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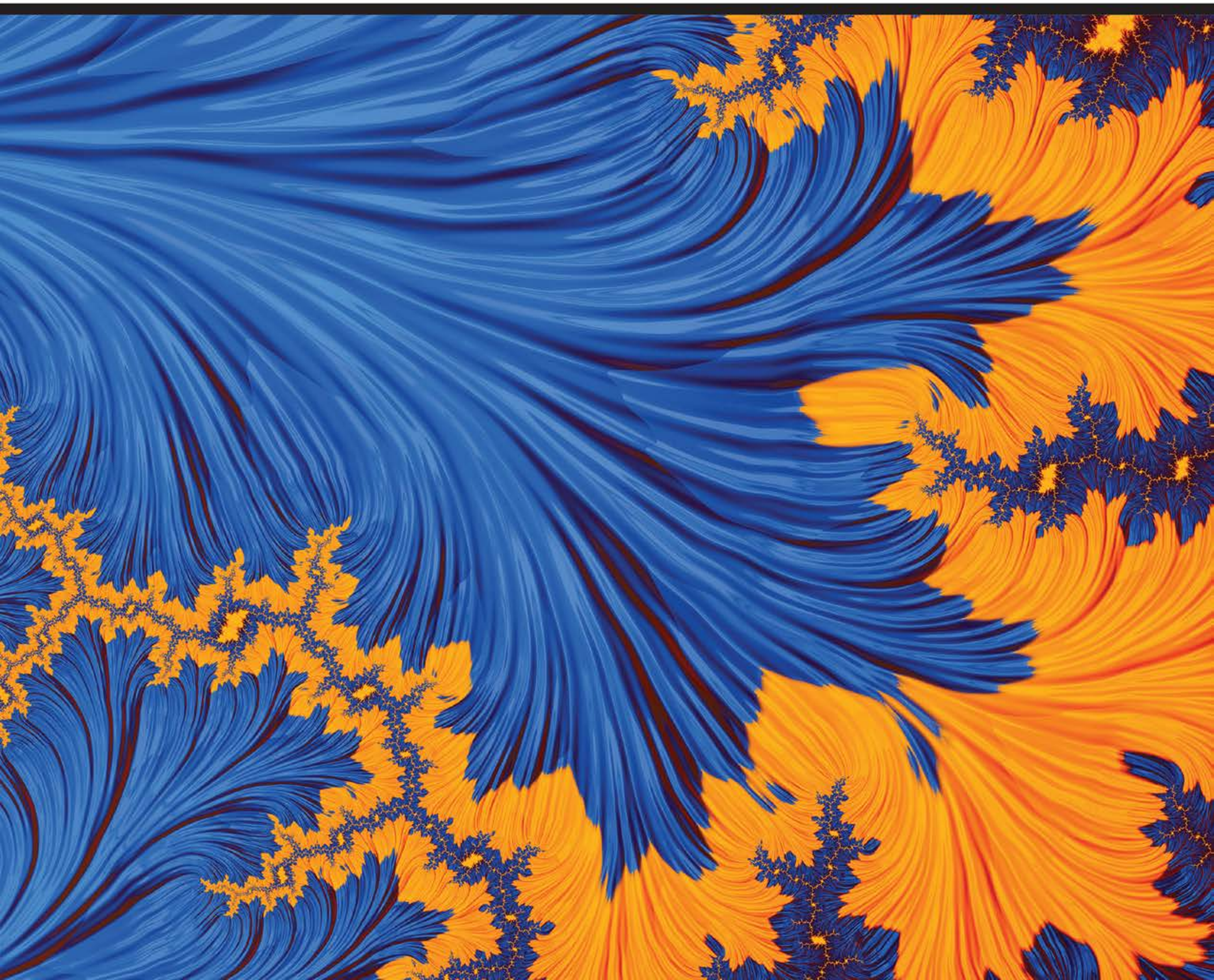

Chemistry

Eleventh Edition

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***Chemistry,* Eleventh Edition**
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Contents

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Chapter 4 | Types of Chemical Reactions and Solution Stoichiometry 116

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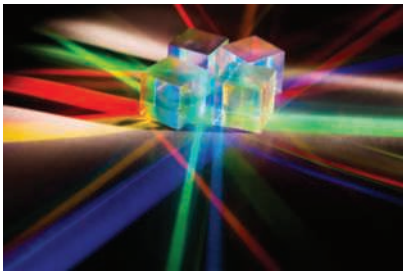
Chapter 5 | Gases 163

Hafsteinn Karlsson / 500px/Getty Images

Chapter 6 | Thermochemistry 209



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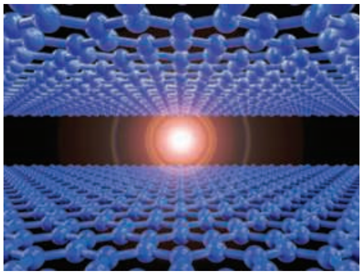
Chapter 7 | Atomic Structure and Periodicity 242

Douglas Klug/Getty Images



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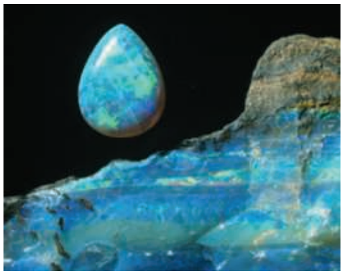

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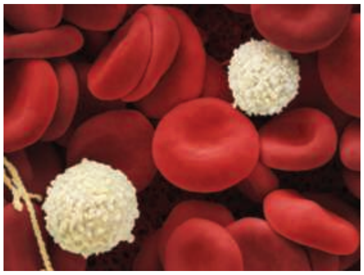

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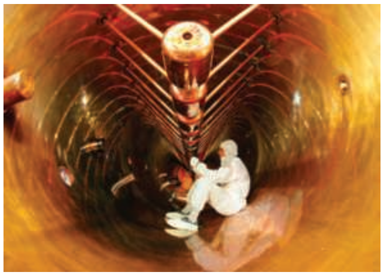

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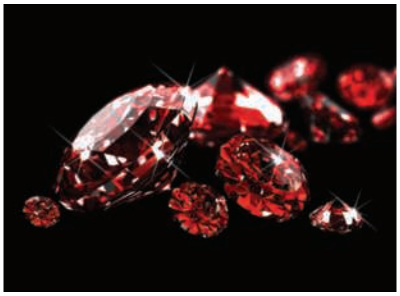
Chapter 20 | The Representative Elements 775


stanislav rishnyak / Alamy Stock Photo

Chapter 21 | Transition Metals and Coordination Chemistry 813


Podlesnyak Nina/Shutterstock

Chapter 22 | Organic and Biological Molecules 858

Appendix 1 | Mathematical Procedures A1

Appendix 2 | The Quantitative Kinetic Molecular Model A14

Appendix 3 | Spectral Analysis A18

To the Professor

Features of *Chemistry*, Eleventh Edition

Conceptual learning and problem solving are fundamental to the approach of ***Chemistry***. Our philosophy is to help students learn to think like chemists so that they can apply the process of problem solving to all aspects of their lives. We give students the tools to become critical thinkers: to ask questions, to apply rules and models, and to evaluate the outcome. It was also our mission to create a media program that embodies this philosophy so that when instructors and students look online for either study aids or online homework, each resource supports the goals of the textbook—a strong emphasis on *models, real-world applications,* and *visual learning*.

What's New

We have made extensive updates to the ***Eleventh Edition*** to enhance the learning experience for students. **Here's what's new:**

- We have added a variety of new assessments to the text:
  - New Active Learning Questions in every chapter
  - 19 New Interactive Examples
- We have added the new subsection:
  - A Review of States of Matter 10.1a
- We have added 12 new Pioneers in Chemistry boxes:
  - Robert Boyle (Chapter 1)
  - Antoine Lavoisier (Chapter 2)
  - John Dalton (Chapter 2)
  - Jennifer Doudna (Chapter 3)
  - St. Elmo Brady (Chapter 3)
  - Dmitri Ivanovich Mendeleev (Chapter 7)
  - Arnold Beckman (Chapter 14)
  - Marie Sklodowska Curie (Chapter 19)
  - Rosalyn Sussman Yalow (Chapter 19)
  - Wallace Hume Carothers (Chapter 22)
- Throughout the text we have updated the colors of figures and graphs for visual accessibility as well as emphasizing accessibility throughout the digital course.
- We had added a new feature in each chapter called "Chemistry in Your Career," providing insight into the diverse and wide-ranging careers students can pursue after taking chemistry.
- 550 new or revised end-of-chapter questions and problems have been added throughout the text.
- The art program has been modified and updated for currency and consistency within molecular structures.
- We have updated chapter opening images and introductions throughout the book.
- We have developed this newest edition with a focus on clarity and conciseness.

