Steven S. Zumdahl

CHEMISTRY
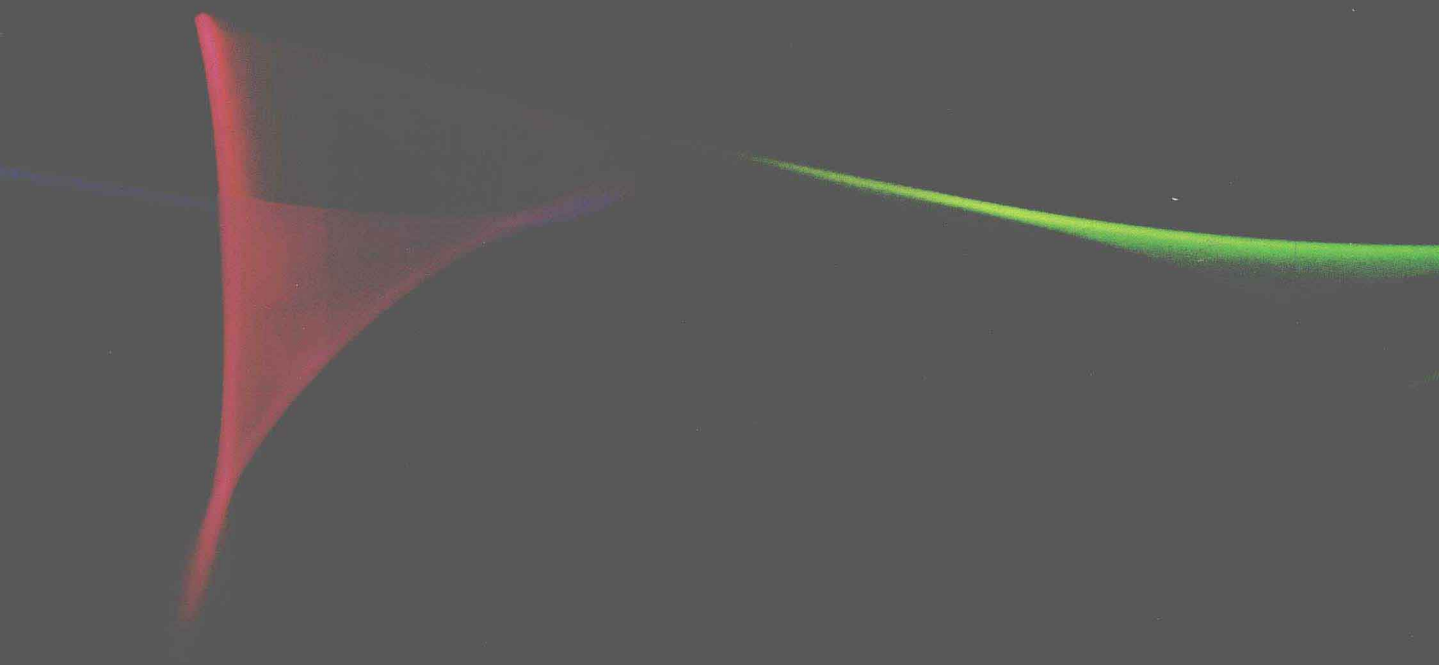
Third Edition

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CHEMISTRY

Third Edition

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◀ To the Professor ▶

Because of the enthusiastic response to the second edition of this text, the third edition of *Chemistry* continues in the same spirit: a presentation of the concepts of chemistry in a clear, interesting, and student-friendly manner. However, I have gone over every page in the second edition thoroughly, fine-tuning in some cases and substantially rewriting in others. In doing so, I have incorporated numerous constructive suggestions from instructors who used the previous edition.

Since visual material is especially important for learning general chemistry, which typically presents a pictorial view of chemical concepts, the use of color has been markedly increased in this edition. Special illustrations and color photographs integrate descriptive chemistry with chemical principles, and many new *Chemical Impact* features emphasize practical applications of newly learned concepts.

Important Features of the Third Edition

- With a strong **problem-solving orientation,** this text talks to the student about how to approach and solve chemical problems. I have made a strong pitch to the student for using a thoughtful and logical approach rather than simply memorizing procedures. In particular, an innovative method is given for dealing with acid–base equilibria, the material the typical student finds most difficult and frustrating. The key to this approach involves first deciding what species are present in solution, then thinking about the chemical properties of these species. This method provides a general framework for approaching all types of solution equilibria.

    The text contains almost 300 sample exercises, with many more examples given in the discussions leading to sample exercises or used to illustrate general strategies. When a specific strategy is presented, it is summarized, and the sample exercise that follows it reinforces the step-by-step attack on the problem (see p. xix).

- I have presented a thorough **treatment of reactions** that occur in solution, including acid–base reactions. This material appears in Chapter 4, directly after the chapter on chemical stoichiometry, to emphasize the connection between solution reactions and chemical reactions in general. The early presentation of this material provides an

opportunity to cover some interesting descriptive chemistry and also supports the lab, which typically involves a great deal of aqueous chemistry. Chapter 4 also includes oxidation–reduction reactions, because a large number of interesting and important chemical reactions involve redox processes. However, coverage of oxidation–reduction is optional at this point and depends on the needs of a specific course.

- **Descriptive chemistry** and chemical principles are thoroughly integrated in this text. Chemical models may appear sterile and confusing without the observations that stimulated their invention. On the other hand, facts without organizing principles may seem overwhelming. A combination of observations and models can make chemistry both interesting and understandable. In addition, in those chapters that deal with the chemistry of the elements systematically, I have made a continuous effort to show how properties and models correlate. Descriptive chemistry is presented in a variety of ways—as applications of the principles in separate sections, in sample exercises and exercise sets, in photographs, and in *Chemical Impact* features.

- Throughout the book a strong **emphasis on models** prevails (see p. xviii). Coverage includes how they are constructed, how they are tested, and what we learn when they inevitably fail. Models are developed naturally, with pertinent observations always presented first to show why a particular model was invented.

- Everyday-life **applications** of chemistry that should be of interest to the students taking general chemistry appear throughout the text. For example, the *Chemical Impact* ''Refurbishing the Lady'' illustrates the chemistry behind the restoration of the Statue of Liberty, while ''Nature Has Hot Plants'' discusses several fascinating species of heat-producing plants, including the voodoo lily. Many industrial applications have also been incorporated into the text. Interesting careers in chemistry are highlighted through profiles of real people who work in the chemical sciences (see p. xv).

- Judging from the favorable comments of instructors and students who have used the second edition, the text seemed to work very well in a variety of courses. I was

especially pleased that **readability** was cited as a key strength when students were asked to assess the text. Thus, although the text has been fine-tuned in many areas, I have endeavored to build on the basic descriptions, strategies, analogies, and explanations that were successful in the second edition.

