicylic

2. Explain, identify, describe or define

a. amphetamines
b. β-phenylethylamines
c. codeine
d. ibuprofen
e. lithium carbonate
f. methadone
g. oil of wintergreen
h. procaine
i. reserpine
j. tetrahydrocannabinol

3. Match each of the following with the corresponding contribution to our understanding of drugs, medicines, and the effects of chemicals on perception.

_____a. Albert Hofman
_____b. Felix Hofmann
_____c. Karl Koller
_____d. Pierre-Jean Robiquet
_____e. Friedrich Sertürner

1. first to isolate codeine
2. first to prepare and to feel the effects of LSD
3. early workers in the field of endorphins and enkephalins

____ f. J. Hughes, H. W. Kosterlitz, C. B. Pert, E. J. Simon, S. H. Snyder, and L. Terenius	4. first to isolate morphine
	5. first to use cocaine to anesthetize the eye
	6. provided proof of aspirin's analgesic effect

4. What is the major, physiologically active substance that comes from each of the following:

a. the bark of the willow tree
b. the coca bush
c. the sap of the poppy
d. the pituitary gland
e. the belladonna plant
f. climbing shrubs of India

5. Describe the connection between the items in the following pairs.

a. acetylsalicylic acid and Reye's syndrome
b. salicylates and prostaglandins
c. methionine enkephalin and leucine enkephalin
d. methionine enkephalin and β-endorphin
e. naloxone and diacetylmorphine
f. carisoprodol and meprobamate
g. reserpine and Li_2CO_3

6. What compound, substance, or other topic of this chapter owes its name to the following?

a. the Latin name for the willow tree
b. the Roman god of dreams
c. a Latin word for something that pleases
d. the Latin word for a physician's art or practice
e. the Greek word for "stupefying"
f. Greek words meaning "in the head"
g. the Italian term for "beautiful lady"
h. the botanical genus of the meadowsweet plant
i. the bodily organ from which they were first isolated
j. a trade name dating from about 1900
k. words meaning "morphine-like compounds produced within the body"

7. Why was the acetylation of salicylic acid important to the introduction of aspirin for general use as an analgesic?

8. What's the difference between an analgesic medication and an antipyretic medication?

9. What is the commercial product called "buffered aspirin" composed of? Why is the use of the term *buffered* incorrect for this product?

10. Name a medication that contains (a) chlorine, but not fluorine; (b) fluorine but not chlorine; (c) both chlorine and fluorine. Give a trade name for each and describe what each is used for.

11. In what way are methadone and heroin alike in their effects on humans? In what way are they different?

12. Name two alkaloids that are used often, in large quantities, and legally throughout most of the world, even though they can be addictive. In what form is each consumed?

13. Name three mood-altering chemicals that are accepted for general, nonmedical use by adults in many countries of the world. Name three mood-altering chemicals whose general, nonmedical use by adults is prohibited in many countries of the world.

14. Name and give the structure of a compound you could use to convert an alcohol or a phenol into an ester.

15. Describe the chemical or biological means by which each of the following affects our perception of pain: (a) aspirin; (b) morphine; (c) naloxone; (d) β-endorphin.

16. What role did the Harrison Narcotics Act of 1914 play in the history of the use of narcotics in the United States?

17. In what way is the combination of a narcotic and an opiate receptor analogous to a key and a lock?

A LITTLE ARITHMETIC AND OTHER QUANTITATIVE PUZZLES

18. In Section 22.17 we learned that total sales of Prozac amount to about $700,000,000 each year and that about a million prescriptions for the medication are filled each month. What is the average cost of filling a prescription for Prozac?

THINK, SPECULATE, REFLECT, AND PONDER

19. Under what conditions or in what circumstances is it dangerous, and possibly fatal, to use aspirin?

20. All acetylations with acetic anhydride always produce one particular organic compound in addition to the desired product. What organic compound is always generated in these reactions?

21. Aspirin tablets kept for many months, especially in hot, humid climates, often smell of vinegar. Why?

22. Under what conditions is acetaminophen a better medication than aspirin? In what circumstances is it inferior to aspirin?

23. What chemical do you think has the longest history of use as a mood altering drug? Describe your reasoning.

24. The 18th Amendment to the U.S. Constitution prohibited the sale and transportation of alcoholic drinks. The 21st Amendment permitted these activities once again. Why do you think the 18th Amendment was adopted? Why do you think the 21st Amendment was adopted? Discuss the factors you think led to each.

25. Describe the evidence that the analgesic effect of some forms of acupuncture is based on release of endorphins.

26. Describe in your own words how you would distinguish between a "medicine" and a "drug."

27. Do you think that the use of all mood-altering or perception-altering drugs should be prohibited except for medical purposes? Describe your reasoning.

28. In some localities, in the United States and in other countries, establishments commonly known to many of us as "drugstores" are called, instead, "pharmacies" or "apothecaries." Do you think we ought to discontinue the use of the term *drugstore* because of its connection with the word *drug*? Describe your reasoning. If you believe we ought to discontinue the use of *drugstore*, what term would you use to replace it?

29. Describe how a double-blind investigation eliminates the possibility that a placebo effect is operating.

30. Do you think that a person who drinks several cups of *decaffeinated* coffee, thinking mistakenly that it is caffeine-containing coffee, might show signs of agitation or sleeplessness as a result? If this would occur in some cases, to what would you attribute the phenomenon? Describe how you might go about determining whether agitation or sleeplessness after drinking several cups of decaffeinated coffee might be due to a placebo effect.

Appendix A

A Short Guide to Exponential Notation

COUNTING BEYOND NINE

Counting is easy, recording numbers isn't. The Romans used letters: I for one, V for five, X for ten, C for a hundred, and so on. To Julius Caesar, eight was VIII, nine was IX.

Roman numerals turned out to be too cumbersome. After the Roman Empire fell, Western civilization adopted a simpler scheme for recording numbers, a system based on Arabic numerals: 1, 2, 3, and so on. One of the beauties of this system is that you can multiply any number by ten simply by appending a zero. Three is 3, ten times 3 is 30, and ten times 30 is 300.

With Arabic numerals, 9 is the largest digit. One more than 9, ten, has to be written as 10, which is really no more than ten times 1, just as 30 is ten times 3. Now, long after the Romans, a hundred isn't C any longer. It's ten times ten, 100. A thousand, 1000, is ten times a hundred, or ten times ten times ten if you wish. Each zero we append multiplies everything to its left by ten.

The trouble with this system is that very soon, with enormously large numbers, the string of zeros becomes as cumbersome as the Roman letter-numbers used to be, long ago. But ingenuity triumphs again. Just as we simplified the recording of numbers by switching from Roman notation to Arabic, we now simplify long strings of zeros by using *exponential notations of ten*.

An exponent itself is just a superscript that tells us how many times the number it's hanging over must be multiplied by itself. The superscript 2 defines 3^2 as 3×3, or 9; the superscript 4 in 3^4 signifies $3 \times 3 \times 3 \times 3$, or 81. In these examples the 2 and 4 are the *exponents* and the 3 is the *base*, which is the number being multiplied by itself any number of times.

(Technically, that paragraph needs a bit of explanation. With 3^2 we surely multiply three *by itself* only *once*, not twice. But that's the great strength that mathematics has over verbal language. The statement

$$3^2 = 3 \times 3$$

is much more elegant in its simplicity than the dozens of words we'd have to use, in cumbersome constructions, to explain the whole thing in proper sentences.)

In exponential notation to the base ten we simply replace a string of zeros by a 10 and its exponent. Since 100 is 10×10, it's also 10^2; similarly, 1000 is 10^3, and 10,000 is 10^4. We can plug other numbers into this system as well. For example, 30 is 3×10, 300 is 3×100 or 3×10^2, and 3000 is 3×1000 or 3×10^3. Because of its great utility in expressing the very large numbers of science (and the very small numbers, too, as we will soon see), this form of exponential notation is often called *scientific notation.*

As a practical matter, the exponent of 10 indicates the number of places the decimal point has to be moved to the right to represent the number in our more common notation. In this way 3×10^3, which can also be written $3. \times 10^3$ (note the decimal behind the 3), becomes 3000 as the decimal moves three places to the right. Again, 3.0173×10^3 translates into 3017.3 with, again, the decimal skipping three places to the right.

As the other side of this coin, *negative* exponents move the decimal to the *left*. The number 3×10^{-1} becomes .3, often written 0.3 to add a bit of clarity. In another example, 3.0173×10^{-5} becomes 0.000030173 as we move the decimal five places to the left.

At the border between mathematics and chemistry, Avogadro's number, 6.02×10^{23}, turns out to be

$$602{,}000{,}000{,}000{,}000{,}000{,}000{,}000$$

Question:	Can you write Avogadro's number in Roman numerals?
Answer:	Probably not.

One final thought. In working with exponential notation we can multiply any two numbers together simply by adding their exponents algebraically *as long as their base numbers are identical.* With the base 2 we see that $2^2 \times 2^3$ is the same as 4×8, or 32. Notice that we get the same result by adding the two exponents $(2 + 3)$ to get 2^5, which is still 32. With base 10, the product of 100 (10^2) and 1000 (10^3) is 100,000 (10^5). Here again, the exponent 5 is the sum of the two exponents $(2 + 3)$. By the use of algebraic addition, 0.01 (10^{-2}) $\times$ 1,000,000 (10^6) is 10,000 (10^4). Here $6 - 2 = 4$, the exponent of 10 needed to give 10,000.

EXERCISES

1. Write each of the following in ordinary Arabic numerals. For example, 3.779×10^2 is 377.9.

a. 2×10^3
b. 4.796×10^3
c. 0.0072553×10^4
d. 142.99×10^{-2}
e. 56.97×10^{-5}

2. Write each of the following in exponential notation to the base ten. For example, 4772.34 is 4.77234×10^3.

a. 47,000
b. 96,723.70
c. 12
d. 0.004195
e. $(5.67 \times 10^3) \times (2 \times 10^{-5})$

3. Write each of the following in common Arabic numerals.

a. 10^8
b. 3^4
c. 4^3
d. $2^3 \times 3^2$
e. $2^4 \times 10^2 \times 2^5 \times 10^{-5}$
f. $2^9 \times 10^{-3}$

Appendix B

The Metric System

THE MEASURE OF ALL THINGS

A Revolution in Measurement

In 1789 the people of France revolted against King Louis XVI. With the success of their great revolution the French not only overthrew their monarch and the system of government he represented, but they began another kind of revolution as well—a revolution in the science and technology of measurement.

Probably since well before recorded history, and surely from the times when the first tribes built complex structures and engaged in trade and commerce, *units* have been vital to any human activity involving measurement: units of length, of area, and of volume; units of mass (or weight) and of time; and units of money. Our dollar is a unit, and so are the second, the pound, and the yard. Ask how many miles per gallon a car gets and you are asking about units of distance and volume. Consider the cost of a piece of fabric and you deal with units of area and money.

Until the matter of the Bastille was settled by the French, units of measurement used by the various peoples of the world suffered from two important defects: (1) they were based on highly arbitrary standards that were sometimes difficult or impossible to reproduce accurately should the original, physical standard of the unit be lost or destroyed, and (2) they were converted to other units only by cumbersome and laborious calculations.

To illustrate this second problem, the matter of interconversions, consider a short example. The English *yard*, whose length was originally established by Edward III in 1353, consists of 3 feet, each of which is made up of 12 inches. Moreover, there are 5280 feet to a mile. Now calculate how many inches there are in 3 miles. It's an easy enough problem, but with the cumbersome English system of units it takes a few moments to solve, even with a hand calculator. To make matters even worse, before the French Revolution, each country of Europe had its own system of units of measurement. International trade thus had a double burden. Added to the conversions required within any particular country were those necessary to switch from the units used by one country to those used by another.

In addition to these intricate and time-consuming interconversions, as well as the additional difficulties of the occasional replacement of lost or damaged standards, there was also another important matter in revolutionary France. As in the other European countries, the French units of weights and measures were based on arbitrary standards and had been maintained by royal decree. With the revolution they had become anachronistic relics of an overthrown regime, relics that were to be replaced in the conduct of the daily life of France by a more natural and a more rational system of measurement, just as autocratic rule by the king had itself been replaced by a more natural and more rational system of government.