Hallmarks of *Chemistry*

- ***Chemistry*** contains numerous discussions, illustrations, and exercises aimed at *overcoming misconceptions*. It has become increasingly clear from our own teaching experience that students often struggle with chemistry because they misunderstand many of the fundamental concepts. In this text, we have gone to great lengths to provide illustrations and explanations aimed at giving students a more accurate picture of the fundamental ideas of chemistry. In particular, we have attempted to represent the microscopic world of chemistry so that students have a picture in their minds of "what the atoms and molecules are doing." The art program along with the animations emphasize this goal. We have also placed a larger emphasis on the qualitative understanding of concepts before quantitative problems are considered. Because using an algorithm to correctly solve a problem often masks misunderstanding—when students assume they understand the material because they got the right "answer"—it is important to probe their understanding in other ways. In this vein, the text includes many *Critical Thinking* questions throughout the text and a number of *Active Learning Questions* at the end of each chapter that are intended for group discussion. It is our experience that students often learn the most when they teach each other. Students are forced to recognize their own lack of understanding when they try and fail to explain a concept to another student.
- With a strong *problem-solving orientation,* this text talks to students about how to approach and solve chemical problems. We emphasize a thoughtful, 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 Examples,* with more given in the text discussions, to illustrate general problem-solving strategies. When a specific strategy is presented, it is summarized in a *Problem-Solving Strategy* box, and the *Example* that follows it reinforces the use of the strategy to solve the problem. In general, we emphasize the use of conceptual understanding to solve problems rather than an algorithm-based approach. This approach is strongly reinforced by the inclusion of many *Interactive Examples,* which encourage students to thoughtfully consider the example step-by-step.
- We have presented a thorough *treatment of reactions* that occur in solution, including acid–base reactions. This material appears in Chapter 4, "Types of Chemical Reactions and Solution Stoichiometry," 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 and balancing by oxidation state, 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 observation and models can make chemistry both interesting and understandable. In the chapter on the chemistry of the elements, we have used tables and charts to show how properties and models correlate. Descriptive chemistry is presented in a variety of ways—as applications of principles in separate sections, in photographs, in *Examples* and exercises, in paragraphs, and in *Chemical Connections*.
- Throughout the book a strong *emphasis on models* prevails. Coverage includes how they are constructed, how they are tested, and what we learn when they inevitably fail. Models are developed naturally, with pertinent observation always presented first to show why a particular model was invented.
- **Chemical Connections** boxes present applications of chemistry in various fields and in our daily lives.
- We offer end-of-chapter exercises for every type of student and for every kind of homework assignment: questions that promote group learning, exercises that reinforce student understanding, and problems that present the ultimate challenge with increased rigor and by integrating multiple concepts. We have added biochemistry problems to make the connection for students in the course who are not chemistry majors.
- Judging from the favorable comments of instructors and students who have used the tenth edition, the text seems to work very well in a variety of courses. We were especially pleased that *readability* was cited as a key strength when students were asked to assess the text.

Supporting Materials

Instructor and student materials are available online.

Acknowledgments

This book represents the efforts of many talented and dedicated people. We want to thank Maureen McLaughlin, Product Director, for her oversight of the project, and Helene Alfaro, Senior Product Manager. We also appreciate the work of Meagan Ford, Senior Content Project Manager, who managed the production of this complex project.

We are especially grateful to Tom Hummel, University of Illinois, Urbana-Champaign, who managed the revision of the end-of-chapter problems. Tom's extensive experience teaching general chemistry and his high standards of accuracy and clarity have resulted in great improvements in the quality of the problems and solutions in this edition. Gretchen Adams supports us in so many ways it is impossible to list all of them. Gretchen performed the entire digital audit for our online course content as well as constructed new hints and targeted feedback throughout our assessments. We are very grateful to Gretchen for her creativity and incredible work ethic and for being such a wonderful colleague.

Special thanks to Sharon Donahue, who did her usual outstanding job finding just the right photos for this edition.

There are many other people who made important contributions to the success of this edition, including Product Managers at Lumina: Amanda Mullins and Nancy Kincade for their professionalism and patience as well as their attention to detail in the production of this complex project. Cover and Interior Designer: Chris Doughman, Product Assistant: Ellie Purgavie who helped in many different ways.

We are especially thankful to all of the reviewers who participated in different aspects of the development process, from reviewing the illustrations and chapters to providing feedback on the development of new features. We sincerely appreciate all of these suggestions.

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To the Student

As you jump into the study of chemistry, we hope that you will find our text helpful and interesting. Our job is to present the concepts and ideas of chemistry in a way you can understand. We hope to encourage you in your studies and to help you learn to solve problems in ways you can apply in all areas of your professional and personal lives.

Our main goal is to help you learn to become a truly creative problem solver. Our world badly needs people who can "think outside the box." Our focus is to help you learn to think like a chemist. Why would you want to do that? Chemists are great problem solvers. They use logic, trial and error, and intuition—along with lots of patience—to work through complex problems. Chemists make mistakes, as we all do in our lives. The important thing that a chemist does is to learn from the mistakes and to try again. This "can do" attitude is useful in all careers.

In this book we develop the concepts in a natural way: The observations come first and then we develop models to explain the observed behavior. Models help us to understand and explain our world. They are central to scientific thinking. Models are very useful, but they also have limitations, which we will point out. By understanding the basic concepts in chemistry we lay the foundation for solving problems.

Our main goal is to help you learn a thoughtful method of problem solving. True learning is more than memorizing facts. Truly educated people use their factual knowledge as a starting point—a basis for creative problem solving. Our strategy for solving problems is explained first in Section 1.6 and is covered in more details in Section 3.5. To solve a problem we ask ourselves questions, which help us think through the problem. We let the problem guide us to the solution. This process can be applied to all types of problems in all areas of life.

As you study the text, use the *Examples* and the problem-solving strategies to help you. The strategies are boxed to highlight them for you, and the *Examples* show how these strategies are applied. It is especially important for you to do the computer-based *Interactive Examples* that are found throughout the text. These examples encourage you to think through the examples step-by-step to help you thoroughly understand the concepts involved.

After you have read and studied each chapter of the text, you'll need to practice your problem-solving skills. To do this we have provided plenty of review questions and end-of-chapter exercises. Your instructor may assign these on paper or online; in either case, you'll want to work with your fellow students. One of the most effective ways to learn chemistry is through the exchange of ideas that comes from helping one another. The online homework assignments will give you instant feedback, and in print, we have provided answers to some of the exercises in the back of the text. In all cases, your main goal is not just to get the correct answer but to understand the process for getting the answer. Memorizing solutions for specific problems is not a very good way to prepare for an exam (or to solve problems in the real world!).

To become a great problem solver, you'll need these skills:

1. Look within the problem for the solution. (Let the problem guide you.)
2. Use the concepts you have learned along with a systematic, logical approach to find the solution.
3. Solve the problem by asking questions and 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 practice, practice, practice and to use your mistakes to find your weaknesses. Be patient with yourself and work hard to understand rather than simply memorize.

We hope you'll have an interesting and successful year learning to think like a chemist!

Steve and Susan Zumdahl
and Don DeCoste

A Guide to Chemistry, Eleventh Edition

Conceptual Understanding Conceptual learning and problem solving are fundamental to the approach of **Chemistry**. The text gives students the tools to become critical thinkers: to ask questions, to apply rules and models, and to evaluate the outcome.

"Before students are ready to figure out complex problems, they need to master simpler problems in various contortions. This approach works, and the authors' presentation of it should have the students buying in."

—**Jerry Burns,** ***Pellissippi State Technical Community College***

The authors' **emphasis on modeling** (or chemical theories) throughout the text addresses the problem of rote memorization by helping students better understand and appreciate the process of scientific thinking. By stressing the limitations and uses of scientific models, the authors show students how chemists think and work.

Molecular Structure: The VSEPR Model

The structures of molecules play a very important role in determining their chemical properties. As we will see later, this is particularly important for biological molecules; a slight change in the structure of a large biomolecule can completely destroy its usefulness to a cell or may even change the cell from a normal one to a cancerous one.

Critical Thinking You have seen that the water molecule has a bent shape and therefore is a polar molecule. This accounts for many of water's interesting properties. What if the water molecule was linear? How would this affect the properties of water, such as its surface tension, heat of vaporization, and vapor pressure? How would life be different?

The text includes a number of open-ended **Critical Thinking** questions that emphasize the importance of conceptual learning. These questions are particularly useful for generating group discussion.

Let's Review Summary of the VSEPR Model

The rules for using the VSEPR model to predict molecular structure are as follows:

- Determine the Lewis structure(s) for the molecule.
- For molecules with resonance structures, use any of the structures to predict the molecular structure.
- Sum the electron pairs around the central atom.
- In counting pairs, count each multiple bond as a single effective pair.
- The arrangement of the pairs is determined by minimizing electron-pair repulsions. These arrangements are shown in Table 8.7.
- Lone pairs require more space than bonding pairs do. Choose an arrangement that gives the lone pairs as much room as possible. Recognize that the lone pairs may produce a slight distortion of the structure at angles less than 120 degrees.