Changes in the Third Edition

- To assist instructors in providing interesting and relevant classroom demonstrations of chemical phenomena for their students, the *Instructor's Edition* indicates via the marginal icon (flask with stirring rod) direct references to more than 750 demonstrations from several authoritative sources. The sources are provided in a separate booklet, the *Lecture Demonstration Guide*, that is available to adopters of the Third Edition.

- In this edition, the effective problem-solving emphasis is further reinforced by the division of the exercise sets into five discrete, increasingly challenging groups (see p. xx). Each set begins with Questions that test students' conceptual grasp of the material. Following these, Exercises, now paired and organized by topic, reinforce students' understanding of each section. Additional Exercises are not keyed by topic, so that students must identify and apply the appropriate concepts themselves. The fourth type of exercises, Challenge Problems, require students to go still further and combine skills and concepts. Finally, Marathon Problems are even more comprehensive (see below).

- New to this edition is the inclusion of ''marathon'' problems at the end of many of the chapters. The use of these problems in the general chemistry course was described in a recent issue of the *Journal of Chemical Education.*[*] Marathon problems can serve several purposes: to introduce chapter material, since they provide a way for the students to see a large number of the concepts in a given chapter in a single problem; to enable students to discern relationships among the main points of a chapter (and sometimes among different chapters) in a way not possible with shorter, narrowly defined problems; and to provide a mechanism for increasing the interaction between the instructor and the students, resulting in a more active learning environment.

- Chapter 4, ''Types of Chemical Reactions and Solution Stoichiometry,'' has been tightened and condensed to

[*]Burness, James H. *J. Chem. Educ*. 1991, *68*, 919.

simplify and clarify this important material as much as possible. In particular, great pains have been taken to explain how to predict the products of reactions. Problem-solving strategies and sample exercises have been increased, while a more detailed discussion of qualitative analysis moves to later chapters. A careful reading of this chapter will show that its length is due mainly to careful explanations of the concepts related to reactions in solution.

- Many of the illustrations have been reconceived for additional visual clarification of chemical concepts and all have been rerendered to achieve a new standard of accuracy and clarity. Pedagogical consistency in the use of color has been a focus in the generation of this new artwork.

Flexibility of Topic Order

The order of topics in the text was chosen because it is preferred by the majority of instructors. However, I consciously constructed the book so that many other orders are possible. For example, at the University of Illinois, for a two-semester sequence we use the chapters in the order 1–6, 13–15, 7–9, 21, 20, 12, 10, 11, 16, 17, and 22. Sections of Chapters 18, 19, and 23 are used throughout the two semesters as appropriate. This order, chosen because of the way the laboratory is organized, is not necessarily recommended, but it illustrates the flexibility of order built into the text.

Some specific points about topic order:

- About half of chemistry courses present kinetics before equilibria, while the other half present equilibria first. This text is written to accommodate either order.

- The introductory aspects of thermodynamics are presented relatively early (in Chapter 6) because of the importance of energy in various chemical processes and models, but the more subtle thermodynamic concepts are left until later (Chapter 16). These two chapters may be used together if desired.

- To make the book more flexible, the derivation of the ideal gas law from the kinetic-molecular theory and quantitative analysis using spectroscopy are presented in the appendixes. While mainstream general chemistry courses typically do not cover this material, some courses may find it appropriate. By using the optional material in the appendixes and by assigning the more difficult end-of-chapter exercises (from the additional exercises section),

an instructor will find the level of the text appropriate for many majors courses or for other courses requiring a more extensive coverage of these topics.

- Because some courses cover bonding using only a Lewis-structure approach, orbitals are not presented in the introductory chapter on bonding (Chapter 8). In Chapter 9 both hybridization and the molecular orbital model are covered, but either or both of these topics may be omitted if desired.

- Chapter 4 can be tailored to fit the specific course involved. Used in its entirety where it stands in the book, it provides interesting examples of descriptive chemistry and supports the laboratory program. Material in this chapter can also be skipped entirely or covered at some later point whenever appropriate. For example, the sections on oxidation and reduction can be taught with electrochemistry. Although many instructors prefer early introduction of this concept, these sections can be omitted without complication since the next few chapters do not depend on this material.

Supplements

An extensive supplements package has been designed to make this book more useful to both student and instructor. These supplements include:

- *Study Guide,* by Paul B. Kelter of the University of Wisconsin, Oshkosh. Written to be a self-study aid for students, this guide includes alternate strategies for solving various types of problems, supplemental explanations for the most difficult material, and self-tests. There are approximately 400 worked examples and 700 practice problems (with answers) designed to give students mastery and confidence.

- *Solutions Guide,* by Kenneth C. Brooks, Thomas J. Hummel, and Steven S. Zumdahl, all of the University of Illinois, Urbana, provides detailed solutions for half of the end-of-chapter exercises (designated by blue question numbers or letters) using the strategies emphasized in the text. To ensure the accuracy of the solutions, this supplement and the *Complete Solutions Guide* were checked independently by several instructors.

- *Complete Solutions Guide,* by Kenneth C. Brooks, Thomas J. Hummel, and Steven S. Zumdahl, presents detailed solutions for **all** of the end-of-chapter exercises in the text for the convenience of faculty and staff in-

volved in instruction and for instructors who wish their students to have solutions for all exercises. Departmental approval is required for the sale of the *Complete Solutions Guide* to students.

- *Instructor's Guide,* by Kenneth C. Brooks, includes suggestions for alternative orders of topics, amplification of strategies used in various chapters, suggested sources of additional information, and a section on notes for teaching assistants.

- *Solving Equilibrium Problems with Applications to Qualitative Analysis,* by Steven S. Zumdahl. Revised from a text successfully used by thousands of students over the last ten years, this book offers thorough, step-by-step procedures for solving problems related to equilibria taking place both in the gas phase and in solution. Containing hundreds of sample exercises, test exercises with complete solutions, and end-of-chapter exercises with answers, the text utilizes the same problem-solving methods found in *Chemistry* and is an excellent source of additional drill-type problems. The last chapter presents an exploratory qualitative analysis experiment with explanations based on the principles of aqueous equilibria.

- *Experimental Chemistry,* Third Edition, by James F. Hall of the University of Lowell, provides an extensively revised laboratory program compatible with the text. The 43 experiments present a wide variety of chemistry, and many experiments offer choices of procedures. Safety is strongly emphasized throughout the program.

- *Instructor's Resource Guide* for *Experimental Chemistry,* Third Edition, by James F. Hall, contains tips including hints on running experiments, approximate times for each experiment, and answers to all prelab and postlab questions posed in the laboratory guide.

- *Test Item File,* by Susan Arena (available to adopters), offers a printed version of more than 2000 exam questions referenced to the appropriate text section. Questions are available in multiple-choice, open-ended, and true-false formats.