That more rational system of measurement, whose units are easily defined and just as easily interconverted, is the *metric system* of weights and measures. Its ease of use is so compelling that the metric system has been adopted as the national system in most countries of the world and has become the universal system of measurement in science. The word itself, *metric*, comes from the Greek word *metron*, "to measure."

A Natural Standard of Length: The Meter

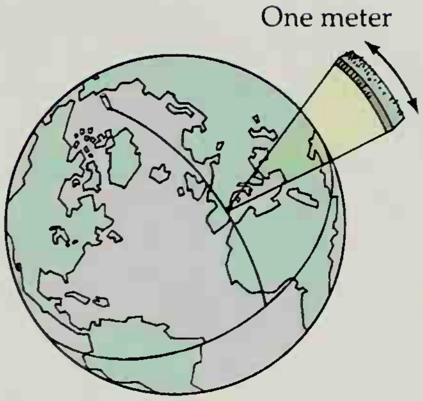


Figure B–1
The original definition of the meter: 1/10,000,000th of the distance from the equator to the pole.

In 1791 the French revolutionaries—by now the French government—asked a commission of 12 learned scientists to develop this new set of weights and measures, to be based on readily available standards and ease of interconversion of units. The commission chose the earth itself as the fundamental standard for all measurements of length. The *meter*, the unit of length they proposed, was to be exactly 10^{-7} (1/10,000,000th) of the distance from the Earth's equator to either of its poles (Fig. B–1).

The meter and all other units of length in the metric system can be interconverted by multiplying or dividing by ten or by some power of ten. There are, for example, 100 *centimeters* to the meter just as, in monetary terms, there are 100 cents to a dollar. Further, 1000 meters make up a *kilometer*. (The prefix *kilo-* is derived from the Greek *khilioi*, "a thousand.") With a relationship based purely on powers of ten it's easy enough to see that there must be 100 × 1000, or 100,000, centimeters to a kilometer. This decimal relationship makes interconversions among metric units extraordinarily simple.

A Natural Standard of Mass: The Gram

Units of area and of volume are the squares and cubes, respectively, of units of length. A square with a side that's 1 kilometer long has an area of 1 square kilometer (1 km^2). Similarly, a cube whose side is 1 meter has a volume of 1 cubic meter (1 m^3). A cube just 1 centimeter on a side is a cubic centimeter (1 cm^3 or 1 cc). A more convenient metric unit of volume, the one in general scientific use today, is the *liter*, a word derived from an ancient French measure of volume, the *litron*. The liter is the volume of a cube almost exactly (as we will soon see) 10 centimeters on a side.

For the unit of mass the French commission chose the *gram*, which was to be the mass of 1 cubic centimeter of water, measured at the temperature of water's maximum density, 4°C. (The word *gram* comes from the Latin and the Greek *gramma*, "a small weight.") For ease of measurement, the actual standard of mass that was adopted was the *kilogram*, the mass of a cube of water 10 cm on edge and therefore occupying a volume of 1000 cm^3. Metric units of mass, like those of length, are all multiples of ten and are easily interconverted.

On December 10, 1799, near the close of the 18th century, the French Legislative Assembly adopted these natural standards of measurement as the metric system, to be used as the legal and official system of weights and measures of the French people. The idealism of the French Revolution was well on its way to touching every scientific measurement made since then.

The Return to Arbitrary Standards: Making Light of the Meter

It wasn't easy, back at the beginning of the 19th century, to measure accurately the arc of the earth from the equator to the pole. But the arc was measured nonetheless, with the best contemporary science and technology available, and a platinum bar was cut and polished to exactly 1 meter. This bar was the standard for the length of the meter during most of the 19th century.

Toward the end of the 19th century came the realization that the platinum bar might be wearing a bit here and there and that its reliability might not last much longer, so a new and sturdier bar was prepared as the standard for the meter. Since it was far easier to duplicate the meter of the old platinum standard than to measure the arc of a quarter of the earth's meridian, and since it had become apparent that the original measurement of the arc—the one that produced the first meter—wasn't very accurate by contemporary standards, the meter was redefined late in the 19th century as the distance between two etched lines on a well-made metal bar. The distance between these two lines duplicated exactly, at least to the best technology available in the late 19th century, the length of the original meter. This 19th-century standard, though, was defined with no idealistic reference to the distance between the equator and the pole, and without even a mention of the original platinum bar. As in olden days, the meter was simply and arbitrarily defined as the distance between two scratches on a certain metal bar, and that was that.

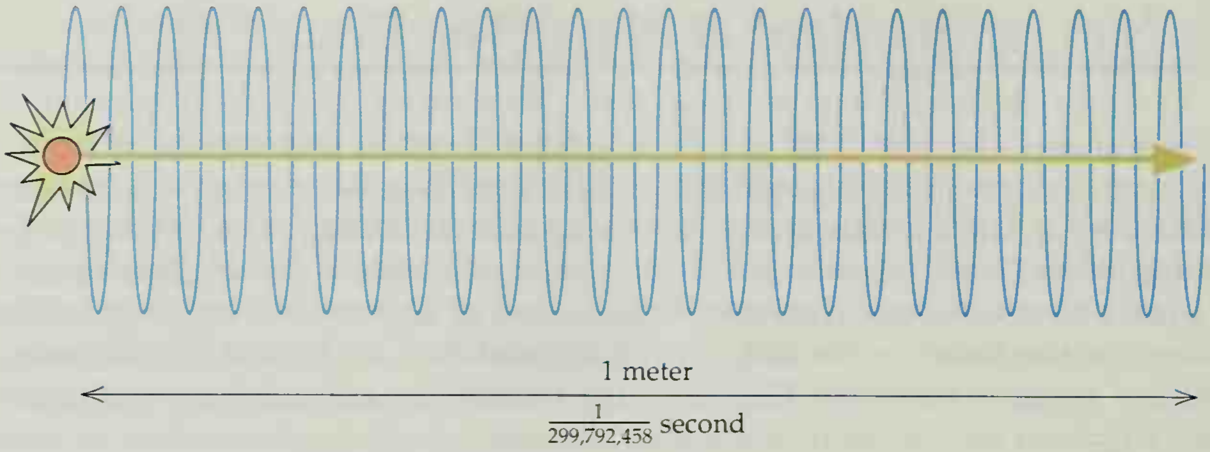


Figure B–2
The modern (1984) meter: the distance light travels, in a vacuum, in 1/299,792,458th second.

Today, with more technical knowledge than was available to 19th-century scientists, and perhaps with more wisdom than was possessed by the French revolutionary idealists, science has abandoned concrete, physical standards of length in favor of an enormously accurate and reproducible standard, the speed of light in a vacuum. Today's meter is defined as the distance covered by light as it travels in a vacuum for exactly 1/299,792,458th of a second (Fig. B–2). It's a far cry from the revolutionary 10^{-7} of the arc of the earth stretching from the equator to the pole, or even from the distance between two lines on a metal rod, but it's the same as the length separating those two etched lines, and it's now a meter we can live with.

Another Arbitrary Standard: The Kilogram

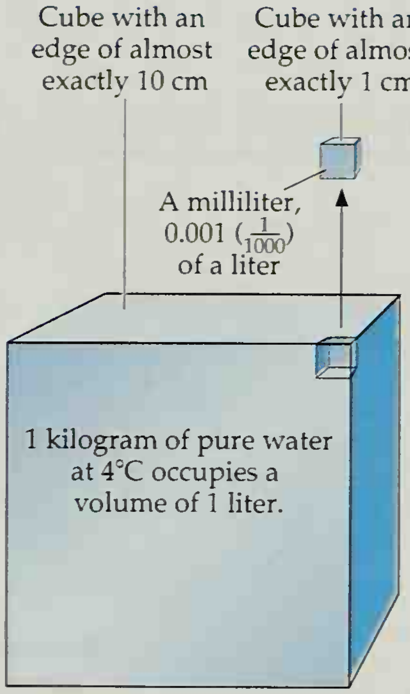


Figure B–3
The liter and the milliliter.

For mass, the original metric ideal was to combine the unit of mass with the unit of length through the density of water. The kilogram was to be the mass of a cube of water exactly a tenth of a meter on edge. It was an elegant combination of cleverness and simplicity. It didn't work.

As with the measurement of the arc of the earth, the problem lay in the matter of accuracy. Early in the 19th century a platinum cylinder was fabricated with a mass identical to that of exactly 1000 cm^3 of water (as measured in those days) at the temperature of water's greatest density. This mass was declared to be the standard for exactly 1000 g, or 1 kg. Later in the 19th century, with progress in the science of measurement, the volume of exactly 1 kg of water—again, at the temperature of its greatest density—was found to be 1000.028 cm^3, off just a bit from the precise 1000 cm^3 of the metric ideal.

That's certainly not enough of a difference to affect anything in our daily lives, but it's an error large enough to give a scientist sleepless nights. With the mass of the kilogram firmly established and easy to reproduce, the simplest solution was to change the standard unit of volume. Now the standard *liter* (abbreviated L) is defined as the volume of exactly 1 kg of pure water at the temperature of its greatest density and also at 1 atmosphere of pressure. A smaller unit of volume, often more convenient, is the *milliliter* (mL), just one-thousandth of a liter (Fig. B–3). There's no noticeable difference between the milliliter and the cubic centimeter in the chemistry we live with daily, but to the theory and practice of a very accurate science the milliliter wins out over the cubic centimeter.

The English System and the Metric System

In the United States the metric system has been a legal system of weights and measures since July 28, 1866. But an older, American adaptation of the English system has been in common use for so long that the two systems, English and metric, are now in competition in the United States. Following are some useful comparisons of the two and more detail on the various metric units.

Metric Units of Length

Unit	Prefix	Abbreviation	Multiple of the Meter
millimeter	milli = one-thousandth	mm	0.001 or 1/1000th of a meter
centimeter	centi = one-hundredth	cm	0.01 or 1/100th of a meter
decimeter	deci = one-tenth	dm	0.1 or 1/10th of a meter
meter		m	
kilometer	kilo = one thousand	km	1000 meters

$$1 \text{ km} = 1000 \text{ m} = 100{,}000 \text{ cm} = 1{,}000{,}000 \text{ mm}$$

$$1 \text{ m} = 100 \text{ cm} = 1000 \text{ mm}$$

$$1 \text{ cm} = 10 \text{ mm}$$

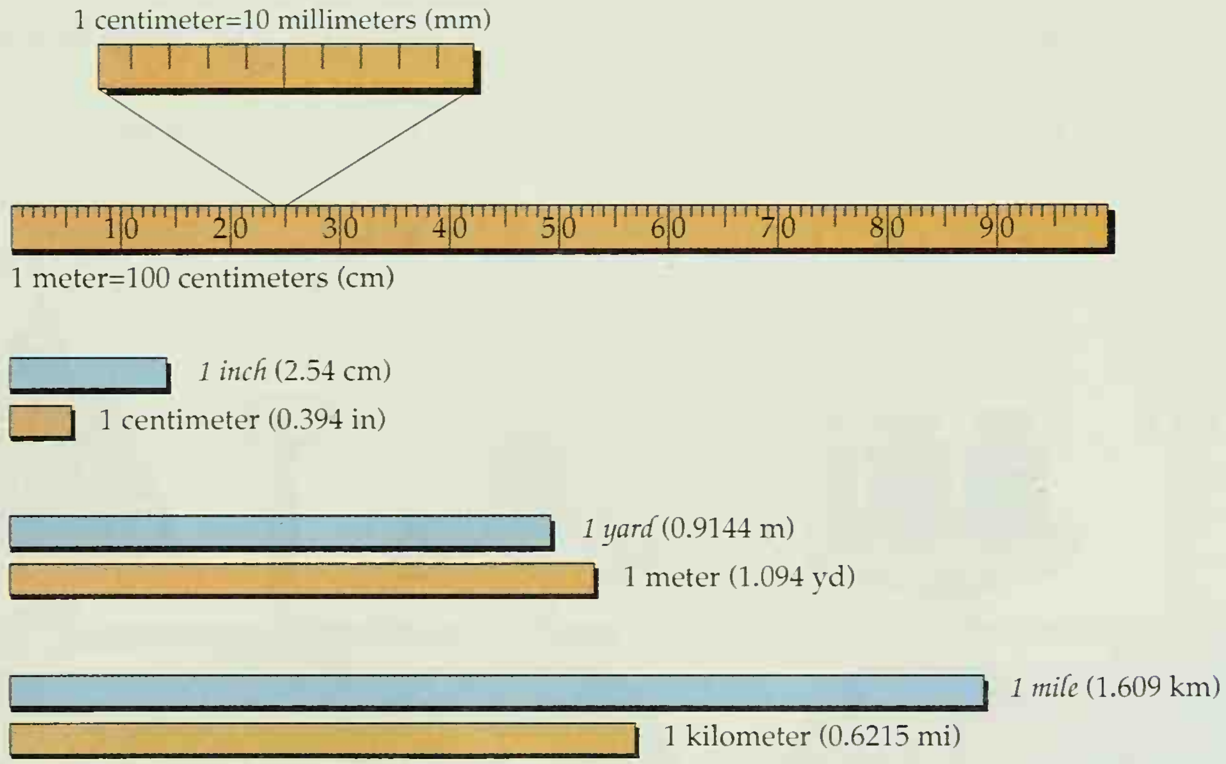


Figure B–4
Measures of length.