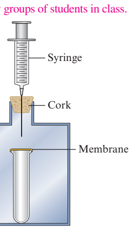
Let's Review boxes help students organize their thinking about the crucial chemical concepts that they encounter.

The text includes a number of **Active Learning Questions** at the end of each chapter that are intended for group discussion, since students often learn the most when they teach each other.

Active Learning Questions

These questions are designed to be used by groups of students in class.

1. Consider the following apparatus: a test tube covered with a nonpermeable elastic membrane inside a container that is closed with a cork. A syringe goes through the cork.



   a. As you push down on the syringe, how does the membrane covering the test tube change?
   b. You stop pushing the syringe but continue to hold it down. In a few seconds, what happens to the membrane?

2. Figure 5.2 shows a picture of a barometer. Which of the following statements is the best explanation of how this barometer works?
   a. Air pressure outside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.

Problem Solving This text talks to the student about how to approach and solve chemical problems, since one of the main goals of general chemistry is to help students become creative problem solvers. The authors emphasize a thoughtful, logical approach rather than simply memorizing procedures.

"The text gives a meaningful explanation and alternative to memorization. This approach and the explanation [to the student] of the approach will supply the 'secret' of successful problem solving abilities to all students."

—**David Boyajian,** ***Palomar College***

In **Chapter 3**, "Stoichiometry," the authors introduce a new section, **Learning to Solve Problems,** which emphasizes the importance of problem solving. This new section helps students understand that thinking their way through a problem produces more long-term, meaningful learning than simply memorizing steps, which are soon forgotten.

Learning to Solve Problems

One of the great rewards of studying chemistry is becoming a good problem solver. Being able to solve complex problems is a talent that will serve you well in all walks of life. It is our purpose in this text to help you learn to solve problems in a flexible, creative way based on understanding the fundamental ideas of chemistry. We call this approach **conceptual problem solving**.

The ultimate goal is for you to be able to solve new problems (that is, problems you have not seen before) on your own. In this text, we will provide problems and offer solutions by explaining how to think about the problems. While the answers to these problems are important, it is perhaps even more important to understand the process—the thinking necessary to get the answer. Although at first we will be solving the problem for you, do not take a passive role. While studying the solution, it is crucial that you interactively think through the problem with us. Do not skip the discussion and jump to the answer. Usually, the solution will involve asking a series of questions. Make sure that you understand each step in the process. This active approach should apply to problems outside of chemistry as well. For example, imagine riding with someone in a car to an unfamiliar destination. If your goal is simply to have the other person get you to that destination, you will probably not pay much attention to how to get there (passive), and if you have to find this same place in the future on your own, you probably will not be able to do it. If, however, your goal is to learn how to get there, you would pay attention to distances, signs, and turns (active). This is how you should read the solutions in the text (and the text in general).

While actively studying our solutions to problems is helpful, at some point you will need to know how to think through these problems on your own. If we help you too much as you solve a problem, you won't really learn effectively. If we always "drive," you won't interact as meaningfully with the material. Eventually you need to learn to drive yourself. We will provide more help at the beginning of the text and less as we proceed to later chapters.

There are two fundamentally different ways you might use to approach a problem. One way emphasizes memorization. We might call this the pigeonholing method. In this approach, the first step is to label the problem—to decide in which pigeonhole it fits. The pigeonholing method requires that we provide you with a set of steps that you memorize and store in the appropriate slot for each different problem you encounter. The difficulty with this method is that it requires a new pigeonhole each time a problem is changed by even a small amount.

Consider the driving analogy again. Suppose you have memorized how to drive from your house to the grocery store. Do you know how to drive back from the grocery store to your house? Not necessarily. If you have only memorized the directions and do not understand fundamental principles such as "I traveled north to get to the store, so my house is south of the store," you may find yourself stranded. In a more complicated example, suppose you know how to get from your house to the store (and back) and from your home to the library (and back). Can you get from the library to the store without having to go back home? Probably not if you have only memorized directions and you do not have a "big picture" of where your house, the store, and the library are relative to one another.

The second approach is conceptual problem solving, in which we help you get the "big picture"—a real understanding of the situation. This approach to problem solving looks within the problem for a solution. In this method, we assume that the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▲ Pigeonholes can be used for sorting and classifying objects like mail.

Chapters 1–6 introduce a series of questions into the in-chapter **Examples** to engage students in the process of problem solving, such as **Where are we going?** and **How do we get there?** This more active approach helps students think their way through the solution to the problem.

Example 1.12 **Temperature Conversions II**

One interesting feature of the Celsius and Fahrenheit scales is that $-40°C$ and $-40°F$ represent the same temperature, as shown in Fig. 1.8. Verify that this is true.

Solution

Where are we going?

To show that $-40°C = -40°F$

What do we know?

› The relationship between the Celsius and Fahrenheit scales

How do we get there?

The difference between 32°F and −40°F is 72°F. The difference between 0°C and −40°C is 40°C. The ratio of these is

$$\frac{72°F}{40°C} = \frac{8 \times 9°F}{8 \times 5°C} = \frac{9°F}{5°C}$$

as required. Thus, −40°C is equivalent to −40°F.

See Exercise 1.73

Problem-Solving Strategy

Determining Molecular Formula from Empirical Formula

» Obtain the empirical formula.

» Compute the mass corresponding to the empirical formula.

» Calculate the ratio:

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

» The integer from the previous step represents the number of empirical formula units in one molecule. When the empirical formula subscripts are multiplied by this integer, the molecular formula results. This procedure is summarized by the equation:

$$\text{Molecular formula} = \text{empirical formula} \times \frac{\text{molar mass}}{\text{empirical formula mass}}$$

Problem-Solving Strategy boxes focus students' attention on the very important process of problem solving.

Interactive Examples engage students in the problem-solving process by requiring them to think through the example step-by-step rather than simply scanning the written example in the text as many students do.

Interactive Example 17.2 **Predicting Entropy Changes**

An interactive version of this example with a step-by-step approach is available online.

Predict the sign of the entropy change for each of the following processes.

a. Solid sugar is added to water to form a solution.

b. Iodine vapor condenses on a cold surface to form crystals.

Solution

a. The sugar molecules become randomly dispersed in the water when the solution forms and thus have access to a larger volume and a larger number of possible positions. The positional disorder is increased, and there will be an increase in entropy. ΔS is positive, since the final state has a larger entropy than the initial state, and $\Delta S = S_{\text{final}} - S_{\text{initial}}$.

b. Gaseous iodine is forming a solid. This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional disorder. For this process, ΔS is negative (the entropy decreases).

See Exercise 17.46

Dynamic Art Program Most of the glassware, orbitals, graphs, flowcharts, and molecules have been redrawn to better serve visual learners and enhance the textbook.

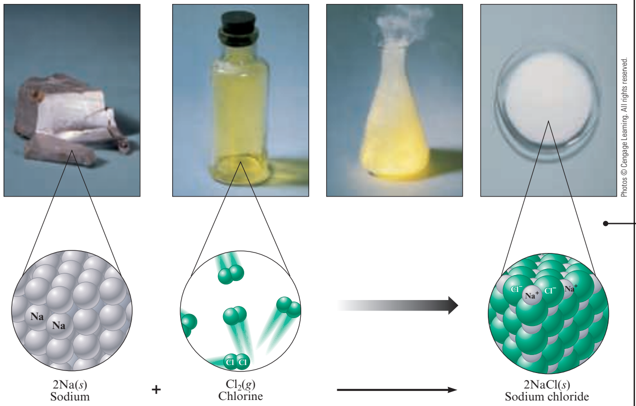


Figure 4.19 The reaction of solid sodium and gaseous chlorine to form solid sodium chloride.

The art program emphasizes molecular-level interactions that help students visualize the “micro/macro” connection.

Realistic drawings of glassware and instrumentation found in the lab help students make real connections.

Figure 4.10 Steps involved in the preparation of a standard aqueous solution. (**a**) Put a weighed amount of a substance (the solute) into the volumetric flask, and add a small quantity of water. (**b**) Dissolve the solid in the water by gently swirling the flask (*with the stopper in place*). (**c**) Add more water (with gentle swirling) until the level of the solution just reaches the mark etched on the neck of the flask. Then mix the solution thoroughly by inverting the flask several times.

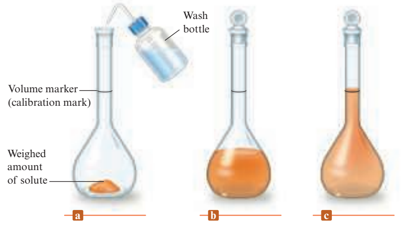


Figure 8.5 (**a**) The charge distribution in the water molecule. (**b**) The water molecule in an electric field. (**c**) The electrostatic potential diagram of the water molecule.