- *Computerized Testing* presents the *Test Item File* questions in a computerized testing program by ESATest. Instructors can produce chapter tests, midterms, and final exams easily and with excellent graphics capability. The instructor can also edit existing questions or add new ones as desired, or preview questions on screen and add them to the test with a single keystroke. The testing program is available for Apple II, Macintosh, and IBM computers.

- *University of Illinois Film Center General Chemistry Videotapes,* which may also be purchased by adopters, reinforce the major concepts found in the text.
- *Transparencies,* a set of 245 transparencies (many in color), are available to adopters of the third edition of the text.

New Supplements

- *Chemistry in Motion Videotape and Videodisc Supplements.* D. C. Heath has two exciting and pedagogically valuable sets of video demonstrations of chemical experiments:

  Available on videotape only is the Project SERAPHIM and JCE:Software 60-minute collection of 37 demonstrations done by John W. Moore of the University of Wisconsin, Madison, with the assistance of Lynn Hunsberger.

  Available on videotape *and* videodisc is a series of 34 demonstrations done by Patricia L. Samuel of Boston University, with the assistance of Lorraine Kelly. The *Chemistry in Motion Videodisc* also includes a complete set of the approximately 550 illustrations in the third edition of *Chemistry.*

- *Chemistry in Motion Software.* This Macintosh software by Leonard J. Soltzberg of Simmons College provides animations of concepts and processes that are best understood when actually viewed in motion and with dimensionality, e.g., Le Châtelier's principle, crystal structure, states of matter, molecular motion, entropy, and so on.

- *Lecture Demonstration Guide.* (See p. vi for a description of this helpful resource reference by Fred Juergens of the University of Wisconsin, Madison.)

Acknowledgments

The success of this text is due to the efforts of many talented people. It is a great privilege and pleasure to work with Kent Porter Hamann, Editorial Director for Science. Kent is simply the best in the business. She combines remarkable market expertise and editorial skills with incredible energy and continuous good humor. Karen Wise, Senior Production Editor, did a truly amazing job of holding everything together. Karen's outstanding organizational and editorial skills, combined with her endless supply of good cheer, made this project a real pleasure.

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Many other people at D. C. Heath supplied invaluable assistance during this project: Jim Porter Hamann, Senior Product Manager, whose energy and thorough understanding of the marketplace have contributed greatly to the success of this book; Mark Corsey, Photo Researcher, who showed real creativity in securing new photos for this edition; Gary Crespo, Art Editor, who coordinated the revision of the entire illustration program; Kenneth Hollman, Senior Designer, who developed a beautiful and functional design; and Joanne Williams, Editorial Associate, whose efficient and cheerful assistance was always greatly appreciated. Last, but surely not least, I want to express my gratitude to the D. C. Heath book reps, a very impressive group of hard-working people, many of whom I am proud to call friends.

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S. S. Z.

◀ To the Student ▶

The major purpose of this book, of course, is to help you learn chemistry. However, this main thrust is closely linked to two other goals: to show how important and how interesting the subject is, and to show how to think like a chemist. To solve complicated problems the chemist uses logic, trial and error, intuition, and, above all, patience. A chemist is used to being wrong. The important thing is to learn from a mistake, recheck assumptions, and try again. A chemist thrives on puzzles that seem to defy solutions.

Many of you using this text do not plan to be practicing chemists. However, the nonchemist can benefit from the chemist's attitude. Problem solving is important in all professions and in all walks of life. The techniques you will learn from this book will serve you well in any career you choose. Thus, I believe that the study of chemistry has much to offer the nonmajor, including an understanding of many fascinating and important phenomena and a chance to hone problem-solving skills.

This book attempts to present chemistry in a manner that is sensible to the novice. Chemistry is not the result of an inspired vision. It is the product of countless observations and many attempts, using logic and trial and error, to account for these observations. In this book the concepts are developed in a natural way: the observations come first and then models are constructed to explain the observed behavior.

Models are a major focus in this book. The uses and limitations of models are emphasized, and science is treated as a human activity, subject to all the normal human foibles. Mistakes are discussed as well as successes.

A central theme of this book is a thoughtful, systematic approach to problem solving. Learning encompasses much more than simply memorizing facts. Truly educated people use their factual knowledge as a starting point—a base for creative approaches to solving problems.

As you have probably heard, learning chemistry can be frustrating. It is easy to lose sight of how really important and interesting chemistry is. You *can* learn chemistry and even enjoy the process, but you must understand that finesse works much better than brute force. Chemistry can be difficult not so much because the concepts are hard, but

because it deals with complicated systems. Before a problem can be solved, a lot of facts must be sifted to find the pertinent ones. There is no alternative to thinking things through.

Read through the material in the text carefully. For most concepts, illustrations or photos will help you visualize what is going on. Often a given type of problem is "walked through" in the text before the corresponding sample exercises appear. Strategies for solving problems are given throughout the text.

Thoroughly examine the sample exercises and the problem-solving strategies. The strategies summarize the approach taken in the text; the sample exercises follow the strategies step-by-step. Schematics in Chapter 15 also illustrate the logical pathways to solving aqueous equilibrium problems.

Throughout the text, I have used margin notes to highlight key points, to comment on an application of the text material, or to reference material in other parts of the book. The boxed features called *Chemical Impacts* discuss especially interesting applications of chemistry to the everyday world.

Each chapter has a summary and key terms list for review, and the glossary gives a quick reference for definitions.

Learning chemistry requires working the end-of-chapter exercises assigned by your professor. Answers to exercises denoted by blue question numbers are in the back of the book, while complete solutions to those exercises are in the *Solutions Guide*.

The *Study Guide* contains extra practice problems and many examples. The supplement *Solving Equilibrium Problems with Applications to Qualitative Analysis* reinforces in great detail the text's step-by-step approach to solving equilibrium problems and contains many worked examples and self-quiz questions to help you assess your level of proficiency.

It is very important to use the exercises to your best advantage. Your main goal should not be to simply get the correct answer but to *understand the process* for getting the answer. Memorizing the solutions for specific problems is

not a very good way to prepare for an exam. There are too many pigeonholes required to cover every possible problem type. Look within the problem for the solution. Use the concepts you have learned along with a systematic, logical approach to find the solution. Learn to trust yourself to think it out. You will make mistakes, but the important thing is to learn from these errors. The only way to gain confidence is to do lots of practice problems and use these to diagnose your weaknesses.

Be patient and thoughtful and work hard to understand rather than simply memorize. I wish you an interesting and satisfying year.