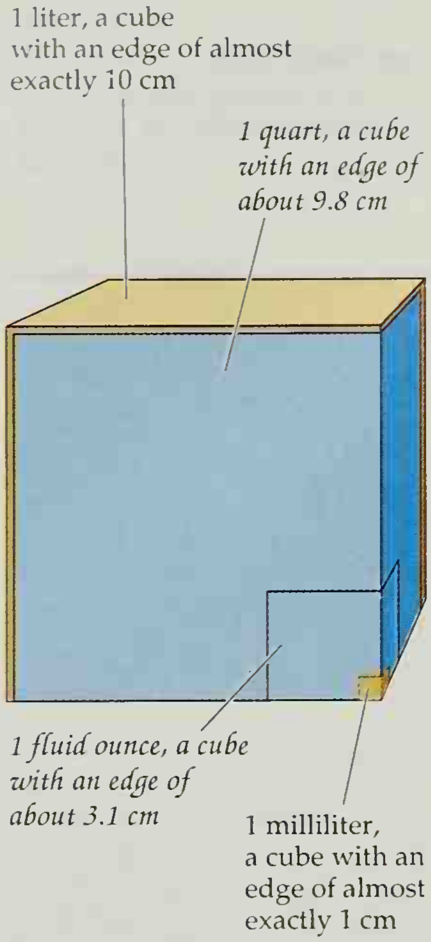


Figure B–5
Measures of volume.

Length in the Metric System and in the U.S.-English System

1 inch = 2.54 cm
1 cm = 0.394 inch

1 foot = 30.48 cm

1 yard = 91.44 cm = 0.9144 m
1 m = 39.37 inches = 1.094 yard

1 mile = 1.609 km
1 km = 0.622 mile

Metric Units of Volume

Unit	Prefix	Abbreviation	Multiple of the Liter
milliliter	milli = one-thousandth	mL	0.001 = 1/1000th of a liter
liter		L	

Volume in the Metric System and in the U.S.-English System

1 fluid ounce = 29.6 mL
1 mL = 0.0338 fluid ounce

1 L = 1.057 quart
1 quart = 0.946 liter

Metric Units of Mass

Unit	Prefix	Abbreviation	Multiple of the Gram
milligram	milli = one-thousandth	mg	0.001 = 1/1000th of a gram
gram		g	
kilogram	kilo = one thousand	kg	1000 grams

Figure B–6
Measures of mass.

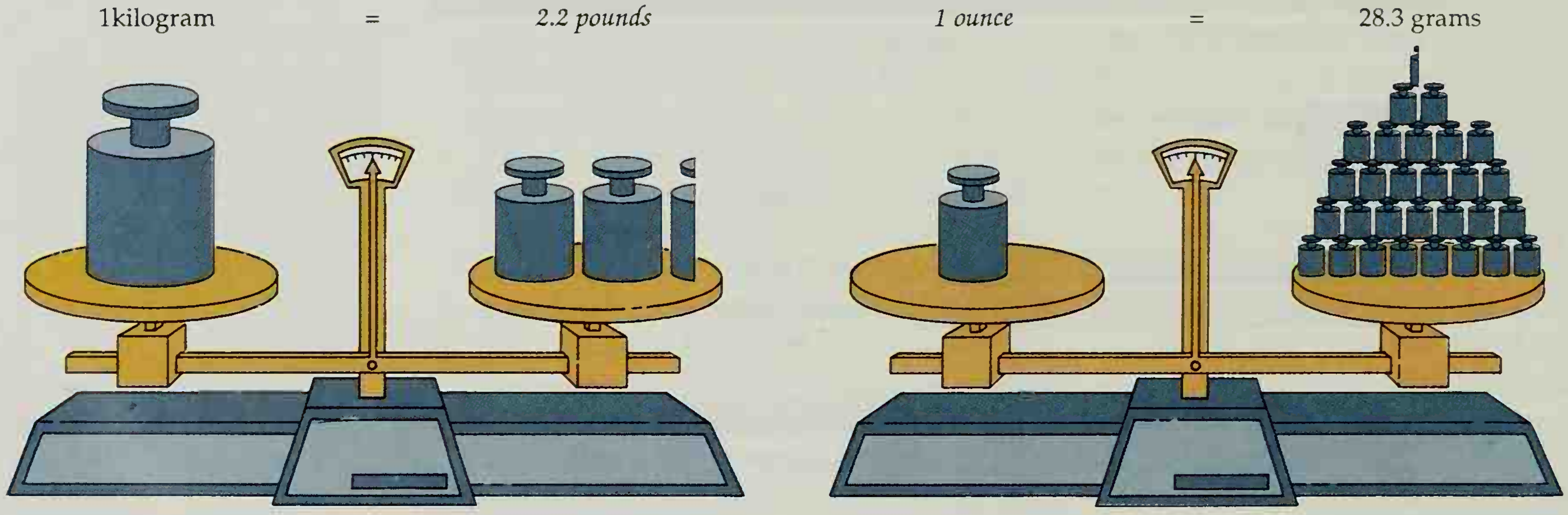


Figure B–7
Typical measurements.

Mass in the Metric System and in the U.S.–English System

1 ounce = 28.3 g
1 g = 0.0353 ounce

1 pound = 0.454 kg
1 kg = 2.20 pounds

Figure B–7 shows some ordinary quantities in both metric and U.S.–English units.

Appendix C

Using Units Cancellation

PETER PIPER PICKED
A PECK OF
PICKLED PEPPERS

Plenty of mathematical problems sound like that old tongue twister, "If Peter Piper picked a peck of pickled peppers, how many pecks of pickled peppers did Peter Piper pick?" Having the right facts and knowing how to use them make working the simple arithmetic of most chemical problems a lot easier than repeating this or any other tongue twister. The puzzle of deciding what to do with the numbers given in the problem is solved easily by using the technique of *units cancellation.*

Units cancellation is no more than the procedure of canceling out any unit that appears both in the numerator of one measure and in the denominator of another. It's a technique that we use, often unconsciously, in working with simple fractions. To return to Peter Piper for an illustration, suppose he picks three-eighths of a peck of pickled peppers in an hour. If Peter works steadily at this rate, how many peppers will he have picked in two-thirds of an hour? We get the answer by multiplying his rate of picking, $\frac{3}{8}$ peck/hour, by the amount of time he works, $\frac{2}{3}$ hour. Writing out the multiplication, we get

$$\frac{3\text{ peck}}{8\text{ hour}} \times \frac{2\text{ hour}}{3}$$

We know that we can divide both the numerator and the denominator by 3 without changing the product of the two fractions. In effect, these two divisions cancel the 3's that appear in the numerator of one fraction and in the denominator of the other

$$\frac{\cancel{3}\text{ peck}}{8\text{ hour}} \times \frac{2\text{ hour}}{\cancel{3}}$$

This gives us

$$\frac{1\text{ peck}}{8\text{ hour}} \times \frac{2\text{ hour}}{1}$$

Now we divide both the numerator and the denominator by 2 to get the answer.

$$\frac{1\text{ peck}}{\cancel{8}\text{ hour}} \times \frac{\cancel{2}\text{ hour}}{1} = \tfrac{1}{4}\text{ peck}$$

We can use this same principle, one in which we divide both the numerator and the denominator by a common term, in the units cancellation technique. In the problem we are dealing with here, we divide both the numerator and the denominator by the same factor—the unit *hour*—to get the answer in the unit we want, *peck*.

$$\frac{1\text{ peck}}{4\ \cancel{\text{hour}}} \times \frac{\cancel{\text{hour}}}{} = \tfrac{1}{4}\text{ peck}$$

Now let's turn from the world of tongue twisters to the real world. Suppose you're going to drive a car that gets 20 miles/gallon on a trip of 500 miles and you use gasoline that costs 90 cents/gallon. What's the total cost of the gasoline for the trip? What do you multiply and what do you divide to get the answer? It's easy with units cancellation.

First, decide what measurement holds in its numerator the unit you want in your final answer. The unit we want here is cents, so start with 90 cents/gallon. Now cancel out the gallon of the denominator by dividing by the term (20 miles/gallon). Carry out this division by *multiplying* by the term's reciprocal (gallon/20 miles):

$$\frac{90\text{ cents}}{\text{gallon}} \times \frac{\text{gallon}}{20\text{ miles}}$$

With cancellation of the unit *gallon*, you learn that the trip is costing you

$$\frac{90\text{ cents}}{20\text{ miles}}$$

Now multiply by 500 miles to cancel out *miles* and you end up with 2250 cents for the entire trip.

$$\frac{90 \text{ cents}}{\cancel{\text{gallon}}} \times \frac{\cancel{\text{gallon}}}{20\ \cancel{\text{miles}}} \times \frac{500\ \cancel{\text{miles}}}{} = 2250 \text{ cents}$$

By recognizing that 100 cents make up one dollar, we express 2250 cents more conveniently as \$22.50.

$$\frac{2250 \text{ cents}}{} \times \frac{1 \text{ dollar}}{100 \text{ cents}} = \$22.50$$

By writing out all the fractions in one long step (with units cancellation always in mind), you can cancel all the units—except the one you want to end up with—in one swoop and have all the arithmetic in front of you. This way we can see that the entire problem becomes simply

$$\frac{90 \text{ cents}}{\text{gallon}} \times \frac{\text{gallon}}{20 \text{ miles}} \times \frac{500 \text{ miles}}{} \times \frac{1 \text{ dollar}}{100 \text{ cents}} = \$22.50$$

With the technique of units cancellation well in hand, we can turn to a problem that involves a chemical principle. Let's look at the question at the end of Section 9.5.

QUESTION

The sun is 150,000,000 km from the earth and the diameter of a penny is 1.9 cm. If Avogadro's number of pennies were used to build a road from the earth to the sun and the road were just one layer of pennies deep, how many pennies wide would the road be? ______________________________

To solve this problem we have to find out how many pennies, 1.9 cm in diameter, we could string out from the earth to the sun. Then, knowing the value of Avogadro's number (Section 9.5), we can calculate how many of these strings of pennies we could lay out, side by side.

We want an answer to the first part of the problem in units of *pennies*, so we start with the length of 1.9 cm/penny and use metric factors (Appendix B) in canceling units of length. Notice that in the following we start with penny/1.9 cm so that the unit *penny* remains in the numerator.

$$\frac{\text{penny}}{1.9 \text{ cm}} \times \frac{100 \text{ cm}}{\text{m}} \times \frac{1000 \text{ m}}{\text{km}} \times \frac{150{,}000{,}000 \text{ km}}{}$$

Since it's much easier to work with powers of ten in this case (Appendix A), we'll rewrite this as

$$\frac{\text{penny}}{1.9 \text{ cm}} \times \frac{10^2 \text{ cm}}{\text{m}} \times \frac{10^3 \text{ m}}{\text{km}} \times \frac{1.5 \times 10^8 \text{ km}}{} = 0.789 \times 10^{13} \text{ pennies}$$

This gives us 0.789×10^{13} (or 7.89×10^{12}) pennies in one line, from here to the sun. Since Avogadro's number of pennies amounts to 6.02×10^{23} pennies our next calculation shows how many of these lines Avogadro's number of pennies would form. The road of pennies that would stretch from the earth to the sun would be

$$\frac{\text{line of pennies}}{7.89 \times 10^{12}\ \text{pennies}} \times \frac{\text{Avogadro's number of pennies}}{} \times \frac{6.02 \times 10^{23}\ \text{pennies}}{\text{Avogadro's number of pennies}} = 0.763 \times 10^{11}\ \text{lines of pennies}$$

Avogardro's number of pennies would therefore be enough to form a roadway 76,300,000,000 pennies wide, from the earth to the sun.