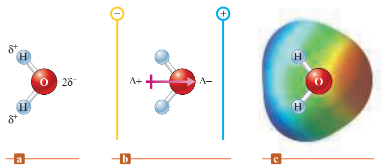
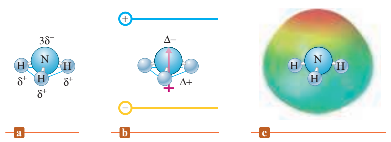


Figure 8.6 (**a**) The structure and charge distribution of the ammonia molecule. The polarity of the N—H bonds occurs because nitrogen has a greater electronegativity than hydrogen. (**b**) The dipole moment of the ammonia molecule oriented in an electric field. (**c**) The electrostatic potential diagram for ammonia.



Electrostatic potential maps help students visualize the distribution of charge in molecules.

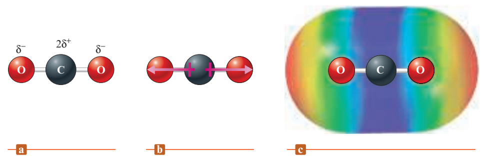
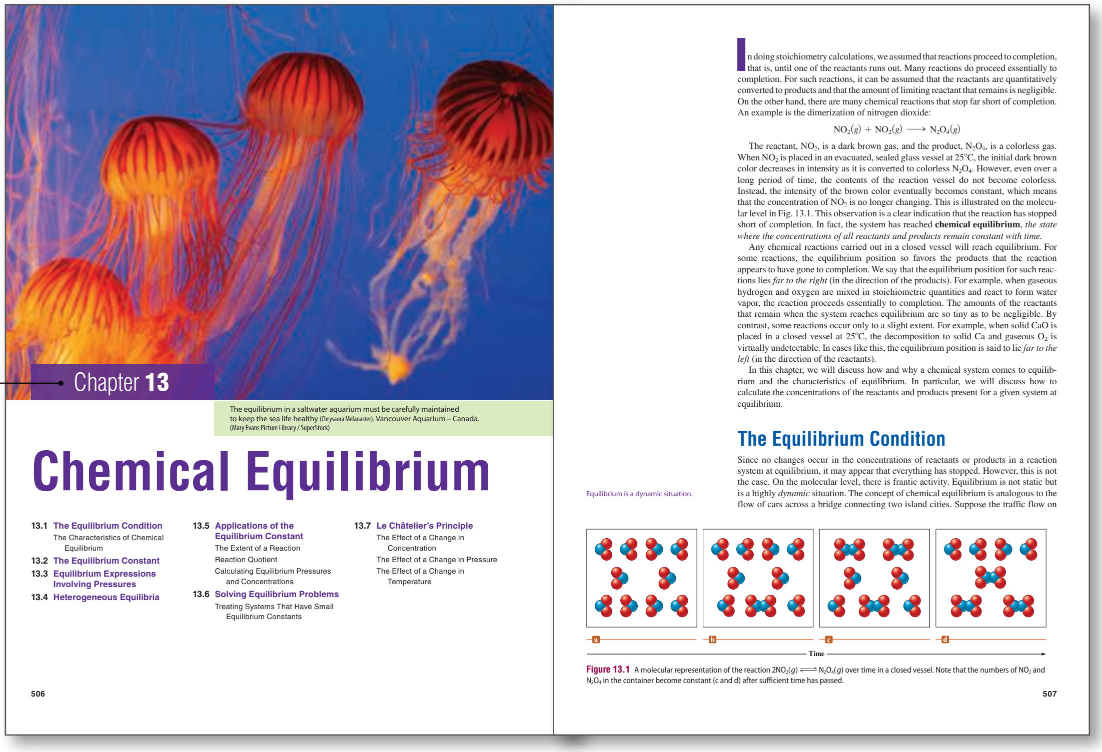


Figure 8.7 (**a**) The carbon dioxide molecule. (**b**) The opposed bond polarities cancel out, and the carbon dioxide molecule has no dipole moment. (**c**) The electrostatic potential diagram for carbon dioxide.

Real-World Applications Interesting applications of modern chemistry show students the relevance of chemistry to their world.

Each chapter begins with an engaging introduction that demonstrates how chemistry is related to everyday life.



Chapter 13

The equilibrium in a saltwater aquarium must be carefully maintained to keep the sea life healthy (Chrysaora Melanaster). Vancouver Aquarium – Canada. (Mary Evans Picture Library / SuperStock)

Chemical Equilibrium

506

In doing stoichiometry calculations, we assumed that reactions proceed to completion, that is, until one of the reactants runs out. Many reactions do proceed essentially to completion. For such reactions, it can be assumed that the reactants are quantitatively converted to products and that the amount of limiting reactant that remains is negligible. On the other hand, there are many chemical reactions that stop far short of completion. An example is the dimerization of nitrogen dioxide:

$$NO_2(g) + NO_2(g) \longrightarrow N_2O_4(g)$$

The reactant, NO_2, is a dark brown gas, and the product, N_2O_4, is a colorless gas. When NO_2 is placed in an evacuated, sealed glass vessel at 25°C, the initial dark brown color decreases in intensity as it is converted to colorless N_2O_4. However, even over a long period of time, the contents of the reaction vessel do not become colorless. Instead, the intensity of the brown color eventually becomes constant, which means that the concentration of NO_2 is no longer changing. This is illustrated on the molecular level in Fig. 13.1. This observation is a clear indication that the reaction has stopped short of completion. In fact, the system has reached **chemical equilibrium**, *the state where the concentrations of all reactants and products remain constant with time.*

Any chemical reactions carried out in a closed vessel will reach equilibrium. For some reactions, the equilibrium position so favors the products that the reaction appears to have gone to completion. We say that the equilibrium position for such reactions lies *far to the right* (in the direction of the products). For example, when gaseous hydrogen and oxygen are mixed in stoichiometric quantities and react to form water vapor, the reaction proceeds essentially to completion. The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible. By contrast, some reactions occur only to a slight extent. For example, when solid CaO is placed in a closed vessel at 25°C, the decomposition to solid Ca and gaseous O_2 is virtually undetectable. In cases like this, the equilibrium position is said to lie *far to the left* (in the direction of the reactants).

In this chapter, we will discuss how and why a chemical system comes to equilibrium and the characteristics of equilibrium. In particular, we will discuss how to calculate the concentrations of the reactants and products present for a given system at equilibrium.

The Equilibrium Condition

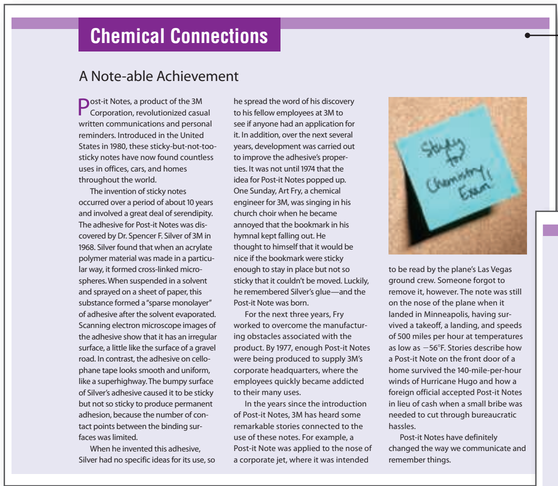
Equilibrium is a dynamic situation.

Since no changes occur in the concentrations of reactants or products in a reaction system at equilibrium, it may appear that everything has stopped. However, this is not the case. On the molecular level, there is frantic activity. Equilibrium is not static but is a highly *dynamic* situation. The concept of chemical equilibrium is analogous to the flow of cars across a bridge connecting two island cities. Suppose the traffic flow on

Figure 13.1 A molecular representation of the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ over time in a closed vessel. Note that the numbers of NO_2 and N_2O_4 in the container become constant (c and d) after sufficient time has passed.

507

Chemical Connections describe current applications of chemistry. These special-interest boxes cover such topics as the invention of Post-it Notes, the metabolic rate of plants, and the use of iron metal to clean up contaminated groundwater.



Chemical Connections

A Note-able Achievement

Post-it Notes, a product of the 3M Corporation, revolutionized casual written communications and personal reminders. Introduced in the United States in 1980, these sticky-but-not-too-sticky notes have now found countless uses in offices, cars, and homes throughout the world.