◄ About the Author ►
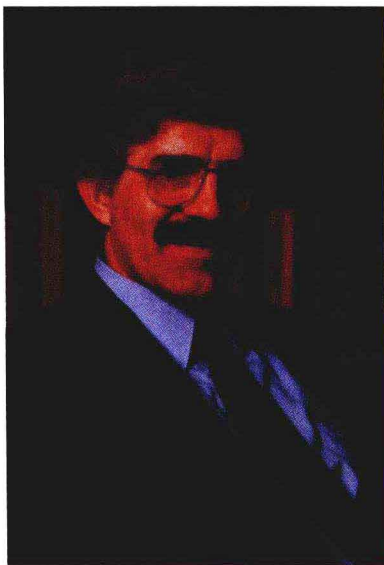
STEVEN S. ZUMDAHL received his B.S. degree in Chemistry from Wheaton College (Illinois) in 1964 and his Ph.D. in Chemistry from the University of Illinois, Urbana, in 1968.

In 25 years of teaching he has been a faculty member at the University of Colorado, Boulder; Parkland College (Illinois); and the University of Illinois, Urbana. Currently he is Professor and Associate Head of Chemistry and Director of Undergraduate Programs in Chemistry at the University of Illinois.

Professor Zumdahl is known at the University of Illinois for his rapport with students and for his outstanding teaching ability. During his tenure at the University, he has received the University of Illinois Award for Excellence in Teaching, the Liberal Arts and Sciences College Award for Distinguished Teaching, and the School of Chemical Sciences Teaching Award (four times).

Dr. Z., as he is known to his students, greatly enjoys ''mechanical things,'' including bicycles and cars. He collects and restores classic automobiles, having a special enthusiasm for vintage Corvettes.

◄ A Note from the Author ►

◄ CHEMICAL IMPACT ►

Titanium Makes Great Bicycles

O ne of the most interesting characteristics of the world of bicycling is the competition among various frame materials. Bicycle frames are now built from steel, aluminum, carbon fiber composites, and titanium, with each material having advantages and disadvantages. Steel is strong, economical, adaptable, and (unfortunately) "rustable." Aluminum is light and stiff but has relatively low fatigue limits (resistance to repeated stresses). Carbon fiber composites have amazing strength-to-mass ratios and have shock- and vibration-dampening properties superior to any metal; however, they are very expensive. Titanium has a density approximately 43% less than that of steel, a yield strength (when alloyed with metals such as aluminum and tin) that is 30% greater than that of steel, an extraordinary resistance to fatigue, and a high resistance to corrosion, but it is expensive and difficult to work.

Of all these materials, titanium gives the bicycle that fanatics seem to love the most. After their first ride on a bicycle with a titanium frame, most experienced cyclists find themselves shaking their heads and searching hard for the right words to describe the experience. Typically, the word *magic* is used a great deal in the ensuing description.

The magic of titanium results from its combination of toughness, stretchability, and resilience. A bicycle that is built stiff to resist pedaling loads usually responds by giving a harsh, uncomfortable ride. A titanium bike is very stiff against high pedaling torques, but it seems to transmit much less road shock than bikes made of competitive materials. Why titanium excels in dampening vibrations is not entirely clear. Despite titanium's significantly lower density than steel's, shock waves travel more slowly in titanium than in steel. Whatever the explanation for its shock-absorbing abilities, titanium pro-

A titanium bicycle.

vides three things that cyclists find crucial: light weight, stiffness, and a smooth ride—magic.

Titanium is quite abundant in the earth's crust, ranking ninth of all the elements and second among the transition elements. The metallurgy of titanium presents special challenges. Carbon, the reducing agent most commonly used to obtain metals from their oxides ores, cannot be used because it forms intractable interstitial carbides with titanium. These carbides are extraordinarily hard and have melting points close to 3000°C. However, if chlorine gas is used in conjunction with carbon to treat the ore, volatile $TiCl_4$ is formed, which can be distilled off and then reduced with magnesium or sodium at approximately 1000°C to form a titanium "sponge." This sponge is then ground up, cleaned with aqua regia (a 1:3 mixture of concentrated HNO_3 and con-

centrated HCl), melted under a blanket of inert gas (to prevent reaction with oxygen), and cast into ingots. Titanium, a lustrous, silvery metal with a high melting point (1667°C), crystallizes in a hexagonal closest packed structure. Because titanium tends to become quite brittle when trace impurities such as C, N, and O are present, it must be fabricated with great care.

Titanium's unusual ability to stretch makes it hard to machine. It tends to push away even from a very sharp cutting blade, giving a rather unpredictable final dimension. Also, because titanium is embrittled by reaction with oxygen, all welding operations must be carried out under a shielding gas such as argon.

However, the bicycle that results is worth all these difficulties. One woman described a titanium bicycle as "the one God rides on Sunday."

- In 25 years of teaching chemistry, I have noticed that students often approach the course with apprehension because they have heard how difficult chemistry can be. One of my main goals is to motivate students by showing them just how important and interesting chemistry really is.

a nationally recognized expert in the areas of monitoring and missions from hazardous substances and is a frequent lecturer at ps. He has over 10 publications and 20 conference presentations

interest in a career in environmental science was fostered by two mistry courses and two ecology courses he took as an undergrad plan to gain several years of industrial experience and then to r a graduate degree was changed when he found that professional a B.S. degree was possible in the environmental research field. ary nature of most environmental problems has allowed him to sts in several fields. His specialty is really in being a generalist. ntal consulting field provides Bart with a number of attractions: ne and solve a number of research problems; the simultaneous of diverse projects (he has had a major role in over 40 projects in k of desk, field, and laboratory work; the travel; and the opportu- warding work that has a positive effect on people's lives. In his manages a research group consisting of two Ph.D., two M.S., ntists with chemistry, physics, and atmospheric science back-

er highlights are

er month doing air sampling in the Grand Tetons, where he also d learned to ski

g pipes by hand into the rocky ground of Death Valley Monument

ly with experts in their fields and with people who enjoy what

- Doing vigorous work in 100°F weather while wearing a rubberized suit, double gloves, and a respirator
- Getting to work in and see Alaska, Yosemite Park, Niagara Falls, Hong Kong, the People's Republic of China, Mesa Verde, New York City, and dozens of other interesting places

Heidi Piper Flatley went to work for Procter and Gamble after her graduation from the University of Illinois at Champaign-Urbana in 1987 with a B.S. degree in chemical engineering. Combining her technical expertise with her interests in psychology and marketing, Ms. Flatley took a position in the area of Products Research, where she tries to discover "unmet consumer needs" and then to design products to meet these needs. Heidi describes herself as a "technology broker"— someone who looks for ways to use her company's technical expertise to improve people's lives. After a possible application is identified, she then works closely with the personnel in Research and Development as the concept is brought from the idea stage to a finished product that can be market tested.

Heidi says, "I have become an expert in market research and am continuing to learn about marketing and about management skills (personal and interpersonal) and am gaining excellent experience in product development."