One final example rounds out Appendix C with a problem in the chemistry of combustion. In Section 7.8 we see that methane burns to give carbon dioxide and water according to the equation

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Notice that for every molecule (or mole) of CH_4 that burns, *two* molecules (or moles) of water form. Our question is, "What weight of water forms when 8 g of methane burn in air?" Using units cancellation we get out answer easily and quickly. We want a weight of water as our answer, so we'll start with the fact that there are 18 g of water per mole of water:

$$\frac{18\ \text{g water}}{\text{mol water}}$$

Since we know from the chemical equation that we get 2 moles water per mole of methane, or (2 mole water)/(mol methane), we can use this factor to cancel out the unit *mol water*. Then we'll use the molecular weight of methane, 16 amu, and the weight of methane that we start with, 8 g, to arrive at our units-canceled answer.

$$\frac{18\ \text{g water}}{\text{mol water}} \times \frac{2\ \text{mol water}}{\text{mol methane}} \times \frac{\text{mol methane}}{16\ \text{g methane}} \times \frac{8\ \text{g methane}}{} = 18\ \text{g water}$$

Once again, units cancellation gives us the answer.

EXERCISES

Work the following using the information contained in Appendixes A to C and the contents of Chapters 1 to 9.

1. What is the distance from New York to San Francisco, expressed in centimeters? (See Fig. B–7.)

2. Light travels at about 3×10^{10} cm/sec in a vacuum. A *light-year* is defined as the distance that light travels in a vacuum in 1 year. What is length of a light-year (a) in meters? (b) in miles?

3. Hydrochloric acid, HCl, forms as hydrogen and chlorine combine according to the chemical equation

$$H_2 + Cl_2 \longrightarrow 2HCl$$

a. What weight of chlorine combines with 40 g of hydrogen to form HCl?
b. What weight of HCl forms when 71 g of chlorine react with an excess of hydrogen?

4. Water forms when hydrogen and oxygen combine according to the chemical equation

$$2H_2 + O_2 \longrightarrow 2H_2O$$

What weight of water forms when 40 g of hydrogen burn in an excess of oxygen?

5. Calculate the number of centuries in the length of time equivalent to Avogadro's number of seconds. Compare your answer with the value given in Section 9.5.

Appendix D

Significant Figures

BUDGETING FOR GASOLINE

Suppose you're going to drive from San Francisco to New York and you want to know how much you should budget for gas. You're driving a car that gets about 19 miles per gallon on the highway, and as a rough estimate you guess that gasoline will cost about $1.25 per gallon. (That's just a guess, but we'll stick with it in the calculation.) A check of a road atlas shows that the distance from San Francisco to New York is 2934 miles. What's the best estimate of the cost of the gasoline: $193.02631, $193.03, $193, $190, or about $200? The first figure, $193.02631, comes from using 19 miles per gallon, $1.25 per gallon, 2934 miles, and a hand calculator. The others come from rounding the answer to different degrees of approximation.

The best answer comes from an understanding of *significant figures*, also called *significant digits*. We'll use both terms here. *Digits* are the symbols from 0 to 9 that make up all the numbers we work with. *Significant* digits are the digits in any number that have real meaning, that we can rely on with confidence. We'll examine what significant figures are and how and why we use them in the measurements and calculations of science and of everyday life.

The Number of Significant Figures

The key to working with measurements and calculations lies in knowing the number of significant figures in any particular quantity. To determine this, we focus on zeros and on the digits that aren't zero, the nonzero digits from 1 to 9. These are the rules to follow:

Rule 1: All nonzero digits are significant. The number 5692 contains four significant figures. The number 27,477.2941 contains nine significant figures. There's one significant figure in 6.

Rule 2: All zeros that lie between nonzero digits are significant. The number 3904 contains four significant figures. The number 40,028 has five, and so does 30,508. There are seven significant figures in 3,000,002.

Rule 3: None of the zeros that lie to the left of the first nonzero digit are significant, regardless of the position of the decimal. There are four significant figures in 0.002911, and five in 0.000039802. The number 10.0083 has six significant figures by rule 1.

Rule 4: Zeros to the right of the last nonzero digit are significant if they lie to the right of a decimal point. There are four significant figures in 341.0, five in 202.40, and seven in 330.0000.

Rule 5: Zeros to the right of the last nonzero digit but to the left of a decimal point may or may not be significant, depending on the context.

Confusion can come by rounding off numbers for approximations. If someone asks you how far you'll have to drive on your trip from San Francisco to New York and you answer "2934 miles," you're using four significant figures. But if you answer "about 3000 miles," you're using only one. Here, the word *about* gives your friend a cue that this is an approximate answer, probably with only one significant digit. Suppose, on the other hand, that you look up road mileages in an atlas and find that the distances from Cincinnati to Atlanta, Boston, Dallas, and Detroit are, respectively, 440, 840, 920, and 259 miles. Because you're using a reference book and the distance to Detroit is given to three significant figures, you can assume that the other distances are also given to three significant figures.

In scientific discussions, powers of 10 are used to indicate significant zeros. For example, 3×10^2 represents 300 to one significant figure; 3.00×10^2 indicates 300 to three significant figures.

Exact Numbers: Counting and Defining

Numbers we use in counting and in defining other quantities are assumed to be exact and to have an infinite number of significant figures. If you *count* the number of pages in a book and find exactly 573, you report this as "573." In this case, "573.000 pages" is meaningless. (Naturally, if you *measure* the length of some typed material and find that it runs over three pages, to 3.76

pages for example, that's another matter. That value comes from a measurement, which we'll get to shortly.) This procedure holds with money as well. We might find, for example, that something costs $34.83. We can look at this as an exact count if we recognize that it's equivalent to exactly 3483 cents. A dollar is, after all, *defined* as the equivalent of 100 pennies. It wouldn't make sense to speak of the cost as $34.830 or 3483.0 pennies, for example, since 3483 cents is an exact count of pennies.

Like counting, defining quantities also involves exact numbers, with an infinite number of significant digits. There are exactly 100 pennies to the dollar, 60 seconds to a minute, 100 cm to a meter, 1000 g to a kilogram, and the like. We say that 60 seconds make up 1 minute and understand that both "60 and "1" are exact numbers.

Approximate Numbers: Measuring

Significant figures are vital when we come to measurements, because all measurements involve some degree of inaccuracy. You can see why if you try this. Get a ruler and a dollar bill and have four friends work with you in measuring the width of the bill, edge to edge. You might find that the bill runs between 155 and 156 mm in length. You and your friends would have to estimate down to the tenth of a millimeter the part of the bill that falls between 155 and 156 mm. You'd get a set of five measurements that would be identical in the first three significant figures (155), but that would vary in your estimates of the fourth, the tenths of a millimeter. You might get a set of measurements like this:

Person	Measurement
1	155.7 mm
2	155.3 mm
3	155.5 mm
4	155.6 mm
5	155.3 mm

Knowing that each of you measured the bill to the best of your ability, and that the fourth digit is an estimate, you would naturally take an average of the five measurements. Adding up all five gives 777.4 mm; dividing by 5 gives an average value of 155.48 mm. That's one more significant figure than any of your five measurements. If your measurements are reliable to 0.1 mm, the average is also reliable to 0.1 mm. You can't very well get an average that's trustworthy to 0.01 mm from individual measurements that are good to only 0.1 mm. So you round the average to 155.5 mm. That's your best estimate of the length of the bill, as measured by five different people. The result of any mathematical manipulation of a set of measurements can't be any more reliable than the least reliable measurement. The end result must not contain more significant figures those in the least reliable measurement.

Rounding

In rounding numbers we use the following rules. (In rounding 155.48 mm to 155.5 mm you used rule 7):

> *Rule 6:* If the digit dropped is less than 5, drop it and all that follow without changing the remaining digits. For four significant figures you would round 1.4033 to 1.403, and 76.584997 to 76.58.
>
> *Rule 7:* If the digit dropped is greater than 5, or if it's 5 and any nonzero digit follows (also to be dropped), increase the last remaining digit by one. For four significant figures, 0.0029817 becomes 0.002982, and 2848.50003 becomes 2849.
>
> *Rule 8:* If the digit dropped is 5 and only zeros follow it, do not change the last remaining digit if it's even; raise it by one if it's odd. Thus, for four significant digits, 34.835000 becomes 34.84, and 937.45 becomes 937.4.

Adding and Subtracting

In adding and subtracting, line up the decimal points and round all numbers down to the one with the fewest decimal digits. To add

$$\begin{array}{l} 45.9930 \\ 5.3501 \\ 25.6 \\ \underline{11.45} \end{array}$$

we recognize that 25.6 has only a single significant digit to the right of the decimal and we round the numbers to

$$\begin{array}{lr} & 46.0 \\ & 5.4 \\ & 25.6 \\ & \underline{11.4} \\ \text{for the total} & 88.4 \end{array}$$

For subtraction we have

$$\begin{array}{r} 12{,}983.006 \\ \underline{-\ \ 1{,}197.355079} \end{array}$$

which rounds to

$$\begin{array}{r} 12{,}983.006 \\ \underline{-\ \ 1{,}197.355} \\ 11{,}785.651 \end{array}$$

Multiplying and Dividing

Regardless of the locations of decimal points, the result must have no more significant digits than those in the factor with the smallest number. Here, two slightly different approaches give the same result. In one, carry out the operation, then round off the result to the same number of significant digits as in the least reliable factor:

$$13.2 \times 242.7 \times 0.023 = 73.68372$$

We round off the answer to 74 since the factor 0.023 has only two significant figures. In another, simpler approach, before you carry out the multiplication or division, round off factors to one digit more than the number in the least reliable factor. With this our multiplication becomes $13.2 \times 243 \times 0.023 = 73.7748$, which once again rounds to 74. This second method gives the same result with a little less work. For division, we have by the first method (and a hand calculator)

$$\frac{143.751}{62} = 2.3185645, \text{ which rounds to } 2.3$$

Using the second, simplified approach we have

$$\frac{143.751}{62} \text{ which rounds to } \frac{144}{62} = 2.3225806, \text{ or again } 2.3$$

Now back to our original problem. Since the factor with the smallest number of significant figures in your trip from San Francisco to New York is the 19 miles per gallon you estimate for your mileage (with its two significant figures), your best guess of the cost also has two significant figures, $190. But common sense also comes into play here. Since your mileage might drop as you go, and since gasoline prices could change during your travel, you ought to play it safe and assume the trip will cost $200 in gas. It would probably be wise to budget even a few dollars more. Common sense is often far more significant than any figures we work with.

EXERCISES

1. Add the following.

a. 21.0884 + 11.79 + 1.34508 + 14.6003 + 33.0650
b. 0.00330 + 1.002001 + 5.704520 + 0.10445
c. 13.6 + 22.9 + 9.45 + 3.350327 + 4

2. Subtract the following.

a. 14.0409 − 8.723
b. 202.3000 − .0040
c. .0072506 − .000419

3. Multiply the following.

a. 2.78 × 0.0035701 × 4.6
b. 3.7 × 414 × 2.601
c. 2 × 7 × 0.035108

4. Divide the following.

a. 6.4/9.2
b. 5.750/3.6
c. 0.01090/0.003266

Appendix E

Working with Avogadro's Number

A REMARKABLE CALCULATION

In effect, Exercise 34 of Chapter 9 asks this question:

- What is the total combined sum of all the protons and all the neutrons in the body of a 165-pound person?

Working this problem requires a good grasp of the contents of Chapter 9 and facility with the material of Appendixes A to D. We know from Chapter 9 that one mole of a chemical substance contains Avogadro's number of chemical particles. We also know that one mole of a substance consists of its atomic, molecular, or ionic weight expressed in grams. These masses are ordinarily expressed in atomic mass units (amu). Since the mass of a proton and of a neutron is 1 amu (Section 2.4), one mole of protons must have a mass of one gram and, similarly, one mole of neutrons must also have a mass of one gram.

What we need to do, then, is calculate the total weight of a 165-pound person in units of grams and we will have the combined sum of the moles of protons and the moles of neutrons in the body. (Recall that the mass of the electron is negligible compared with the mass of the proton or the mass of the neutron; see Section 2.4).