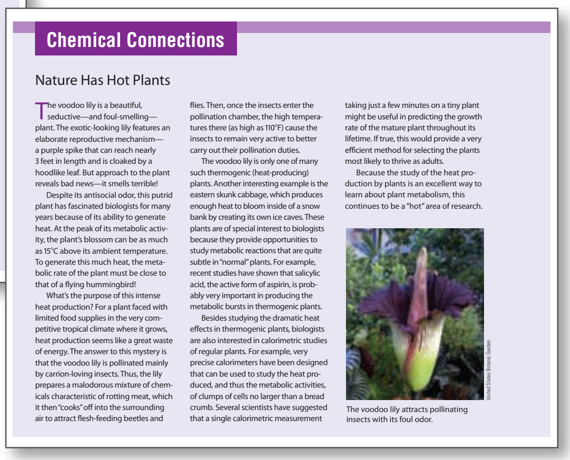
The invention of sticky notes occurred over a period of about 10 years and involved a great deal of serendipity. The adhesive for Post-it Notes was discovered by Dr. Spencer F. Silver of 3M in 1968. Silver found that when an acrylate polymer material was made in a particular way, it formed cross-linked microspheres. When suspended in a solvent and sprayed on a sheet of paper, this substance formed a "sparse monolayer" of adhesive after the solvent evaporated. Scanning electron microscope images of the adhesive show that it has an irregular surface, a little like the surface of a gravel road. In contrast, the adhesive on cellophane tape looks smooth and uniform, like a superhighway. The bumpy surface of Silver's adhesive caused it to be sticky but not so sticky to produce permanent adhesion, because the number of contact points between the binding surfaces was limited.

When he invented this adhesive, Silver had no specific ideas for its use, so he spread the word of his discovery to his fellow employees at 3M to see if anyone had an application for it. In addition, over the next several years, development was carried out to improve the adhesive's properties. It was not until 1974 that the idea for Post-it Notes popped up. One Sunday, Art Fry, a chemical engineer for 3M, was singing in his church choir when he became annoyed that the bookmark in his hymnal kept falling out. He thought to himself that it would be nice if the bookmark were sticky enough to stay in place but not so sticky that it couldn't be moved. Luckily, he remembered Silver's glue—and the Post-it Note was born.

For the next three years, Fry worked to overcome the manufacturing obstacles associated with the product. By 1977, enough Post-it Notes were being produced to supply 3M's corporate headquarters, where the employees quickly became addicted to their many uses.

In the years since the introduction of Post-it Notes, 3M has heard some remarkable stories connected to the use of these notes. For example, a Post-it Note was applied to the nose of a corporate jet, where it was intended to be read by the plane's Las Vegas ground crew. Someone forgot to remove it, however. The note was still on the nose of the plane when it landed in Minneapolis, having survived a takeoff, a landing, and speeds of 500 miles per hour at temperatures as low as −56°F. Stories describe how a Post-it Note on the front door of a home survived the 140-mile-per-hour winds of Hurricane Hugo and how a foreign official accepted Post-it Notes in lieu of cash when a small bribe was needed to cut through bureaucratic hassles.

Post-it Notes have definitely changed the way we communicate and remember things.



Chemical Connections

Nature Has Hot Plants

The voodoo lily is a beautiful, seductive—and foul-smelling—plant. The exotic-looking lily features an elaborate reproductive mechanism—a purple spike that can reach nearly 3 feet in length and is cloaked by a hoodlike leaf. But approach to the plant reveals bad news—it smells terrible!

Despite its antisocial odor, this putrid plant has fascinated biologists for many years because of its ability to generate heat. At the peak of its metabolic activity, the plant's blossom can be as much as 15°C above its ambient temperature. To generate this much heat, the metabolic rate of the plant must be close to that of a flying hummingbird!

What's the purpose of this intense heat production? For a plant faced with limited food supplies in the very competitive tropical climate where it grows, heat production seems like a great waste of energy. The answer to this mystery is that the voodoo lily is pollinated mainly by carrion-loving insects. Thus, the lily prepares a malodorous mixture of chemicals characteristic of rotting meat, which it then "cooks" off into the surrounding air to attract flesh-feeding beetles and flies. Then, once the insects enter the pollination chamber, the high temperatures there (as high as 110°F) cause the insects to remain very active to better carry out their pollination duties.

The voodoo lily is only one of many such thermogenic (heat-producing) plants. Another interesting example is the eastern skunk cabbage, which produces enough heat to bloom inside of a snow bank by creating its own ice caves. These plants are of special interest to biologists because they provide opportunities to study metabolic reactions that are quite subtle in "normal" plants. For example, recent studies have shown that salicylic acid, the active form of aspirin, is probably very important in producing the metabolic bursts in thermogenic plants.

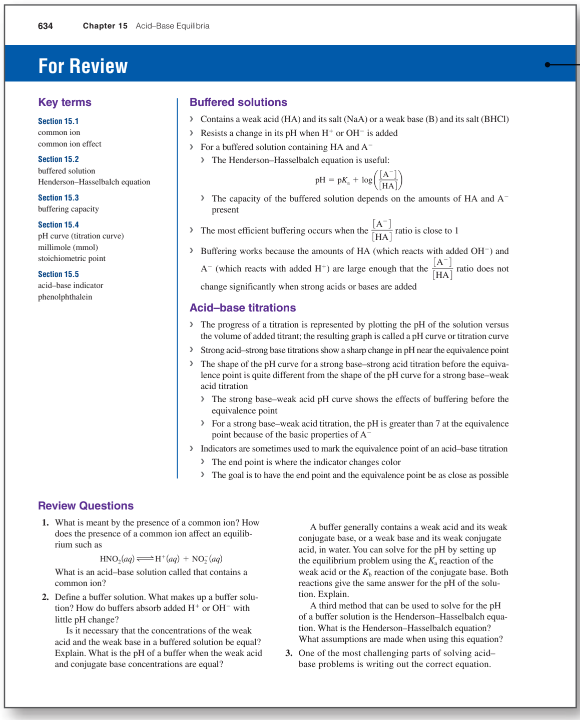
Besides studying the dramatic heat effects in thermogenic plants, biologists are also interested in calorimetric studies of regular plants. For example, very precise calorimeters have been designed that can be used to study the heat produced, and thus the metabolic activities, of clumps of cells no larger than a bread crumb. Several scientists have suggested that a single calorimetric measurement taking just a few minutes on a tiny plant might be useful in predicting the growth rate of the mature plant throughout its lifetime. If true, this would provide a very efficient method for selecting the plants most likely to thrive as adults.

Because the study of the heat production by plants is an excellent way to learn about plant metabolism, this continues to be a "hot" area of research.

United States Botanic Garden

The voodoo lily attracts pollinating insects with its foul odor.

Comprehensive End-of-Chapter Practice and Review We offer end-of-chapter exercises for every type of student and for every kind of homework assignment.



634 **Chapter 15** Acid–Base Equilibria

For Review

Key terms

Section 15.1
common ion
common ion effect

Section 15.2
buffered solution
Henderson–Hasselbalch equation

Section 15.3
buffering capacity

Section 15.4
pH curve (titration curve)
millimole (mmol)
stoichiometric point

Section 15.5
acid–base indicator
phenolphthalein

Buffered solutions

- Contains a weak acid (HA) and its salt (NaA) or a weak base (B) and its salt (BHCl)
- Resists a change in its pH when H^+ or OH^- is added
- For a buffered solution containing HA and A^-
  - The Henderson–Hasselbalch equation is useful:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

  - The capacity of the buffered solution depends on the amounts of HA and A^- present
- The most efficient buffering occurs when the $\frac{[\text{A}^-]}{[\text{HA}]}$ ratio is close to 1
- Buffering works because the amounts of HA (which reacts with added OH^-) and A^- (which reacts with added H^+) are large enough that the $\frac{[\text{A}^-]}{[\text{HA}]}$ ratio does not change significantly when strong acids or bases are added

Acid–base titrations

- The progress of a titration is represented by plotting the pH of the solution versus the volume of added titrant; the resulting graph is called a pH curve or titration curve
- Strong acid–strong base titrations show a sharp change in pH near the equivalence point
- The shape of the pH curve for a strong base–strong acid titration before the equivalence point is quite different from the shape of the pH curve for a strong base–weak acid titration
  - The strong base–weak acid pH curve shows the effects of buffering before the equivalence point
  - For a strong base–weak acid titration, the pH is greater than 7 at the equivalence point because of the basic properties of A^-
- Indicators are sometimes used to mark the equivalence point of an acid–base titration
  - The end point is where the indicator changes color
  - The goal is to have the end point and the equivalence point be as close as possible

Review Questions

1. What is meant by the presence of a common ion? How does the presence of a common ion affect an equilibrium such as

$$\text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq)$$

What is an acid–base solution called that contains a common ion?

2. Define a buffer solution. What makes up a buffer solution? How do buffers absorb added H^+ or OH^- with little pH change?

Is it necessary that the concentrations of the weak acid and the weak base in a buffered solution be equal? Explain. What is the pH of a buffer when the weak acid and conjugate base concentrations are equal?