By 1990, Heidi was living in a French-speaking neighborhood in Brussels, Belgium, where she does market research throughout Europe for Procter and Gamble. Heidi says, "As a sample slice of my job, I'll tell you what I did last week. I spent Monday, Tuesday, and Wednesday in London with a Belgian woman I hired to help

Heidi Piper Flatley

- Chemistry is a *human activity,* and throughout the text I try to show not just the history of chemistry but also that chemists are indeed real people.

Notice from Sample Exercise 4.12 that the procedures for doing stoichiometric calculations for solution reactions are very similar to those for other types of reactions. It is useful to think in terms of the following steps for reactions in solution.

STOICHIOMETRY FOR REACTIONS IN SOLUTION

STEP 1
Identify the species present in the combined solution, and determine what reaction occurs.

STEP 2
Write the balanced net ionic equation for the reaction.

STEP 3
Calculate the moles of reactants.

STEP 4
Determine which reactant is limiting.

STEP 5
Calculate the moles of product or products, as required.

STEP 6
Convert to grams or other units, as required.

Sample Exercise 4.13

When aqueous solutions of Na_2SO_4 and $Pb(NO_3)_2$ are mixed, $PbSO_4$ precipitates. Calculate the mass of $PbSO_4$ formed when 1.25 L of 0.0500 M $Pb(NO_3)_2$ and 2.00 L of 0.0250 M Na_2SO_4 are mixed.

Solution

STEP 1

Identify the species present in the combined solution, and determine what reaction occurs. When the aqueous solutions of Na_2SO_4 (containing Na^+ and SO_4^{2-} ions) and $Pb(NO_3)_2$ (containing Pb^{2+} and NO_3^- ions) are mixed, the resulting solution contains the ions Na^+, SO_4^{2-}, Pb^{2+}, and NO_3^-. Since $NaNO_3$ is soluble and $PbSO_4$ is insoluble (see Rule 4 in Table 4.1), solid $PbSO_4$ will form.

STEP 2

Write the balanced net ionic equation for the reaction. The net ionic equation is

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

STEP 3

Calculate the moles of reactants. Since 0.0500 M $Pb(NO_3)_2$ c[ontains] Pb^{2+} ions, we can calculate the moles of Pb^{2+} ions in 1.25 L [as] follows:

$$1.25 \, L \times \frac{0.0500 \text{ mol } Pb^{2+}}{L} = 0.0625 \text{ mol } Pb^{2+}$$

The 0.0250 M Na_2SO_4 solution contains 0.0250 M SO_4^{2-} ions, a[nd the] moles of SO_4^{2-} ions in 2.00 L of this solution is

$$2.00 \, L \times \frac{0.0250 \text{ mol } SO_4^{2-}}{L} = 0.0500 \text{ mol } SO_4^{...}$$

• Chemistry is not the result of an inspired vision. It is the product of countless observations and many attempts, using logic and trial and error, to account for these observations. In this book I try to develop key chemical concepts in the same way—to show the observations first and then discuss the models that have been constructed to explain the observed behavior. I hope students will practice ''thinking like a chemist'' by carefully studying the observations to see if they can follow the thought process, rather than just jumping ahead to the equation or model that will follow.

• Another goal I have is to show students how to think like a chemist. Most students using this text do not plan to be practicing chemists. However, problem solving is important in all professions and all walks of life. The same skills and attitudes a chemist uses—logic, trial and error, intuition, and above all, patience—students will find useful whatever their career goals.

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relationships among the properties can be discovered. These relationships are often represented pictorially by means of graphs (plots).

We will take an historical approach to these laws to give you some perspective on the scientific method in action.

Boyle's Law

The first quantitative experiments on gases were performed by an Irish chemist, Robert Boyle (1627–1691). Using a J-shaped tube closed at one end (Fig. 5.4), which he reportedly set up in the multistory entryway of his house, Boyle studied the relationship between the pressure of the trapped gas and its volume. Representative values from Boyle's experiments are given in Table 5.1. These data show that the product of the pressure and volume for the trapped air sample is constant within the accuracies of Boyle's measurements (note the third column in Table 5.1). This behavior can be represented by the equation

$$PV = k$$

which is called **Boyle's law** and where k is a constant for a given sample of air at a specific temperature.

It is convenient to represent the data in Table 5.1 by using two different plots. The first type of plot, P versus V, forms a curve called a **hyperbola** shown in Fig. 5.5(a) on p. 188. Looking at this plot, note that as the pressure drops by about half (from 58.8 to 29.1), the volume doubles (from 24.0 to 48.0). In other words, there is an *inverse relationship* between pressure and volume. The second type of plot can be obtained by rearranging Boyle's law to give

$$V = \frac{k}{P} = k\frac{1}{P}$$

which is the equation for a straight line of the type

$$y = mx + b$$

where m represents the slope and b the intercept of the straight line. In this case, $y = V$, $x = 1/P$, $m = k$, and $b = 0$. Thus a plot of V versus $1/P$ using Boyle's data gives a straight line with an intercept of zero, as shown in Fig. 5.5(b).
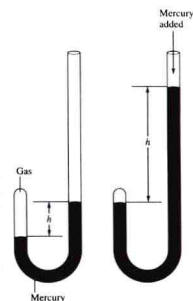
Figure 5.4
A J-tube similar to the one used by Boyle.

Boyle's law: $V \propto 1/P$ at constant temperature.

Graphing is reviewed in Appendix 1.3.

Table 5.1		
Actual Data from Boyle's Experiment		
Volume (in^3)	Pressure (in Hg)	Pressure × Volume (in Hg × in^3)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

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4.1 Water, the Common Solvent

Purpose

• To show why the polar nature of water makes it an effective solvent.

Water is one of the most important substances on earth. It is essential for sustaining the reactions that keep us alive, but it also affects our lives in many indirect ways. Water helps moderate the earth's temperature; it cools automobile engines, nuclear power plants, and many industrial processes; it provides a means of transportation on the earth's surface and a medium for the growth of a myriad of creatures we use as food; and much more.