Knowing that each mole of chemical particles contains Avogadro's number of particles gives us the answer we're looking for. The following sequence of fractions makes clear the units cancellation required:

$$\frac{6.02 \times 10^{23} \text{ particles}}{\text{mol}} \times \frac{\text{mol}}{1 \text{ g particles}} \times \frac{10^3 \text{ g}}{\text{kg}} \times \frac{\text{kg}}{2.20 \text{ pound}} \times \frac{165 \text{ pounds}}{\text{body}}$$
$$= 452 \times 10^{26} \text{ particles/body}$$

or a combined total of 4.52×10^{28} protons and neutrons in the body of a 165-pound person.

Glossary

A

Absolute zero The lowest possible temperature; 0 K, or −273°C.

Acceptable daily intake (ADI) One percent of the maximum daily amount of a food additive that produces no observable effect on laboratory animals.

Acid By the Arrhenius definition, any substance that can produce a proton (hydrogen ion) in water. By the Brønsted–Lowry definition, any substance that can transfer a proton to another substance. By the Lewis definition, a chemical species capable of accepting a pair of electrons. Turns blue litmus red, tastes sour, and reacts with iron, zinc, and certain other metals to generate hydrogen gas.

Acid–base indicator A dye that changes, loses, or acquires color as a solution containing the dye changes in acidity or basicity.

Acidity constant (ionization constant, K_a) The ratio of the concentrations of the ionization products of an acid to the concentration of the un-ionized acid. It is a measure of the strength of the acid since it represents the fraction of the acid that ionizes.

Adipose tissue The fatty tissue of the body; it stores chemical energy at a ratio of about 3500 Cal per pound.

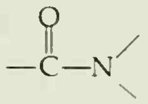
Aldehyde A class of organic compounds whose molecules contain a carbonyl group bonded to at least one hydrogen.

Alkaloid A basic, bitter-tasting, nitrogen-containing compound found in plants that produces physiological reactions of various kinds and intensities.

Alkane A hydrocarbon whose molecular formula fits the general formula C_nH_{2n+2}.

Alpha (α) Particle A high energy helium nucleus travelling at 5%–7% the speed of light.

Amide An organic compound containing the *amide* functional group,



$$—\overset{\overset{\displaystyle O}{\|}}{C}—N\langle$$

Amine An organic base whose molecules bear the *amino* group, $—NH_2$.

Amino acid A compound whose molecules carry both a carboxyl group and an amino group. Amino acids have properties of both acids and bases.

Ampere (amp) A unit of electrical current; the rate of flow of electrons.

Analgesic A substance that reduces or eliminates pain.

Anion A negatively charged ion.

Anode The part of a battery that provides the electrons flowing through the external circuit.

Anti-inflammatory agent A substance that reduces or eliminates inflammations.

Antioxidant A chemical so easily oxidized itself that it protects other chemicals from oxidation.

Antiperspirant A substance that inhibits sweating and keeps the body relatively dry.

Antipyretic A substance that reduces or eliminates fever.

Aromatic compound A compound that contains at least one benzene ring as part of its molecular structure.

Aromatization The conversion of cyclohexane rings into aromatic rings.

Aspirin The common name or trade name of *acetylsalicylic acid*, an analgesic, antipyretic, and anti-inflammatory medication.

Atmospheric pressure At any particular point on or above the earth's surface, the pressure generated by the combined weight of all the atmospheric gases above that point.

Atom The smallest particle of an element that can be identified as that element.

Atomic weight The average of the masses of all an element's isotopes, weighted for the abundance of each.

Atomic number The sum of all of an atom's protons.

Atomic mass unit (amu) One-twelfth the mass of the most common isotope of carbon.

Avogadro's number The experimentally determined number of chemical particles in a mole: 6.02×10^{23}.

Avogadro's law Equal volumes of gases (at the same temperature and pressure) contain equal numbers of atoms or molecules.

B

Background radiation The low level of natural radiation to which we are all exposed.

Balanced equation An equation containing the same number of atoms of each of the elements among both the reactants and the products.

Base By the Arrhenius definition, any substance that can produce a hydroxide ion in water. By the Brønsted–Lowry definition, any substance that can accept a proton. By the Lewis definition, a chemical species capable of donating a pair of electrons. Turns red litmus blue, tastes bitter, and feels slippery when dissolved in water.

Beta (β) particle A high energy electron moving at up to 90% the speed of light.

Binary compound A compound made up of two elements.

Binding energy The energy that holds an atom's nucleus together as a coherent whole; the energy equivalent of an atom's mass defect.

Biodegradable A substance that can be converted, by the action of microorganisms within the environment, into the simpler substances that form our natural environment.

Boiling point The temperature at which a liquid boils to become a gas, and at which the gas condenses to become a liquid, usually measured at normal atmospheric pressure.

Boyle's law With the temperature and the number of moles of a quantity of gas held constant, the volume of the gas varies inversely with its pressure.

Breeder reactor A nuclear reactor that produces more fissionable fuel than it consumes.

Buffer A combination of a weak acid or a weak base and one of its salts.

"Buffered" aspirin A combination of acetylsalicylic acid and one or more bases. The combination accelerates the disintegration of the tablet.

C

Caffeine An alkaloid that occurs in coffee beans and in tea leaves. It stimulates the central nervous system and heightens a sense of awareness.

Calorie The amount of heat (or energy) needed to raise the temperature of one gram of water by one degree Celsius. When capitalized, it represents 1000 calories.

Carcinogen A cancer-causing agent.

Catalyst A substance that increases the rate of a reaction but is not itself a reactant.

Catalytic cracking A process by which large hydrocarbon molecules are converted into two or more smaller hydrocarbon molecules.

Catalytic hydrogenation The addition of hydrogen atoms to atoms joined by double or triple bonds, through the use of a catalyst.

Catalytic reforming A process by which hydrocarbon molecules are reorganized into more useful molecular structures of the same carbon content.

Cathode The part of a battery that receives the returning electrons from an external circuit.

Cation A positively charged ion.

Chain reaction A continuing series of nuclear fissions that occurs when neutrons released in the fission of one atom cause fission among several additional atoms, which in turn release still more neutrons and produce still more fissions, and so on.

Charles' law With the pressure and the number of moles of a quantity of gas held constant, the volume of the gas varies directly with its absolute temperature.

Chemical formula A sequence of chemical symbols and subscripts that shows what elements are present in a compound and the ratio of their ions in a lattice, or the actual number of their atoms in an molecule.

Chemistry The branch of science that studies the composition and properties of matter and the changes that matter undergoes.

Chirality The characteristic "handedness" of right and left hands, as applied to chemical structures.

Circuit The path electrons follow.

Colloid A mixture made up of particles of one substance dispersed throughout another. The particles of the dispersed substance range in diameter from about 10^{-7} to 10^{-4} cm.

Cologne A highly diluted, inexpensive version of a perfume.

Complementary protein A combination of incomplete or low-quality proteins that, taken together, provide about the same ratio of essential amino acids as do complete or high-quality proteins.

Complete protein (high quality protein) Protein that contains all the essential amino acids in about the same ratio as they occur, on average, in human proteins.

Compound A pure substance formed by the chemical combination of two or more different elements, in a specific ratio.

Compression ratio The ratio of the maximum volume of a cylinder's gasoline–air mixture at the beginning of the compression stroke to the volume of the compressed mixture as the spark plug fires.

Concentration The quantity of solute dissolved in a specific quantity, often a specific volume, of solution.

Corrosion The erosion and disintegration of a material as a result of chemical reactions.

Cortex The central core of a strand of hair. The cortex forms the bulk of the strand and contains its pigments.

Cosmetic A substance applied directly to the human body to make it more attractive.

Covalent bond A bond consisting of a pair of electrons shared between two atoms.

Critical mass The minimum mass of fissionable material needed to sustain a chain reaction.

Crystal lattice The orderly, three-dimensional arrangement of the chemical particles that make up a crystal.

Cuticle The scaly sheath that covers the cortex of a strand of hair.

Cyclization A chemical process that converts noncyclic molecules into cyclic molecules.

D

Dalton's law The total pressure of a mixture of gases equals the sum of the partial pressures of each of the gases in the mixture.

Density The mass per unit volume of a substance. Density is normally stated in grams per milliliter or grams per cubic centimeter.

Deodorant A substance that masks or nullifies bodily odors.

Dermis The portion of the skin that contains nerves, blood vessels, sweat glands, and the active portion of the hair follicles, and also supports the upper layer, the *epidermis*.

Dextrorotation The rotation of a plane of polarized light to the right, or clockwise.

Disaccharide A molecule formed by the combination of two monosaccharides.

Distillation The process of purifying a liquid by boiling it in one container, condensing its vapors again to a liquid, and collecting the separated, condensed liquid in another container.

DNA (deoxyribonucleic acid) A polymeric acid that resides in the nucleus of every cell and that carries within its structure the genetic code.

Drug A chemical used medically for treating diseases and injuries, with the added connotation of narcotics and addiction.

E

Elastomer A substance that stretches easily and returns readily to its original shape.

Electric current A flow of electrons.

Electrochemical cell A cell or battery that produces electricity from chemical reactions.

Electrochemical reaction A reaction that can produce a flow of electrons from one location to another; a reaction that is caused by such a flow.

Electrolysis The decomposition of a substance by means of electricity.

Electrolyte A substance that conducts electricity when it is dissolved in water or melted.

Electron A subatomic particle with negligible mass and a charge of $1-$.

Electron structure The distribution of electrons in an atom's quantum shells.

Element A substance whose atoms all have the same atomic number.

Enantiomer One member of a pair of molecular structures that are nonsuperposable mirror images of each other.

Endorphin An opiate produced within the bodies of animals.

Endothermic reaction A reaction that absorbs heat as it proceeds.

Epidermis The upper layer of the skin.

Essential amino acid An amino acid that our bodies cannot synthesize from other chemicals and that we must obtain from our foods.

Exothermic reaction A reaction that releases heat as it proceeds.

F

Fallout Fine radioactive debris that is released into the atmosphere by nuclear explosions and accidents and that settles to the earth.

Family of compounds A group of compounds of similar structure and similar properties.

Family of elements A group of elements all of which lie in the same column of the Periodic Table and have similar chemical properties.

Fat-soluble vitamin One of a group of vitamins that are much more soluble in fats, hydrocarbons, and similar solvents than in water; vitamins A, D, E, and K.

Fat A solid triester of glycerol and fatty acids; constitutes one of the macronutrients of our foods and furnishes 9 Cal/g.

Fatty acid An acid formed on hydrolysis of fats and oils.

Fiber (also known as **bulk** and **roughage**) A component of our foods made up of the carbohydrate *cellulose;* indigestible because of our lack of the enzyme *cellobiase*.

Fischer projection A two-dimensional projection used to show the stereochemistry of a three-dimensional, chiral carbon.

Follicle A microscopic sac, under the surface of the skin, that holds the root of a strand of hair.

Food additive By a practical definition, anything intentionally added to a food to produce a specific, beneficial result.

Frequency The number of waves of electromagnetic radiation that pass a fixed point in a specific period.

Functional group A small set of atoms held together by covalent bonds in a specific, characteristic arrangement that is responsible for the principal chemical and physical properties of a compound.

G

Galvanic (bimetallic) corrosion Corrosion that results from the contact of two different metals separated by a thin layer of electrolyte.

Galvanizing A process that provides a protective zinc coating to metals.

Gamma (γ) ray A form of high-energy electromagnetic radiation; has no mass and carries no electrical charge.

Gas A phase or state of matter that takes both the shape and volume of the container that holds it.

Gay-Lussac's law When gases react with each other at constant temperature and pressure, they combine in volumes that are related to each other as ratios of small, whole numbers.

Genetic code The genetic information contained in the sequence of four bases strung out along the polymeric nucleic acid, DNA.

Genetic damage Damage that is transmitted to future generations.

Geometric isomer One of a pair of different compounds that have the same four groups bonded to the carbons of a double bond, but with different geometries.

Gluon A subatomic particle that holds quarks in their clusters.

GRAS list A list of food additives that are generally recognized as safe by a panel of experts, without having been subjected to laboratory testing.

Greenhouse effect The warming of the earth by solar radiation trapped as heat through the insulating effect of atmospheric gases.

H

Half-cell reaction Each of the oxidation and reduction reactions that combine to form a redox reaction.

Half-life The time it takes for exactly half of any given quantity of a radioisotope to decay.