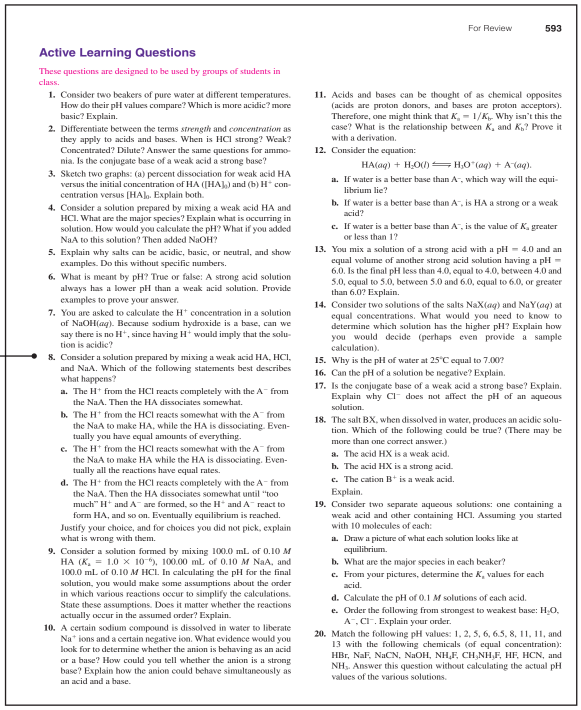
A buffer generally contains a weak acid and its weak conjugate base, or a weak base and its weak conjugate acid, in water. You can solve for the pH by setting up the equilibrium problem using the K_a reaction of the weak acid or the K_b reaction of the conjugate base. Both reactions give the same answer for the pH of the solution. Explain.

A third method that can be used to solve for the pH of a buffer solution is the Henderson–Hasselbalch equation. What is the Henderson–Hasselbalch equation? What assumptions are made when using this equation?

3. One of the most challenging parts of solving acid–base problems is writing out the correct equation.

Each chapter has a **For Review** section to reinforce key concepts and includes review questions for students to practice independently.

Active Learning Questions are designed to promote discussion among groups of students in class.



For Review 593

Active Learning Questions

These questions are designed to be used by groups of students in class.

1. Consider two beakers of pure water at different temperatures. How do their pH values compare? Which is more acidic? more basic? Explain.
2. Differentiate between the terms *strength* and *concentration* as they apply to acids and bases. When is HCl strong? Weak? Concentrated? Dilute? Answer the same questions for ammonia. Is the conjugate base of a weak acid a strong base?
3. Sketch two graphs: (a) percent dissociation for weak acid HA versus the initial concentration of HA ($[\text{HA}]_0$) and (b) H^+ concentration versus $[\text{HA}]_0$. Explain both.
4. Consider a solution prepared by mixing a weak acid HA and HCl. What are the major species? Explain what is occurring in solution. How would you calculate the pH? What if you added NaA to this solution? Then added NaOH?
5. Explain why salts can be acidic, basic, or neutral, and show examples. Do this without specific numbers.
6. What is meant by pH? True or false: A strong acid solution always has a lower pH than a weak acid solution. Provide examples to prove your answer.
7. You are asked to calculate the H^+ concentration in a solution of NaOH(*aq*). Because sodium hydroxide is a base, can we say there is no H^+, since having H^+ would imply that the solution is acidic?
8. Consider a solution prepared by mixing a weak acid HA, HCl, and NaA. Which of the following statements best describes what happens?
   a. The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat.
   b. The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA, while the HA is dissociating. Eventually you have equal amounts of everything.
   c. The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA while the HA is dissociating. Eventually all the reactions have equal rates.
   d. The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat until "too much" H^+ and A^- are formed, so the H^+ and A^- react to form HA, and so on. Eventually equilibrium is reached.

   Justify your choice, and for choices you did not pick, explain what is wrong with them.
9. Consider a solution formed by mixing 100.0 mL of 0.10 *M* HA ($K_a = 1.0 \times 10^{-6}$), 100.00 mL of 0.10 *M* NaA, and 100.0 mL of 0.10 *M* HCl. In calculating the pH for the final solution, you would make some assumptions about the order in which various reactions occur to simplify the calculations. State these assumptions. Does it matter whether the reactions actually occur in the assumed order? Explain.
10. A certain sodium compound is dissolved in water to liberate Na^+ ions and a certain negative ion. What evidence would you look for to determine whether the anion is behaving as an acid or a base? How could you tell whether the anion is a strong base? Explain how the anion could behave simultaneously as an acid and a base.
11. Acids and bases can be thought of as chemical opposites (acids are proton donors, and bases are proton acceptors). Therefore, one might think that $K_a = 1/K_b$. Why isn't this the case? What is the relationship between K_a and K_b? Prove it with a derivation.
12. Consider the equation:

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq).$$

   a. If water is a better base than A^-, which way will the equilibrium lie?
   b. If water is a better base than A^-, is HA a strong or a weak acid?
   c. If water is a better base than A^-, is the value of K_a greater or less than 1?
13. You mix a solution of a strong acid with a pH = 4.0 and an equal volume of another strong acid solution having a pH = 6.0. Is the final pH less than 4.0, equal to 4.0, between 4.0 and 5.0, equal to 5.0, between 5.0 and 6.0, equal to 6.0, or greater than 6.0? Explain.
14. Consider two solutions of the salts NaX(*aq*) and NaY(*aq*) at equal concentrations. What would you need to know to determine which solution has the higher pH? Explain how you would decide (perhaps even provide a sample calculation).
15. Why is the pH of water at 25°C equal to 7.00?
16. Can the pH of a solution be negative? Explain.
17. Is the conjugate base of a weak acid a strong base? Explain. Explain why Cl^- does not affect the pH of an aqueous solution.
18. The salt BX, when dissolved in water, produces an acidic solution. Which of the following could be true? (There may be more than one correct answer.)
   a. The acid HX is a weak acid.
   b. The acid HX is a strong acid.
   c. The cation B^+ is a weak acid.

   Explain.
19. Consider two separate aqueous solutions: one containing a weak acid and other containing HCl. Assuming you started with 10 molecules of each:
   a. Draw a picture of what each solution looks like at equilibrium.
   b. What are the major species in each beaker?
   c. From your pictures, determine the K_a values for each acid.
   d. Calculate the pH of 0.1 *M* solutions of each acid.
   e. Order the following from strongest to weakest base: H_2O, A^-, Cl^-. Explain your order.
20. Match the following pH values: 1, 2, 5, 6, 6.5, 8, 11, 11, and 13 with the following chemicals (of equal concentration): HBr, NaF, NaCN, NaOH, NH_4F, CH_3NH_3F, HF, HCN, and NH_3. Answer this question without calculating the actual pH values of the various solutions.

Comprehensive End-of-Chapter Practice and Review

A magenta question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*, as found on the Instructor Companion Site.

Questions

13. The common ion effect for weak acids is to significantly decrease the dissociation of the acid in water. Explain the common ion effect.

14. Consider a buffer solution where [weak acid] > [conjugate base]. How is the pH of the solution related to the pK_a value of the weak acid? If [conjugate base] > [weak acid], how is pH related to pK_a?

15. A best buffer has about equal quantities of weak acid and conjugate base present as well as having a large concentration of each species present. Explain.

16. Determining which reaction to use to solve an acid–base problem can be difficult. If a weak acid is present in water, we use the K_a reaction of the weak acid reacting with water to solve the equilibrium problem. If a weak base is present in water, we use the K_b reaction of the weak base reacting with water to solve the equilibrium problem. A buffer solution contains a weak acid and its weak conjugate base or a weak base and its weak conjugate acid. Since both a weak acid and a weak base are present in a buffer solution, what equation do you use to solve the equilibrium problem when you have a buffer solution?

17. Determining which reaction to use to solve an acid–base problem can be difficult. If strong acid or strong base is added to a solution, what is the first reaction to consider when solving for the pH of the solution? What assumption is always made when a strong acid or a strong base is reacted?

18. H_3PO_4 is a triprotic acid with $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, and $K_{a_3} = 4.8 \times 10^{-13}$. What phosphoric acid components would you use to prepare a pH = 7.0 buffer?

Questions are homework problems directed at concepts within the chapter and in general don't require calculation.

Exercises

In this section similar exercises are paired.

The Localized Electron Model and Hybrid Orbitals

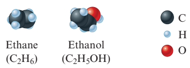
27. Use the localized electron model to describe the bonding in H_2O.

28. Use the localized electron model to describe the bonding in CCl_4.

29. Use the localized electron model to describe the bonding in H_2CO (carbon is the central atom).

30. Use the localized electron model to describe the bonding in C_2H_2 (exists as HCCH).

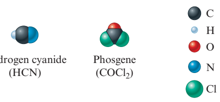
31. The space-filling models of ethane and ethanol are shown below.



Ethane (C_2H_6) Ethanol (C_2H_5OH)

Use the localized electron model to describe the bonding in ethane and ethanol.

32. The space-filling models of hydrogen cyanide and phosgene are shown below.



Hydrogen cyanide (HCN) Phosgene ($COCl_2$)

Use the localized electron model to describe the bonding in hydrogen cyanide and phosgene.