One of the most valuable properties of water is its ability to dissolve many different substances. For example, salt disappears when you sprinkle it into the water used to cook vegetables, as does sugar when you add it to your iced tea. In each case the "disappearing" substance is obviously still present—you can taste it. What happens when a solid dissolves? To understand this process, we need to consider the nature of water. Liquid water consists of a collection of H_2O molecules. An individual H_2O molecule is "bent" or V-shaped, with an H—O—H angle of approximately 105 degrees:

$$H \overset{105°}{\underset{O}{\frown}} H$$
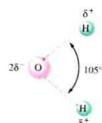
The O—H bonds in the water molecule are covalent bonds formed by electron sharing between the oxygen and hydrogen atoms. However, the electrons of the bond are not shared equally between these atoms. For reasons we will discuss in later chapters, oxygen has a greater attraction for electrons than does hydrogen. If the electrons were shared equally between the two atoms, both would be electrically neutral because, on average, the number of electrons around each would equal the number of protons in that nucleus. However, because the oxygen atom has a greater attraction for electrons, the shared electrons tend to spend more time close to the oxygen than to either of the hydrogens. Thus the oxygen atom gains a slight excess of negative charge, and the hydrogen atoms become slightly positive. This is shown in Fig. 4.1, where δ (delta) indicates a *partial* charge *(less than one unit of charge).* Because of this unequal charge distribution, water is said to be a **polar molecule.** It is this polarity that gives water its great ability to dissolve compounds.

A schematic of an ionic solid dissolving in water is shown in Fig. 4.2. Note that the "positive ends" of the water molecules are attracted to the negatively charged anions and that the "negative ends" are attracted to the positively charged cations. This process is called **hydration.** The hydration of its ions tends to cause a salt to "fall apart" in the water, or to dissolve. The strong forces present among the positive and negative ions of the solid are replaced by strong water–ion interactions.

It is very important to recognize that when ionic substances (salts) dissolve in water, they break up into the *individual* cations and anions. For instance, when ammonium nitrate (NH_4NO_3) dissolves in water, the resulting NH_4^+ and NO_3^- ions moving around independently. This process is represented as

$$NH_4NO_3(s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-(aq)$$
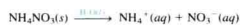
where (*aq*) designates that the ions are hydrated by unspecified molecules.
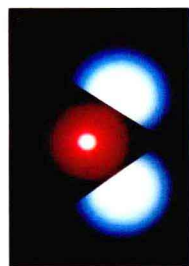
Figure 4.1
(a) The water molecule is polar.
(b) A space-filling model of the water molecule.

Figure 4.2
Polar water molecules interact with the positive and negative ions of a salt, assisting in the dissolving process.

The solubility of ionic substances in water varies greatly. For example, sodium chloride is quite soluble in water, whereas silver chloride (contains Ag^+ and Cl^- ions) is only very slightly soluble. The differences in the solubilities of ionic compounds in water typically depend on the relative attractions of the ions for each other (these forces hold the solid together) and the attractions of the ions for water molecules (which cause the solid to disperse [dissolve] in water). Solubility is a complex

• Visual material is especially important for learning general chemistry, which typically presents a pictorial view of chemical concepts. All of the illustrations in this edition have been reworked to increase student understanding.

The first law of thermodynamics is used mainly for energy bookkeeping, that is, to answer such questions as

How much energy is involved in the change?
Does energy flow into or out of the system?
What form does the energy finally assume?

The first law of thermodynamics: the energy of the universe is constant
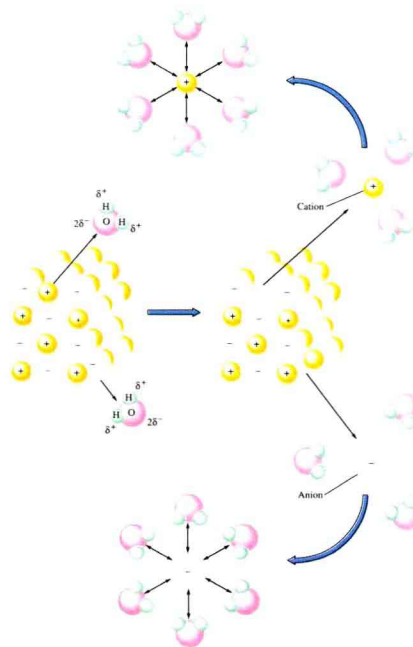
Although the first law of thermodynamics provides the means for accounting for energy, it gives no hint as to *why* a particular process occurs in a given direction. This is the main question to be considered in this chapter.

16.1 Spontaneous Processes and Entropy

Purpose

• To define a spontaneous process.
• To define entropy in terms of positional probability.

Spontaneous does not mean fast

A process is said to be **spontaneous** if it *occurs without outside intervention*. **Spontaneous processes** may be fast or slow. As we will see in this chapter, thermodynamics can tell us the *direction* in which a process will occur but can say nothing about the *speed* of the process. As we saw in Chapter 12, the rate of a reaction depends on many factors, such as activation energy, temperature, concentration, and catalysts, and we were able to explain these effects using a simple collision model. In describing a chemical reaction, the discipline of chemical kinetics focuses on the pathway between reactants and products; thermodynamics only considers the initial and final states and does not require knowledge of the pathway between reactants and products (see Fig. 16.2).

In summary, thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process. For example, according to the principles of thermodynamics, a diamond should change spontaneously to graphite. The fact that we do not observe this process does not mean the prediction is wrong; it simply means the process is very slow. Thus we need both thermodynamics and kinetics to describe reactions fully.

To explore the idea of spontaneity, consider the following physical and chemical processes:

A ball rolls down a hill but never spontaneously rolls back up the hill.

If exposed to air and moisture, steel rusts spontaneously. However, the iron oxide in rust does not spontaneously change back to iron gas.

A gas fills its container uniformly. It never spontaneously col the container.

Heat flow always occurs from a hot object to a cooler one. T never occurs spontaneously.

Wood burns spontaneously in an exothermic reaction to form c water, but wood is not formed when carbon dioxide and together.

• Throughout the text I have used margin notes to highlight key points, to comment on an application of the text material, or to reference material in other parts of the text. I have also included ''Purpose'' statements at the beginning of each section of a chapter to identify the key concepts that will be covered. This book attempts to present chemistry in a manner that makes sense to the student.

• Models are a central theme in this book. The uses and limitations of models are emphasized to show chemistry as a dynamic process. Mistakes are discussed as well as the successes to further illustrate this process. Throughout the text I emphasize that *a model does not equal reality*.

◀ CHEMICAL IMPACT ▶

Testing for Toxicity by Computer

When a new compound that will come in contact with humans is synthesized, the compound's safety must be tested. Currently this is done with expensive bacterial or animal tests. However, computers are now being introduced to screen new compounds to detect those which are likely to be toxic in some way.

The fundamental idea is that the toxicity of a compound is due to some part or parts of the molecular structure. That is, certain types of molecular fragments seem to always lead to a particular kind of toxicity, such as carcinogenicity (ability to cause cancer). The new procedure involves entering known structure–toxicity relationships into the computer database. When a new compound is prepared, its structure is compared by the computer with this database. If the computer finds a fragment in the new molecule that is known to cause a toxic response, this information will alert the researcher to the possible problems. The hope is that this approach will prevent many compounds from being tested only to be rejected after much time and money have already been spent. This should make products both safer and less expensive.

as constructed of individual bonds, C—C, C—H, C—N, C—O, N—H, and so on, it helps tremendously in predicting and understanding the protein's behavior. The essential idea is that we expect a given bond to behave about the same in any molecular environment. Used in this way, the model of the chemical bond has helped chemists to systematize the reactions of the millions of existing compounds.