Health food By one definition, a food that supplies a large number of micronutrients compared with its calories. This definition does not take into consideration the food's content of saturated fats, cholesterol, or other factors that can affect health.

Henry's law At a fixed temperature, the quantity of a gas that dissolves in a liquid depends directly on the pressure of that gas above the liquid.

Heroin *Diacetylmorphine,* a strongly addicting compound in which the two —OH functional groups of morphine have been converted into ester functional groups.

Hydrocarbon A compound composed exclusively of hydrogen and carbon.

Hydrogen bond A weak chemical bond formed through the attraction of a nitrogen, oxygen, or halogen atom for a hydrogen bonded to a different nitrogen, oxygen, or halogen.

Hydrolysis The decomposition of a substance, or its conversion to other substances, through the action of water.

Hydronium ion (H_3O^+) The ion that forms when a proton bonds to a water molecule.

I

Incomplete protein (low quality protein) Protein that is deficient in one or more of the essential amino acids.

Inorganic chemistry The chemistry of compounds that do not contain carbon.

Inorganic compound A compound that does not contain carbon.

Invert sugar A mixture of equal quantities of glucose and fructose.

Iodine number The number of grams of iodine that add to 100 g of a triglyceride.

Ion An atom or a group of atoms that carries an electrical charge.

Ionic bond A chemical bond resulting from the mutual attraction of oppositely charged ions.

Ionic compound A compound composed of ions.

Ionization The transformation of a covalent molecule into a pair of ions.

Ionizing radiation Any form of radiation capable of converting electrically neutral matter into ions.

Ionosphere A region of the upper atmosphere that is filled with ionized gases and that serves to reflect shortwave radio transmissions.

Isomer One of two or more different compounds that have the same molecular formula.

Isomerization The conversion of one compound into another of the same molecular formula.

Isotope An atom of any particular element that differs in mass number from other atoms of that same element.

J

Joule The work done by 1 watt of electricity in 1 second; equivalent to 0.24 cal.

Junk food By one definition, a food that supplies a large number of calories but few micronutrients.

K

Ketone A class of organic compounds whose molecules contain a carbonyl group bonded to two carbon atoms.

Kilocalorie 1000 cal; 1 Cal.

Kinetic energy The energy of motion.

Kinetic–molecular theory of gases A theory that explains the behavior of gases by assuming that they are made up of point-sized, perfectly resilient, constantly moving chemical particles.

Knocking A rapid pinging or knocking sound produced by pre-ignition or irregular combustion of the gasoline–air mixture in the cylinders of an internal combustion engine.

L

Law of Conservation of Energy Energy can be neither created nor destroyed as a result of chemical transformations.

Law of Conservation of Mass Mass can be neither created nor destroyed as a result of chemical transformations.

LD_{50} The amount of a chemical that kills exactly half of a large population of animals.

Le Châtelier's principle When a stress is placed on a system in equilibrium, the system tends to change in a way that relieves the stress.

Lethal dose The amount of a substance that causes death.

Levorotatory The rotation of a plane of polarized light to the left, or counterclockwise.

Lipoprotein A combination of a protein with cholesterol and triglycerides, in varying proportions, that carries these substances through the blood.

Liquid A phase or state of matter that retains its own volume but takes the shape of the container that holds it.

M

Mass A body's resistance to acceleration.

Mass defect The difference between the mass of the atom as a whole and the sum of the masses of all the individual protons, neutrons, and electrons that compose it.

Mass number The sum of the protons and neutrons in an atom's nucleus.

Medicine A chemical used medically for treating diseases and injuries.

Melanin The dark brown pigment of the skin and hair.

Melting point The temperature at which a solid melts to become a liquid, and at which the liquid crystallizes to become a solid.

Meta The orientation of substituents on a benzene ring that are on carbons separated from each other by a single ring carbon.

Micelle A submicroscopic globule or sphere distributed in large numbers throughout another substance, which is usually a liquid.

Micronutrient A component of food, especially a vitamin or a mineral, that we need in very small amounts for life and good health.

Mineral In nutrition, a chemical element we need for life and good health, other than the elements that make up the macronutrients (that is, other than carbon, hydrogen, oxygen, nitrogen, and sulfur).

Molarity The concentration of solute in a solution expressed as the number of moles of solute per liter of solution.

Mole The number of atoms of carbon-12 in exactly 12 g of carbon-12. In practice, the number of chemical particles contained in a quantity of any pure substance equal to its atomic, molecular, or ionic weight expressed in grams.

Molecular formula The chemical formula of a covalent compound.

Molecule A discrete chemical structure held together by covalent bonds.

Monomer One of a set of individual molecules that are linked to each other to form a polymer.

Monosaccharide The smallest molecular unit of a carbohydrate, such as glucose, fructose, or galactose.

Monounsaturated fatty acid A fatty acid with a single carbon–carbon double bond in its carbon chain.

Morphine A narcotic; the major alkaloid of opium.

N

Narcotic A substance that produces a stupefying, dulling effect, induces sleep, and is often addictive.

Neutralization The combination of an acid and a base to produce a salt (and often water as well).

Neutron A subatomic particle with a mass of 1 amu and no electrical charge; occurs in the nucleus of every atom except protium.

Nicotine A highly poisonous alkaloid that occurs in tobacco leaves.

Nonessential amino acid An amino acid our bodies can synthesize from other chemicals.

Nuclear fission The splitting of an atomic nucleus into two or more large fragments.

Nuclear fusion The combination of two or more nuclei of small mass to form a single nucleus of larger mass.

Nucleus The positively charged central core of an atom; consists of protons and, except for atoms of protium, neutrons.

O

Octane rating (octane number) A measure of a gasoline's resistance to knocking.

Oil In nutrition, a liquid triester of glycerol and fatty acids; constitutes one of the macronutrients of our foods and furnishes 9 Cal/g.

Opiate antagonist A compound that counteracts or nullifies the effects of opiates.

Opiate receptor One of a set of extremely large molecules within the nervous system. When a narcotic molecule connects with an opiate receptor, it blocks or alters signals flowing through the nervous system.

Opium The dried sap of the poppy, composed principally of morphine.

Optical activity The ability to rotate the plane of polarized light.

Organic chemistry The chemistry of carbon compounds.

Ortho The orientation of substituents on a benzene ring that are on carbons bonded to each other.

Oxidation The loss of electrons.

Oxidation potential The voltage produced by or required for the removal of electrons from an atom or ion.

Oxidizing agent An agent that acquires electrons from some other substance and thereby causes it to be oxidized.

Ozone layer A layer of ozone lying within the stratosphere and centered some 30–35 kilometers (about 20 miles) above the earth. It protects life at the surface of the earth by absorbing a portion of the sun's ultraviolet radiation.

P

Para The orientation of substituents on a benzene ring that are on carbons directly across the ring from each other.

Partial pressure The pressure each gas of a mixture of gases would exert, at the same temperature and in the same volume, in the absence of all the other gases.

Parts per million (ppm) A concentration term referring to the number of units of weight of a solute per million units of weight of solution, such as milligrams of solute per kilogram of solution.

Peptide bond (peptide link) The carbon–nitrogen bond of an amide group that links two amino acids. The resulting compound is a *dipeptide*, a *tripeptide*, a *tetrapeptide*, and so on, depending on the total number of amino acids joined by peptide links.

Perfume A pleasantly fragrant blend of synthetic chemicals, animal oils, and extracts of plants, all dissolved as a 10 to 25% solution in alcohol.

Petroleum fraction A mixture of components of petroleum with similar boiling points; obtained through the distillation of petroleum.

pH A measure of a solution's acidity; the negative logarithm of a solution's hydronium ion concentration.

Phaeomelanin A red-brown or yellow-brown pigment chemically similar to melanin.

Placebo A harmless and normally ineffective substance given simply to please and pacify a patient.

Placebo effect The relief or generation of symptoms by the administration of a placebo that results from a patient's expectation of such results.

Plaque A thin layer of a polysaccharide that adheres to the surface of teeth and harbors bacteria.

Plastic A material capable of being shaped into virtually any form.

Plasticizer A liquid that is mixed with a plastic to soften it.

Poison A substance that can cause illness or death when it enters our bodies, usually as a component of our food or drink.

Polarized light Light with electromagnetic oscillations in only one plane, known as the *plane of polarization*.

Polymer A molecule of very large molecular weight formed by the repeated chemical linking of a great many simpler, smaller molecules.

Polymerization The linking of many individual monomers to each other, resulting in the formation of a polymer.

Polyolefin A polymer produced by the polymerization of alkenes or compounds closely related to them.

Polypeptide A polyamide consisting of a chain of 10 or more amino acids.

Polysaccharide A molecule that exists as a chain of hundreds of monosaccharides.

Polyunsaturated fatty acid A fatty acid containing two or more carbon–carbon double bonds.

Positron A subatomic particle that carries a charge of 1+ but is otherwise identical to an electron.

Positron emission tomography (PET) A diagnostic medical technique in which images of planes within an organ are generated through the analysis of γ-rays emitted by collisions of positrons with electrons.

Potential energy The energy stored in an object or a substance, often as a consequence of its location or composition.

Primary (1°) carbon A carbon bonded to exactly one other carbon.

Protein A polypeptide with a molecular weight greater than about 10,000 amu.

Proton A subatomic particle with a mass of 1 amu and a charge of 1+; occurs in the nucleus of every atom.

Q

Quantum shell An electron shell surrounding an atomic nucleus.

Quark A fundamental particle that, in combination with other quarks, composes larger subatomic particles such as protons and neutrons.

R

Radical (free radical) A chemical species that carries an unpaired electron.

Radioactivity The spontaneous emission of radiant energy and or high-energy particles from the nucleus of an atom.

Radioisotope An isotope that emits radioactivity.

Rate-determining step The single step in a sequence of steps that, by itself alone, determines the rate of the entire, multistep process.

Redox reaction A reaction that takes place with a transfer of one or more electrons from one chemical species to another.

Reducing agent An agent that transfers electrons to some other substance and thereby causes it to be reduced.

Reduction The gain of electrons.

Reduction potential The voltage produced by or required for the addition of electrons to an atom or ion.

Rust The corrosion of iron to form various reddish-brown oxides of iron.

S

Safety By one useful definition, the acceptability of risk.

Salt A compound (other than water) produced by the reaction of an acid with a base; commonly, sodium chloride.

Saponification The hydrolysis of an ester carried out in the presence of a base.

Saturated hydrocarbon A hydrocarbon whose molecules contain the maximum number of hydrogen atoms possible and contain only single covalent bonds.

Science A way of knowing and understanding the universe.

Scientific method The process by which science operates, involving the formulation of hypotheses and theories based on experimental tests of the universe.

Sebaceous gland A gland, located in the skin near a hair follicle, that secretes *sebum,* an oily substance that lubricates the cuticle of the hair and gives it a gloss.

Secondary (2°) carbon A carbon bonded to exactly two other carbons.

Sequestering agent A molecule or ion that bonds with a metal so firmly that it removes the metal from chemical contact with other substances.

Solid A phase or state of matter that retains its own shape and volume regardless of the container that holds it.

Solute A substance that is dissolved in some other substance to form a solution; the minor component of a solution.

Solution A homogeneous mixture of one substance, the *solute,* dissolved in another, the *solvent.* In a solution, the solute is present in a smaller proportion than the solvent.

Solvent A substance in which a solute is dissolved to form a solution; the major component of a solution.

Somatic damage Injury to a living body, causing illness or death to that body.

Standard reduction potential The numerical value of a substance's reduction potential, in volts, as compared with the reduction of the hydrogen ion.

Stereochemistry The three-dimensional, spatial arrangement of the atoms of a molecule.

Stratosphere The region of the earth's atmosphere that lies above the troposphere and contains the ozone layer.

Stratum corneum The outermost layer of skin, a protective shield consisting of 25 to 30 layers of dead cells.

Sublimation The conversion of a solid to a gas without the intermediate formation of a liquid.

Substituent An atom or group of atoms bonded to one of the atoms that forms part of the carbon chain of an organic molecule.

Sunscreen protection factor (SPF) The inverse of fraction of ultraviolet radiation a suntan or sunscreen lotion allows to pass through to the skin.

Superposability The capability of two structures to be merged in space so that each point on one coincides exactly with its corresponding point on the other; a test used to determine whether two molecular structures represent identical or different molecules.

T

Teratogen A substance that produces severe birth defects.