33. Give the expected hybridization of the central atom for the molecules or ions in Exercises 97 and 107 from Chapter 8.

34. Give the expected hybridization of the central atom for the molecules or ions in Exercises 98 and 108 from Chapter 8.

35. Give the expected hybridization of the central atom for the molecules or ions in Exercise 101 from Chapter 8.

36. Give the expected hybridization of the central atom for the molecules in Exercise 102 from Chapter 8.

37. Give the expected hybridization of the central atom for the molecules in Exercises 133 and 134 from Chapter 8.

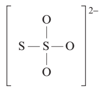
38. Give the expected hybridization of the central atom for the molecules in Exercises 135 and 136 from Chapter 8.

39. For each of the following molecules, write the Lewis structure(s), predict the molecular structure (including bond angles), give the expected hybrid orbitals on the central atom, and predict the overall polarity.

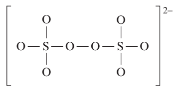
a. CF_4 **c.** OF_2 **e.** BeH_2
b. NF_3 **d.** BF_3

40. For each of the following molecules or ions that contain sulfur, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybrid orbitals for sulfur.

a. SO_2
b. SO_3
c. $S_2O_3^{2-}$



d. $S_2O_8^{2-}$



e. SO_3^{2-} **g.** SF_2
f. SO_4^{2-}

41. For each of the following molecules, write the Lewis structure(s), predict the molecular structure (including bond angles), give the expected hybrid orbitals on the central atom, and predict the overall polarity.

a. TeF_4 **e.** SeF_6
b. AsF_5 **f.** IF_5
c. KrF_2 **g.** IF_3
d. KrF_4

42. For each of the following molecules or ions, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybrid orbitals for sulfur.

a. SF_4 **c.** $F_3S\text{-}SF$
b. SF_6 **d.** SF_5^+

43. A compound has a formula QF_5 where Q is an unknown element. The compound has an even number of valence electrons, and the central Q atom is d^2sp^3 hybridized. What are some possible identities for Q?

44. Which of the following molecular structures do *not* require the central atom to use *d* orbital(s) to form the hybrid orbitals?

a. T-shape
b. see-saw
c. square planar
d. square pyramid
e. trigonal pyramid

45. Draw the Lewis structure for ICl_5. Which of the following statements is/are *true* regarding ICl_5?

a. The central atom in ICl_5 has one lone pair of electrons.
b. Some of the Cl—I—Cl bond angles are approximately 90°.
c. ICl_5 is polar.
d. The molecular structure of ICl_5 is square pyramid.
e. The central iodine atom is dsp^3.

46. What do the following molecules all have in common?

XeF_2, ICl_3, SCl_4, AsF_5

a. All have 90° bond angles.
b. All have central atoms that are dsp^3 hybridized.
c. All are polar.

There are numerous **Exercises** to reinforce students' understanding of each section. These problems are paired and organized by topic so that instructors can review them in class and assign them for homework.

ChemWork Problems

The asterisked multiconcept problems below are found online with the same type of interactive assistance a student would get from an instructor.

109. Derive an equation analogous to the Henderson–Hasselbalch equation but relating pOH and pK_b of a buffered solution composed of a weak base and its conjugate acid, such as NH_3 and NH_4^+.

110. a. Calculate the pH of a buffered solution that is 0.100 *M* in $C_6H_5CO_2H$ (benzoic acid, $K_a = 6.4 \times 10^{-5}$) and 0.100 *M* in $C_6H_5CO_2Na$.

b. Calculate the pH after 20.0% (by moles) of the benzoic acid is converted to benzoate anion by addition of a strong base. Use the dissociation equilibrium

$$C_6H_5CO_2H(aq) \rightleftharpoons C_6H_5CO_2^-(aq) + H^+(aq)$$

to calculate the pH.

c. Do the same as in part b, but use the following equilibrium to calculate the pH:

$$C_6H_5CO_2^-(aq) + H_2O(l) \rightleftharpoons C_6H_5CO_2H(aq) + OH^-(aq)$$

d. Do your answers in parts b and c agree? Explain.

111. Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies. Its buffering range is pH 7 to 9, and K_b is 1.19×10^{-6} for the aqueous reaction

$$\underset{\text{TRIS}}{(HOCH_2)_3CNH_2} + H_2O \rightleftharpoons \underset{\text{TRISH}^+}{(HOCH_2)_3CNH_3^+} + OH^-$$

a. What is the optimal pH for TRIS buffers?

b. Calculate the ratio [TRIS]/[TRISH⁺] at pH = 7.00 and at pH = 9.00.

New **ChemWork** end-of-chapter problems are now included, with many additional problems available to assign online for more practice.

Wealth of End-of-Chapter Problems

The text offers an unparalleled variety of end-of-chapter content with problems that increase in rigor and integrate multiple concepts.

Challenge Problems

136. Another way to treat data from a pH titration is to graph the absolute value of the change in pH per change in milliliters added versus milliliters added ($\Delta pH/\Delta mL$ versus mL added). Make this graph using your results from Exercise 85. What advantage might this method have over the traditional method for treating titration data?

137. A buffer is made using 45.0 mL of 0.750 M $HC_3H_5O_2$ ($K_a = 1.3 \times 10^{-5}$) and 55.0 mL of 0.700 M $NaC_3H_5O_2$. What volume of 0.10 M NaOH must be added to change the pH of the original buffer solution by 2.5%?

138. A 0.400-M solution of ammonia was titrated with hydrochloric acid to the equivalence point, where the total volume was 1.50 times the original volume. At what pH does the equivalence point occur?

139. What volume of 0.0100 M NaOH must be added to 1.00 L of 0.0500 M HOCl to achieve a pH of 8.00?

140. Consider a solution formed by mixing 50.0 mL of 0.100 M H_2SO_4, 30.0 mL of 0.100 M HOCl, 25.0 mL of 0.200 M NaOH, 25.0 mL of 0.100 M $Ba(OH)_2$, and 10.0 mL of 0.150 M KOH. Calculate the pH of this solution.

141. Cacodylic acid, $(CH_3)_2AsO_2H$, is a toxic compound that is a weak acid with $pK_a = 6.19$. It is used to prepare buffered solutions. Calculate the masses of cacodylic acid and sodium cacodylate that should be used to prepare 500.0 mL of a pH = 6.60 buffer so that the buffer has a total of arsenic-containing species equal to 0.25 M, that is, so that:

$$[(CH_3)_2AsO_2H] + [(CH_3)_2AsO_2^-] = 0.25\ M$$

Challenge Problems take students one step further and challenge them more rigorously than the Additional Exercises.

Marathon Problems also combine concepts from multiple chapters; they are the most challenging problems in the end-of-chapter material.

209. A certain acid, HA, has a vapor density of 5.11 g/L when in the gas phase at a temperature of 25°C and a pressure of 1.00 atm. When 1.50 g of this acid is dissolved in enough water to make 100.0 mL of solution, the pH is found to be 1.80. Calculate K_a for the acid.

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation.

210. An aqueous solution contains a mixture of 0.0500 M HCOOH ($K_a = 1.77 \times 10^{-4}$) and 0.150 M CH_3CH_2COOH ($K_a = 1.34 \times 10^{-5}$). Calculate the pH of this solution. Because both acids are of comparable strength, the H^+ contribution from both acids must be considered.

211. For the following, mix equal volumes of one solution from Group I with one solution from Group II to achieve the indicated pH. Calculate the pH of each solution.

Group I: 0.20 M NH_4Cl, 0.20 M HCl, 0.20 M $C_6H_5NH_3Cl$, 0.20 M $(C_2H_5)_3NHCl$

Group II: 0.20 M KOI, 0.20 M NaCN, 0.20 M KOCl, 0.20 M $NaNO_2$

a. the solution with the lowest pH
b. the solution with the highest pH
c. the solution with the pH closest to 7.00

"The end-of-chapter content helps students identify and review the central concepts. There is an impressive range of problems that are well graded by difficulty."