In addition to being very useful, the bonding model is also physically sensible. It makes sense that atoms can form stable groups by sharing electrons; shared electrons give a lower energy state because they are simultaneously attracted by two nuclei.

Also, as we will see in the next section, bond energy data support the existence of discrete bonds that are relatively independent of the molecular environment. It is very important to remember, however, that the chemical bond is only a model. Although our concept of discrete bonds in molecules agrees with many of our observations, some molecular properties require that we think of a molecule as a whole, with the electrons free to move through the entire molecule. This is called **delocalization** of the electrons, a concept that will be discussed more completely in the next chapter.

Fundamental Properties of Models

• Models are human inventions, always based on an incomplete understanding of how nature works. *A model does not equal reality.*
• Models are often wrong. This property derives from the first property. Models are based on speculation and are always oversimplifications.
• Models tend to become more complicated as they age. As flaws are discovered in our models, we ''patch'' them and thus add more detail.
• It is very important to understand the assumptions inherent in a particular model before you use it to interpret observations or to make predictions. Simple models usually involve very restrictive assumptions and can only be expected to yield qualitative information. Asking for a sophisticated explanation from a simple model is like expecting to get an accurate mass for a diamond using a bathroom scale.

For a model to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the

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Since C_2H_5OH contains six hydrogen atoms, the hydrogen atoms can be balanced by placing a 3 before the H_2O:

$$C_2H_5OH(l) + O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$
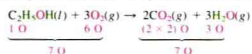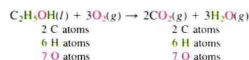$$(5 + 1)\ H \qquad\qquad (3 \times 2)\ H$$
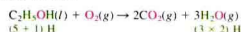
Last, we balance the oxygen atoms. Note that the right side of the preceding equation contains seven oxygen atoms, whereas the left side has only three. We can correct this by putting a 3 before the O_2 to produce the balanced equation:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$
$$1\ O \qquad 6\ O \qquad (2 \times 2)\ O \quad 3\ O$$
$$7\ O \qquad\qquad 7\ O$$

Now we check:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$
$$2\ C\ atoms \qquad 2\ C\ atoms$$
$$6\ H\ atoms \qquad 6\ H\ atoms$$
$$7\ O\ atoms \qquad 7\ O\ atoms$$

The equation is balanced.

WRITING AND BALANCING THE EQUATION FOR A CHEMICAL REACTION

STEP 1
Determine what reaction is occurring. What are the reactants, the products, and the physical states involved?

STEP 2
Write the *unbalanced* equation that summarizes the reaction described in Step 1.

STEP 3
Balance the equation by inspection, starting with the most complicated molecule(s). Determine what coefficients are necessary so that the same number of each type of atom appears on both reactant and product sides. Do not change the identities (formulas) of any of the reactants or products.

Sample Exercise 3.14

Chromate and dichromate compounds are carcinogens (cancer-inducing agents) and should be handled very carefully.

Chromium compounds exhibit a variety of bright colors. When solid ammonium dichromate, $(NH_4)_2Cr_2O_7$, a vivid orange compound, is ignited, a spectacular reaction occurs, as shown in the two photographs. Although the reaction is actually somewhat more complex, let's assume here that the pro[...] chromium(III) oxide, nitrogen gas (consisting of N_2 molecules), [...] Balance the equation for this reaction.

Solution

STEP 1
From the description given, the reactant is solid ammoni[...] $(NH_4)_2Cr_2O_7(s)$, and the products are nitrogen gas, $N_2(g)$, wate[...] and solid chromium(III) oxide, $Cr_2O_3(s)$. The formula for chromi[...]

3.3

be determined by recognizing that the Roman numeral III means that Cr^{3+} ions are present. For a neutral compound, the formula must then be Cr_2O_3, since each oxide ion is O^{2-}.

STEP 2
The unbalanced equation is

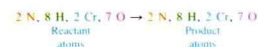$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + H_2O(g)$$

STEP 3
Note that nitrogen and chromium are balanced (two nitrogen atoms and two chromium atoms on each side), but hydrogen and oxygen are not. A coefficient of 4 for H_2O balances the hydrogen atoms:

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$$
$$(4 \times 2)\ H \qquad\qquad (4 \times 2)\ H$$

Note that in balancing the hydrogen we also have balanced the oxygen, since there are seven oxygen atoms in the reactants and in the products.

CHECK:

$$2\ N,\ 8\ H,\ 2\ Cr,\ 7\ O \rightarrow 2\ N,\ 8\ H,\ 2\ Cr,\ 7\ O$$
$$\text{Reactant} \qquad\qquad \text{Product}$$
$$\text{atoms} \qquad\qquad \text{atoms}$$

The equation is balanced.

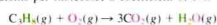Decomposition of ammonium dichromate.

Sample Exercise 3.15

Propane (C_3H_8), a liquid at 25°C under high pressure, is often used as a fuel in rural areas where there is no natural gas pipeline. When liquid propane is released from its storage tank, the pressure on it is lowered and it changes to a gas. Propane gas reacts with oxygen gas (a combustion reaction) in a furnace to produce gaseous carbon dioxide and water vapor. Balance the equation for this reaction.

Solution

The reactants are propane and oxygen; the products are carbon dioxide and water. All are in the gaseous state. Thus the unbalanced equation for the reaction is

$$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$
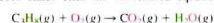
We start with C_3H_8 because it is the most complicated molecule. Since C_3H_8 contains three carbon atoms per molecule, a coefficient of 3 is needed for CO_2:

$$C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + H_2O(g)$$

Also, each C_3H_8 molecule contains eight hydrogen atoms, so a coefficient of 4 is required for H_2O:

$$C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$
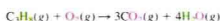
The final element to be balanced is oxygen. Note that the left side of the equation

Propane burns readily in the presence of oxygen, giving this characteristic blue flame.

• A central theme of this book is to present a thoughtful, systematic approach to problem solving. Often I will "walk through" a problem in the text and provide guidelines for developing effective problem-solving techniques. Whenever you see problem-solving strategies set apart in the text followed by a Sample Exercise, you will find that the exercise follows the strategies step-by-step. My goal is to help the student *understand the process*, not *memorize the example*.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the Solutions Guide.

Questions

1. The atomic mass of boron (B) is given in the periodic table as 10.81, yet no single atom of boron has a mass of 10.81 amu. Explain.

2. The listed atomic mass of chromium is 52.00 amu. Does this mean that chromium can have only a single isotope with mass 52.00 amu? Explain.