Tertiary (3°) carbon A carbon bonded to exactly three other carbons.

Tetraethyllead ("lead") A chemical originally added to gasoline to inhibit knocking.

Tetrahedral carbon A carbon atom that lies at the center of a tetrahedron and forms covalent bonds to the four atoms lying at the apexes or corners of the tetrahedron.

Thermal inversion An atmospheric condition in which a layer of warm air lies above a layer of cooler air, trapping it and any pollutants within it.

Thermoplastic A plastic that softens when heated, then hardens again as it cools.

Thermoset A plastic that remains firm and holds its shape, even when heated.

Toxin A harmful substance that usually has a biological origin.

Trace element A dietary element we need in our diets at levels of less than 100 mg per day.

Transmutation The conversion of one element into another.

Triglyceride A triester of glycerol and fatty acids; the principal organic component of fats and oils.

Troposphere The region of the earth's atmosphere that rises from the planet's surface and is responsible for our weather.

U

Unsaturated molecule A molecule to which hydrogen can be added.

V

Valence electron An electron located in the outermost electron shell of an atom.

Valence shell The outermost electron shell of an atom.

Vasoconstrictor A drug or medicine that constricts blood vessels.

Vitamin An organic compound of our food that is essential in very small amounts for life and good health.

Volatility A measure of the ease and speed of a substance's transformation from a liquid to a vapor.

Volt A unit of electrical potential, the pressure that moves electrons from one point to another.

W

Water-soluble vitamin A vitamin that is much more soluble in water than in fats and hydrocarbons; vitamins B and C.

Wavelength The distance from the crest of one wave to the crest of the next wave.

Weight The characteristic of a body of matter that results from the pull of gravity.

[illegible]

W

W[illegible]. A [illegible]

Wavelength. The [illegible] of the [illegible] wave.

Weight. The characteristic of a body of matter that results from the pull of gravity.

T[illegible]. A [illegible]

Troposphere. The region of the earth's atmosphere [illegible]

U

Unsaturated molecule. A molecule [illegible] added.

V

Valence electron. An electron [illegible] shell of [illegible]

Valence shell. The [illegible]

V[illegible]. [illegible]

Answers to Selected Exercises

Answers are provided for fill-in and matching exercises, and for additional selected odd-numbered exercises. Words and phrases for the fill-in exercises are presented in the sequence in which they are used.

CHAPTER 1

1. Water; sodium chloride; ions; cations; anions; electrical charges; negatively; positively; electrolyte; sucrose; nonelectrolyte.
2. Chemistry; science; scientific method; experiments; hypothesis; theory.
3. 5a; 7b; 3c; 2d; 8e; 1f; 6g; 4h.
9. A solution of sodium chloride in water is capable of conducting an electric current; a solution of sucrose in water is not.
11. Pure sodium chloride, with neither elemental chlorine nor elemental sodium left over, is produced when 15.4 g of chlorine reacts with 10.0 g sodium.

$$10.0 \text{ g sodium} \times \frac{35.5 \text{ g chlorine}}{23.0 \text{ g sodium}} = 15.4 \text{ g chlorine}$$

With less chlorine, excess sodium remains; with more chlorine, excess chlorine remains.

CHAPTER 2

1. Atoms; element; nucleus; protons; protium; isotope; neutrons; electrons; quantum shells; atomic number; *Z*; mass number; *A*; neutral; two; eight.
3. Lithium and beryllium.
5. 109.
7. Number of protons = atomic number. Number of neutrons = mass number minus atomic number. Number of electrons = number of protons.
9. Tritium.
11. Hydrogen, H; helium, He; lithium, Li; beryllium, Be; boron, B; carbon, C; nitrogen, N; oxygen, O; fluorine, F; neon, Ne.
13. No. An atom must contain at least one proton (mass = 1 amu) in its nucleus.
15. a. Hydrogen, lithium, sodium; b. beryllium, magnesium; c. helium, neon, argon; d. hydrogen, whose lone shell can be considered outermost or innermost.
17. a. Oxygen; b. magnesium; c. carbon.
21. Mass = 1 amu; electrical charge = 0. A neutron.

CHAPTER 3

1. Periodic table; atomic number; column; properties; valence electrons; family; symbol; atomic weight; isotopes; abundance; elements; valence shells; transfer; ions; sharing; covalent bond; lattices; molecules.
3. Elements: a, c, e, g, i, j. Compounds: b, d, f, h.
5. a. LiBr; b. CaS; c. Na_2S; d. BeO; e. Cl_2; f. SiH_4.
7. a. Liquid household bleach; b. "iodized" table salt; c. the relaxant Valium; d. Teflon, CFCs; e. common table salt; f. any of the sulfa drugs, such as sulfanilamide; g. tincture of iodine.
9. a. Nitrogen; b. sulfur; c. hydrogen; d. argon; e. magnesium; f. helium; g. neon; h. beryllium; i. carbon.
11. a. Al; b. Ar; c. Ca; d. C; e. Cs; f. F; g. Au; h. H; i. Pb; j. Mn.
13. a. 6; b. losing six electrons would give the resulting cation a very large positive charge, $6+$.
15. An explosion would occur.
17. They move farther from the nucleus.
19. O_3.
21. a. $2+$; b. $2+$; c. $3+$; d. $2+$; e. $3+$.
23. NO_2, $4+$.
25. $7+$.

27. No, a compound consists of *two* or more elements combined with each other in a specific ratio.

29. 4; 2.

31. The compound hydrogen chloride, H—Cl, does not ionize when it dissolves in benzene.

CHAPTER 4

1. Radioactivity; radioisotope; α particle; β particle; γ ray; ionizing radiation; helium nucleus; electron; transmutation; stable isotope; chain of radioactive decay.

2. Matter; energy; nuclear fission; plutonium-239; uranium-235; uranium-238; gaseous diffusion; critical mass; chain reaction; nuclear fusion; deuterium; tritium; helium.

3. 5a; 3b; 6c; 1d; 4e; 2f.

7. They are all stable isotopes, and are not radioactive.

11. Quarks.

13. a. ${}^{222}_{86}Rn$; b. ${}^{13}_{6}C$; c. ${}^{7}_{3}Li$; d. ${}^{37}_{17}Cl$; e. ${}^{99}_{43}Tc$; f. ${}^{4}_{2}He^{2+}$; g. ${}^{1}_{1}H^{+}$; h. ${}^{0}_{0}\gamma$; i. ${}^{0}_{1-}\beta^{-}$; j. ${}^{35}_{17}Cl^{-}$ or ${}^{37}_{17}Cl^{-}$; k. ${}^{23}_{11}Na^{+}$.

15. a. No effect on either mass number or atomic number. b. Decrease by one unit in atomic number; no effect on mass number.

17. No known form of radioactivity occurs with an *increase* in mass number, which would require the addition of one or more protons or neutrons to the nucleus.

25. Radon can build up in the atmosphere of a well-sealed house. A house with a continual flow of air through it will be purged of radon coming up from underground rock and mineral deposits.

CHAPTER 5

1. Electrical power; diagnosis and therapy; radioisotopic dating; fission reactor; atomic pile; uranium-235; breeder reactor; uranium-238; plutonium-239; fusion reactor; iodine-131; technetium-99*m*; half-lives; carbon-14.

3. A chain reaction could be made to occur and thus could be used to produce commercially useful energy.

5. The kinetic energy of falling water turns the rotor of a turbine. The turbine operates an electric generator.

7. 1. Real and imagined fears of accidents at the power plants; 2. limited supplies of nuclear fuels; 3. disposal of radioactive wastes; 4. the cost of nuclear power.

9. Chernobyl.

13. Technetium. Its name comes from the Greek word *tekhnetos*, "synthetic" or "artificial."

15. Decreases atomic number by one; has no effect on mass number.

19. α, β, γ; γ, β, α.

21. 5.2 seconds.

23. No detectable amount of Te-137 would have been left after 4 days. The Zr-97 would have been detectable.

25. Younger.

29. To reveal the cumulative dose of radiation to which they have been exposed.

31. It must have a short half-life, emit γ radiation alone, and must not be toxic chemically in the doses used.

CHAPTER 6

1. Redox; half-cell; loses electrons; gains electrons; standard reduction potentials; positive; negative; electrochemical cell; Daniell cell; zinc; copper; lead–acid storage battery; lead; lead dioxide; lead sulfate.

3. Zinc.

5. Batteries.

7. To accept the returning electrons and produce the electrochemical reactions of a reduction half-cell.

9. From reducing agents to oxidizing agents.

11. By adding energy to it.

13. $2H^{+} + 2e^{-} \rightarrow H_2$.

15. Because it easily acquires electrons from some other substance, thereby oxidizing the other substance.

23. $+0.80$ volts $+$ $(-0.34$ volts$)$ $=$ $+0.46$ volts.

CHAPTER 7

1. Organic; hydrocarbons; alkanes; paraffins; IUPAC; isomers; *n*-butane; isobutane; butane; 2-methylpropane; Law of Conservation of Mass; balanced equation.

3. a. petroleum or gasoline; b. natural gas; c. coal.

7. They form covalent bonds with each other.

8. 4a; 3b; 1c; 2d.

9. Determine whether its molecular formula fits C_nH_{2n+2}.

13. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

15. a. Hydrocarbons: a, b, c, d, f, g; b. alkanes: a, c, g; c. aromatic: f, h.

19. 9.

23. a. alkene, cycloalkane; b. alkane; c. alkyne, cycloalkene; d. alkene, cycloalkane; e. alkane.

25. The water might not have condensed inside the beaker.
31. Unsaturated hydrocarbon since it is possible to add hydrogen to it.
35. Less CO_2 would be emitted.

CHAPTER 8

1. Gasoline; hydrocarbons; chemical energy; kinetic energy; internal combustion engine; spark plug; compression stroke; power stroke; compression ratio; knock; octane rating; *n*-heptane; 2,2,4-trimethylpentane; petroleum; distillation; catalytic cracking; kerosene.
5. CO_2, H_2O, and energy; CO.
7. Molecular weight and branching.
11. The gasoline contains no tetraethyllead.
13. Separating hydrocarbons of different boiling points.
17. e, b, c, d, a.
19. d, b, c, e, a.
29. Kinetic: a, c, e, g, h; potential: b, d, f.
35. Power is unaffected. Spark plug merely ignites gasoline–air mixture.

CHAPTER 9

1. Mole; grams; Avogadro's number; chemical particles; atomic or molecular weights; volumes; concentration; solute; solution; liter; molar.
3. a. $C + O_2 \rightarrow CO_2$; b. $2C + O_2 \rightarrow 2CO$.
5. Weigh its atomic or molecular weight in grams.
11. Its identity and concentration.
13. Ozone.
15. 1. Soaking into the earth; 2. running off to lakes and rivers; 3. evaporating.
19. a. 15; b. 0.5; c. 0.5.
21. a. water, 17; isopropyl alcohol, 12; b. solvent; c. solute.
25. a. 0.1; b. 0.1; c. 9.8 g.
37. a, c, b; chlorine.

CHAPTER 10

1. Sour; litmus; zinc; hydrogen gas; bases; bitter; red; blue; slippery; Arrhenius; proton; hydroxide ion; Brønsted–Lowry; proton transfer; Lewis; electron pair; hydronium; pH; smaller; greater.
3. H_2CO_3 and $CH_3—CO_2H$; NH_3.
5. Red: b, d, e; blue: a, c.
6. 7a, 8b, 3c, 9d, 5e, 4f, 2g, 6h, 11i, 10j, 1k.
9. A hydronium ion, $H^+ + H_2O \rightarrow H_3O^+$.
13. Sulfuric acid, H_2SO_4; nitric acid, HNO_3; carbonic acid, H_2CO_3.
15. CO_2; $NaHCO_3 + H^+ \rightarrow H_2CO_3 + Na^+$; $H_2CO_3 \rightarrow H_2O + CO_2$.
17. Accumulations of lactic acid.
23. a. 0.01, or 10^{-2}; b. 10^{-12}; c. 12.
29. a. 1; b. 1; c. 0.3.
33. d, a base; c, not a carboxylic acid.
37. Digestion of protein would stop.

CHAPTER 11

1. Hydrophobic; hydrophilic; carboxylate; soap; alkylbenzenesulfonates; sulfonate; surface tension; surfactants; hard water; calcium, iron, and magnesium; carboxylic acids; curd; synthetic detergents.
3. All but the paper clip and the tack are floating.
5. Only butter and asphalt soften over a range.
9. a, c, and f are true.
13. —OH and $—CO_2H$.
15. Glycerol.
19. Antiseptic.
21. *A* floats; *B* sinks; *C* floats.
23. 1.47 cm^3.
29. Sublimation.
33. They don't combine chemically with detergent anions.
37. Solid NH_4Cl forms.

CHAPTER 12

1. Heat; energy; work; Calorie; 1000 g of water; 1° Celsius; joule; electricity; chemical bonds; products; reactants; calorimetry; fats and oils; specific dynamic action; basal metabolism.
3. Energy In = Energy Out + Energy Stored; Energy In comes from food; Energy Out represents exercise, specific dynamic action, and basal metabolism; Energy Stored is fat.
5. Yes, by losing even fewer Calories through exercise, specific dynamic action, and basal metabolism.
9. From the effects of specific dynamic action.
11. Fats and oils.
13. Triglycerides.
19. 250.

21. 44°C.
23. 36%.
27. 7 minutes.
31. 10 cents.
35. Basal metabolism.
37. From the potential chemical energy of the gasoline; into heat.

CHAPTER 13

1. Triglycerides; glycerol; fatty acids; fats; oils; length; carbon chains; unsaturation; hydrolysis; hydrogen; catalytic hydrogenation; iodine number; saturated side chains; cholesterol.
3. Leads to an increase.
5. Determine whether it's a solid or a liquid.
7. Compare it with iodine numbers of other triglycerides.
9. Stearic acid for all.
11. Cholesterol.
15. Too hard and brittle.
21. a. Butter; b. whole milk; c. white meat of chicken; d. cheddar cheese.
27. It has a large percentage (about 59%) of saturated fatty acid side chains.
29. a. Incapable; b. *cis;* c. *trans;* d. incapable.

CHAPTER 14

1. Carbohydrates; monosaccharides; aldohexose; fructose; ketohexose; dextrose; plane-polarized light; disaccharides; glucose; lactose; galactose; polysaccharides; starch; α links; cellulose; β links; maltase; cellobiase; lactase.
3. a. Glucose; b. glucose; c. lactose; d. sucrose; e. invert sugar.
7. a. Sweetness; b. sugar; c. right, clockwise; d. hand; e. milk; f. carbon and water.
9. Provides quick energy.
19. 2^n.
27. Sucrase.

CHAPTER 15

1. Protein; amino acids; nonessential; alanine; essential; leucine; glycine; chiral; L-series; primary structure; peptide; amide; dipeptide; tripeptide; polypeptides.
3. Secondary and higher structures change.
5. Globular, spherical; fibrous, ropelike strands.
9. Arginine, histidine.
11. a. Alanine; b. glycine; c. phenylalanine; d. serine; e. aspartic acid; f. cysteine.
13. They contain sulfur.
15. 27.
21. a. T; b. F.
25. Met–Ala–Lys.
27. 2.

CHAPTER 16

1. Vitamins; micronutrients; minerals; calcium; bones and teeth; potassium; chloride; fat-soluble; water-soluble; ascorbic acid; scurvy; rickets; night blindness; β-carotenes.
7. a. C; b. D.
11. All need dietary vitamin C.
13. 0.003% by weight.
19. Avoid losses of water-soluble vitamins.

CHAPTER 17

1. Food additive; desirable effect; more appealing to the senses; ethyl acetate; sweeteners; titanium dioxide; color; nutritional value; potassium iodide; ferrous sulfate; BHA and BHT; EDTA; metal ions; catalyze; mono- and diglycerides; emulsify.
3. Citric acid.
7. Keeps food moist; glycerine; shredded coconut.
9. Prevents microbial contamination.
17. Decreasing order by weight.
19. Through listing as individual ingredients.

CHAPTER 18

1. Injury; acceptability; risk; LD_{50}; body weight; lethal; half; botulinum toxin A; tetanus toxin; diphtheria toxin; 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; dioxin; teratogens; mutagens; carcinogens; safrole; oil of sassafras; saccharin; Delaney Amendment; Food and Drug Administration, or FDA.
5. a. Milk; b. licorice; c. nutmeg; d. rhubarb, spinach; e. smoked and broiled meat; f. pufferfish.
7. Sleeping pill.
11. a. Arsenic trioxide; b. aspirin; c. caffeine; d. acetaminophen.
13. 280 L.

19. a. Gastrointestinal distress; b. hypertension and cardiovascular damage; c. hallucinations; d. kidney damage; e. gastrointestinal cancer; f. paralysis.

CHAPTER 19

1. Atmosphere; troposphere; stratosphere; ozone layer; triatomic; oxygen; ultraviolet; ionosphere.
2. Kinetic-molecular theory of gases; ideal gas; volume; elastic; energy; pressure; increases; absolute temperature; constant temperature; decreases.
4. 4a; 2b; 9c; 3d; 8e; 6f; 1g; 7h; 5i.
5. a. Inversely; b. directly; c. directly.
7. Nitrogen.
11. Excessive ultraviolet radiation.
15. 100 K, or −173°C.
19. As external pressure drops, volume of helium increases.
21. Most, helium; least, water.
23. Heating.
29. Flammability.

CHAPTER 20

1. Polymers; monomers; homopolymer; copolymer; cellulose; glucose; nylon; adipic acid; 1,6-diaminohexane; condensation; addition; polyethylene; low-density; high-density; linear.
3. 4a; 6b; 1c; 5d; 3e; 8f; 2g; 7h.
11. Carbohydrates (cellulose, starch), proteins.
13. Bakelite.
15. a. Polystyrene; b. polyvinylchloride, poly(vinylidene chloride); c. Teflon; d. nylon; e. polyvinylacetate.
21. Sunlight.
27. a. Cellulose, starch; b. protein; c. rubber.
29. a. Teflon; b. poly(vinylidene chloride); c. polyvinylacetate; d. nylon; e. Bakelite; f. neoprene; g. poly(ethylene terephthalate).

CHAPTER 21

1. Surfactants; lauryl sulfonates; pH; chelate; cortex; hydrogen peroxide; coupler; waving; thioglycolic acid; cysteine; cystine.
2. Abrasive; surfactant; caries; polysaccharides; hydroxyapatite; calcium; phosphate; sodium *N*-lauroyl sarcosinate; enzymes.
3. Emulsions; stratum corneum; sebum; eccrine; apocrine; aluminum chlorohydrates; zinc; neomycin.
4. Castor oil; triglyceride; lanolin; sebum; tetrabromofluorescein; dibromofluorescein; ultramarine blue; carbon black; titanium dioxide, TiO_2; polymer; nitrocellulose; hydrocarbons; ethyl acetate.
5. Ultraviolet radiation; UV-B; UV-A; vitamin D; melanin; skin cancer; *p*-aminobenzoic acid, or PABA; benzophenone; dihydroxyacetone; amino acids.
11. Antibacterial agent.
15. UV-A: longer wavelength, less energetic.
17. Orientation on benzene ring.
21. a. 2 hours; b. 3.3 hours; c. 5 hours; d. 10 hours.
25. Increases contrast with skin.

CHAPTER 22

1. Analgesic; aspirin; acetylsalicylic acid; salicyclic acid; acetic anhydride; prostaglandins; acetaminophen; plants; alkaloids; morphine; narcotic; opium; heroin; cocaine; local anesthetic; naloxone; opiate antagonists; polypeptides; endorphins and enkephalins; placebo effect.
3. 2a; 6b; 5c; 1d; 4e; 3f.
7. Made it easier to take orally.
11. Both are addictive; methadone doesn't produce the psychological effects of heroin.
17. Exact fit is required in each case.
21. Hydrolyzed to salicylic acid and acetic acid, major acid of vinegar.

APPENDIX A

1. a. 2000; b. 4796; c. 72.553; d. 1.4299; e. 0.0005697.
3. a. 100,000,000; b. 81; c. 64; d. 72; e. 0.512; f. 0.512.

APPENDIX C

1. 4.722×10^8 cm.

APPENDIX D

1. a. 81.89; b. 6.81427; c. 53.
3. a. 0.046; b. 40×10^2; c. 0.5.

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Symbols of the Elements

Symbol	Name	Symbol	Name
Ac	Actinium	N	Nitrogen
Ag	Silver	Na	Sodium
Al	Aluminum	Nb	Niobium
Am	Americium	Nd	Neodymium
Ar	Argon	Ne	Neon
As	Arsenic	Ni	Nickel
At	Astatine	No	Nobelium
Au	Gold	Np	Neptunium
B	Boron	O	Oxygen
Ba	Barium	Os	Osmium
Be	Beryllium	P	Phosphorus
Bi	Bismuth	Pa	Protactinium
Bk	Berkelium	Pb	Lead
Br	Bromine	Pd	Palladium
C	Carbon	Pm	Promethium
Ca	Calcium	Po	Polonium
Cd	Cadmium	Pr	Praseodymium
Ce	Cerium	Pt	Platinum
Cf	Californium	Pu	Plutonium
Cl	Chlorine	Ra	Radium
Cm	Curium	Rb	Rubidium
Co	Cobalt	Re	Rhenium
Cr	Chromium	Rh	Rhodium
Cs	Cesium	Rn	Radon
Cu	Copper	Ru	Ruthenium
Dy	Dysprosium	S	Sulfur
Er	Erbium	Sb	Antimony
Es	Einsteinium	Sc	Scandium
Eu	Europium	Se	Selenium
F	Fluorine	Si	Silicon
Fe	Iron	Sm	Samarium
Fm	Fermium	Sn	Tin
Fr	Francium	Sr	Strontium
Ga	Gallium	Ta	Tantalum
Gd	Gadolinium	Tb	Terbium
Ge	Germanium	Tc	Technetium
H	Hydrogen	Te	Tellurium
He	Helium	Th	Thorium
Hf	Hafnium	Ti	Titanium
Hg	Mercury	Tl	Thallium
Ho	Holmium	Tm	Thulium
I	Iodine	U	Uranium
In	Indium	Une	Unnilennium
Ir	Iridium	Unh	Unnilhexium
K	Potassium	Unp	Unnilpentium
Kr	Krypton	Unq	Unnilquadium
La	Lanthanum	Uns	Unnilseptium
Li	Lithium	V	Vanadium
Lr	Lawrencium	W	Tungsten
Lu	Lutetium	Xe	Xenon
Md	Mendelevium	Y	Yttrium
Mg	Magnesium	Yb	Ytterbium
Mn	Manganese	Zn	Zinc
Mo	Molybdenum	Zr	Zirconium

Table of Atomic Weights

Elements by Name, Symbol, Atomic Number, and Atomic Weight
(Atomic weights are given to four significant figures for elements below atomic number 104. See Appendix D.)

		Atomic	
Name	Symbol	Number	Weight
Actinium	Ac	89	227.0
Aluminum	Al	13	26.98
Americium	Am	95	243.1
Antimony	Sb	51	121.8
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210.0
Barium	Ba	56	137.3
Berkelium	Bk	97	247.1
Beryllium	Be	4	9.012
Bismuth	Bi	83	209.0
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.08
Californium	Cf	98	252.1
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.55
Curium	Cm	96	247.1
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	252.1
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	257.1
Fluorine	F	9	19.00
Francium	Fr	87	223.0
Gadolinium	Gd	64	157.2
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.003
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9
Lawrencium	Lr	103	260.1
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.30
Manganese	Mn	25	54.94
Mendelevium	Md	101	256.1
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.2
Neon	Ne	10	20.18
Neptunium	Np	93	237.0
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	259.1
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.1
Plutonium	Pu	94	239.1
Polonium	Po	84	210.0
Potassium	K	19	39.10
Praseodymium	Pr	59	140.9
Promethium	Pm	61	144.9
Protactinium	Pa	91	231.0
Radium	Ra	88	226.0
Radon	Rn	86	222.0
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.9
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.07
Tantalum	Ta	73	180.9
Technetium	Tc	43	98.91
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.88
Tungsten	W	74	183.8
Unnilennium	Une	109	
Unnilhexium	Unh	106	(263)
Unnilpentium	Unp	105	(262)
Unnilquadium	Unq	104	(261)
Unnilseptium	Uns	107	(262)
Uranium	U	92	238.0
Vanadium	V	23	50.94
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.91
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.22

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ISBN 0-471-62971-5
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9 780471 629719