3. What is the difference between the empirical and molecular formulas of a compound? Can they ever be the same? Explain.

4. Why is the actual yield of a reaction often less than the theoretical yield?

Exercises

In this section similar exercises are paired.

Atomic Masses and the Mass Spectrometer

5. The element magnesium (Mg) has three stable isotopes with the following masses and abundances:

Isotope	Mass (amu)	Abundance
^{24}Mg	23.9850	78.99%
^{25}Mg	24.9858	10.00%
^{26}Mg	25.9826	11.01%

Calculate the average atomic mass (the atomic weight) of magnesium from these data.

6. Assume that element Uus is synthesized and that it has the following stable isotopes:

^{284}Uus (283.4 amu)	34.60%	
^{285}Uus (284.7 amu)	21.20%	
^{288}Uus (287.8 amu)	44.20%	

What is the value of the average atomic mass for Uus that would be listed on the periodic table?

7. The element europium exists in nature as two isotopes: ^{151}Eu has a mass of 150.9196 amu, and ^{153}Eu has a mass of 152.9209 amu. The average atomic mass of europium is 151.96 amu. Calculate the relative abundance of the two europium isotopes.

8. The element silver (Ag) has two naturally occurring isotopes: ^{109}Ag and ^{107}Ag with a mass of 106.905 amu. Silver consists of 51.82% ^{107}Ag and has an average atomic mass of 107.868 amu. Calculate the mass of ^{109}Ag.

9. The mass spectrum of bromine (Br$_2$) consists of three peaks with the following characteristics:

Mass (amu)	Relative size
157.84	0.2534
159.84	0.5000
161.84	0.2466

How do you interpret these data?

10. Naturally occurring tellurium (Te) has the following isotopic abundances:

Isotope	Abundance	Mass (amu)
^{120}Te	0.09%	119.90
^{122}Te	2.46%	121.90
^{123}Te	0.87%	122.90
^{124}Te	4.61%	123.90
^{125}Te	6.99%	124.90
^{126}Te	18.71%	125.90
^{128}Te	31.79%	127.90
^{130}Te	34.48%	129.91

Draw the mass spectrum of H$_2$Te, assuming that the only hydrogen isotope present is ^{1}H (mass 1.008).

b. What masses of anthraquinone and of water are produced assuming 100% yield?

c. If 1.96×10^3 g anthraquinone is actually obtained, what is the percent yield of the reaction?

Additional Exercises

85. Calculate the molar mass for each of the following substances:

a. Cu(H$_2$O)$_6$Cl$_2$

b. NaBrO$_3$

c. (C$_2$F$_4$)$_{500}$ (the polymer Teflon), which is made of the unit

[structure of C$_2$F$_4$ unit]

d. H$_3$PO$_4$

e. CaCO$_3$

86. Chloral hydrate (C$_2$H$_3$Cl$_3$O$_2$) is a drug formerly used as a sedative and hypnotic. It is the compound used to make "Mickey Finns" in detective stories.

a. Calculate the molar mass of chloral hydrate.

b. How many moles of C$_2$H$_3$Cl$_3$O$_2$ molecules are in 500.0 g chloral hydrate?

c. What is the mass in grams of 2.0×10^{-2} mol chloral hydrate?

d. How many chlorine atoms are in 5.0 g chloral hydrate?

87.

is made from 1.00×10^3 g adipic acid?

Challenge Problems

104. In the spring of 1984 concern arose over the presence of ethylene dibromide, or EDB, in grains and cereals. EDB has the molecular formula C$_2$H$_4$Br$_2$ and until 1984 was commonly used a plant fumigant. The federal limit for EDB in finished cereal products is 30.0 parts per billion (ppb), where 1.0 ppb = 10^{-9} g EDB for every 1.0 g sample. How many molecules of EDB are in 1.0 lb flour if 30.0 ppb EDB is present?

105. When aluminum metal is heated with an element from Group 6A of the periodic table, an ionic compound forms. When the experiment is performed with an unknown Group 6A element, the product is 18.56% Al by mass. What is the formula of the compound?

106. A salt contains only barium and one of the halide ions. A 0.158-g sample of the salt was dissolved in water, and an excess of sulfuric acid was added to form barium sulfate (BaSO$_4$), which was filtered, dried, and weighed. Its mass was found to be 0.124 g. What is the formula of the barium halide?

107. Hydrogen cyanide is produced industrially from the reaction of gaseous ammonia, oxygen, and methane:

$$2NH_3(g) + 3O_2(g) + 2CH_4(g) \rightarrow 2HCN(g) + 6H_2O(g)$$

If 5.00×10^3 kg each of NH$_3$, O$_2$, and CH$_4$ are reacted, what mass of HCN and of H$_2$O would be produced, assuming 100% yield?

111. A 1.500-g sample of a mixture containing only Cu$_2$O and CuO was treated with hydrogen to produce 1.252 g pure copper metal. Calculate the percentage composition (by mass) of the mixture.

Marathon Problem*

112. From the information below, determine the mass of substance C that will be formed if 45.0 grams of substance A reacts with 23.0 grams of substance B. (Assume that the reaction between A and B goes to completion.)

a. Substance A is a gray solid that consists of an alkaline earth metal and carbon (37.5% by mass). It reacts with substance B to produce substances C and D. Forty million trillion formula units of A have a mass of 4.26 milligrams.

b. 47.9 grams of substance B contains 5.36 grams of hydrogen and 42.5 grams of oxygen.

c. When 10.0 grams of C is burned in excess oxygen, 33.8 grams of carbon dioxide and 6.92 grams of water are produced. A mass spectrum of substance C shows a parent molecular ion with a charge-to-mass ratio of 26.

d. Substance D is the hydroxide of the metal in substance A.

*This Marathon Problem was developed by James H. Burness of Penn State University, York Campus.

(Excerpts from pp. 123 and 125.)

• It is very important that students use the exercise sets to their best advantage. And in this edition the exercise sets have undergone a major change. First there are the "Questions," which require a short written answer. These test conceptual understanding rather than number crunching. Next are the "Exercises," generally drill-type in nature, keyed by topic in the chapter and now in matched pairs. Students will have access to the answer to each odd-numbered problem in the back of the book, and the solution for each is included in the *Solutions Guide*. For the matching even-numbered problems, there is no student help. This both gives versatility to homework assignments and builds student self-confidence in mastering problem-solving skills. The third group, "Additional Exercises," requires more student thought—these exercises require more synthesis of various concepts and are not listed by chapter topic. "Challenge Exercises" are exactly that, and have been included to offer a wider range of difficulty in the problem sets. The final "Marathon Problem" is more comprehensive, helping students to see relationships. It may be done in class as a group problem, helping students to develop yet another problem-solving technique—working as a member of a team.