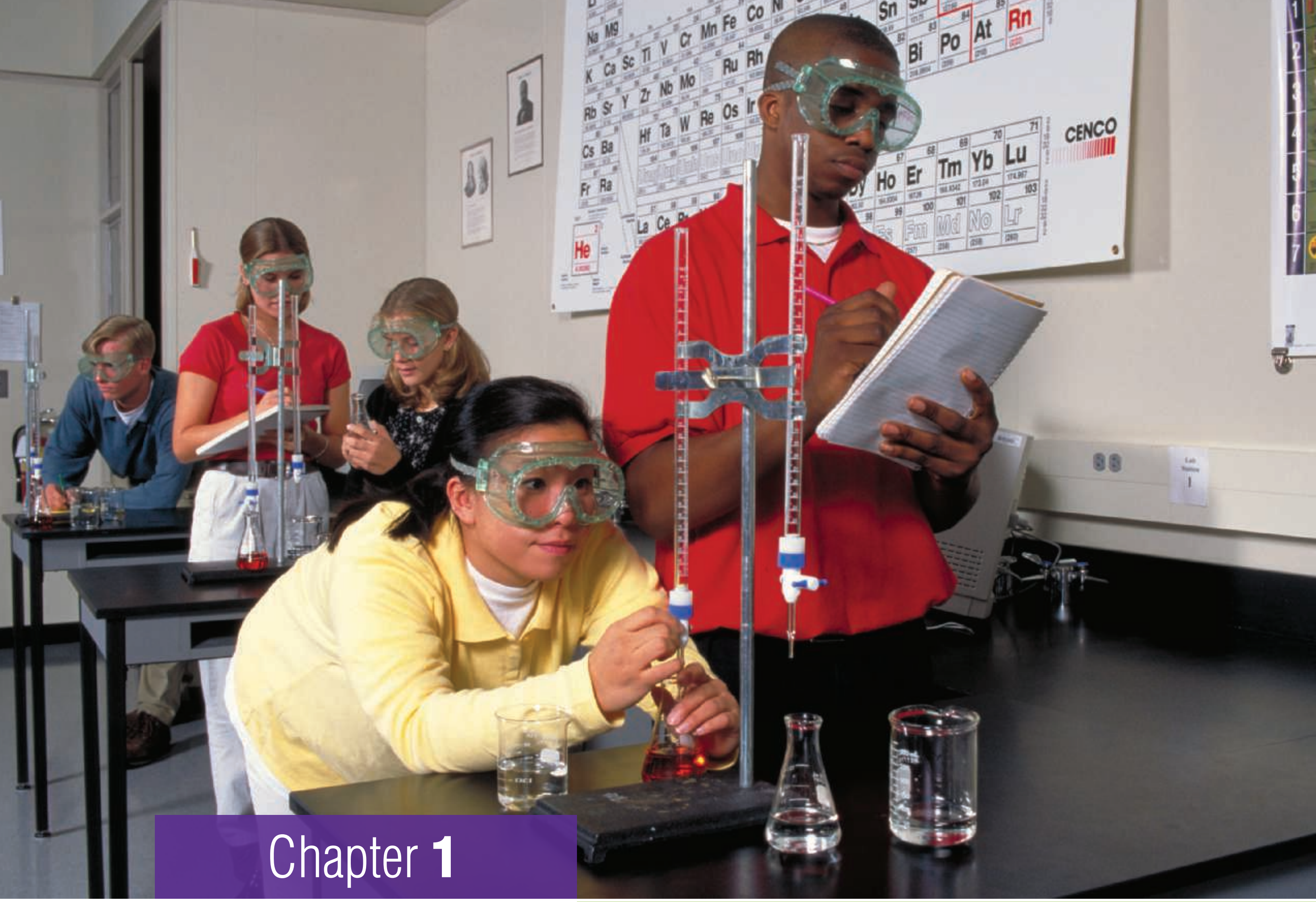
—Alan M. Stolzenberg, ***West Virginia University***

About the Authors

Steven S. Zumdahl earned a B.S. in Chemistry from Wheaton College (IL) and a Ph.D. from the University of Illinois, Urbana-Champaign. He has been a faculty member at the University of Colorado–Boulder, Parkland College (IL), and the University of Illinois at Urbana-Champaign (UIUC), where he is Professor Emeritus. He has received numerous awards, including the National Catalyst Award for Excellence in Chemical Education, the University of Illinois Teaching Award, the UIUC Liberal Arts and Sciences Award for Excellence in Teaching, UIUC Liberal Arts and Sciences Advising Award, and the School of Chemical Sciences Teaching award (five times). He is the author of several chemistry textbooks. In his leisure time he enjoys traveling and collecting classic cars.

Susan A. Zumdahl earned a B.S. and M.A. in Chemistry at California State University–Fullerton. She has taught science and mathematics at all levels, including middle school, high school, community college, and university. At the University of Illinois at Urbana-Champaign, she developed a program for increasing the retention of minorities and women in science and engineering. This program focused on using active learning and peer teaching to encourage students to excel in the sciences. She has coordinated and led workshops and programs for science teachers from elementary through college levels. These programs encourage and support active learning and creative techniques for teaching science. For several years she was director of an Institute for Chemical Education (ICE) field center in Southern California, and she has authored several chemistry textbooks. Susan spearheaded the development of a sophisticated web-based electronic homework system for teaching chemistry. She enjoys traveling, classic cars, and gardening in her spare time—when she is not playing with her grandchildren.

Donald J. DeCoste is Associate Director of General Chemistry at the University of Illinois, Urbana-Champaign, and has been teaching chemistry at the high school and college levels for over 30 years. He earned a B.S. in Chemistry and a Ph.D. from the University of Illinois, Urbana-Champaign. At Illinois he teaches courses in introductory chemistry and the teaching of chemistry and has developed chemistry courses for non-science majors, preservice secondary teachers, and preservice elementary/middle school teachers. He has received the LAS Award for Excellence in Undergraduate Teaching by Instructional Staff Award, the Provost's Excellence in Undergraduate Teaching Award, and the School of Chemical Sciences Teaching Award (five times). Don has led workshops for secondary teachers and graduate student teaching assistants, discussing the methods and benefits of getting students more actively involved in class. When not involved in teaching and advising, Don enjoys spending time with his wife and three children.



Chapter **1**

Chemistry lab. High school chemistry students working in a chemistry lab. (Doug Martin/Science Source)

Chemical Foundations

When you start your car, do you think about chemistry? Probably not, but you should. Your car may actually be powered by lithium-ion batteries (several hundred of them). If your car has a traditional internal combustion engine, the power to start your car is furnished by a lead storage battery. How does this battery work, and what does it contain? When a battery goes dead, what does that mean? If you use a friend's car to "jump-start" your car, did you know that your battery could explode? How can you avoid such an unpleasant possibility? If your car requires gasoline, how does it furnish energy to your car so that you can drive it to school? What is the vapor that comes out of the exhaust pipe, and why does it cause air pollution? Your car's air conditioner might have a substance in it that is leading to the destruction of the ozone layer in the upper atmosphere. What are we doing about that? And why is the ozone layer important anyway?

All of these questions can be answered by understanding some chemistry. In fact, we'll consider the answers to all of these questions in this text.

Chemistry is around you all the time. You are able to read and understand this sentence because chemical reactions are occurring in your brain. The food you ate for breakfast or lunch is now furnishing energy through chemical reactions. Trees and grass grow because of chemical changes.

Chemistry is also very important in determining a person's behavior. Various studies have shown that many personality disorders can be linked directly to imbalances of trace elements in the body. Studies on the inmates at Stateville Prison in Illinois have linked low cobalt levels with violent behavior. Lithium salts have been shown to be very effective in controlling the effects of manic-depressive disease.

You have probably at some time in your life felt a special "chemistry" for another person. Studies suggest there is literally chemistry going on between two people who are attracted to each other. "Falling in love" apparently causes changes in the chemistry of the brain; chemicals are produced that give that "high" associated with a new relationship. Unfortunately, these chemical effects seem to wear off over time, even if the relationship persists and grows.

The importance of chemistry in the interactions of people should not really surprise us. We know that insects communicate by emitting and receiving chemical signals via molecules called *pheromones*. For example, ants have a very complicated set of chemical signals to signify food sources, danger, and so forth. Also, various female sex attractants have been isolated and used to lure males into traps to control insect populations. It would not be surprising if humans also emitted chemical signals that we were not aware of on a conscious level. Thus, chemistry is pretty interesting and pretty important. The main goal of this text is to help you understand the concepts of chemistry so that you can better appreciate the world around you and can be more effective in whatever career you choose.

1.1 Chemistry: An Overview

Since the time of the ancient Greeks, people have wondered about the answer to the question: What is matter made of? For a long time, humans have believed that matter is composed of atoms, and in the previous three centuries, we have collected much indirect evidence to support this belief. Since the 1980s, we have been able to visualize individual atoms using a special microscope called a *scanning tunneling microscope* (STM), which uses an electron current from a tiny needle to probe the surface of a substance and produce an image (Fig. 1.1).

The nature of atoms is complex, and the components of atoms don't behave much like the objects we see in the *macroscopic world*—the world of cars, tables, baseballs, rocks, oceans, and so forth. One of the main jobs of a scientist is to delve into the macroscopic world and discover its "parts." For example, when you view a beach

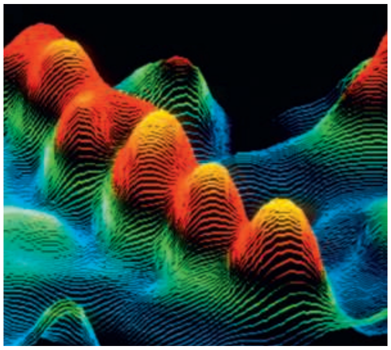
Chemistry in Your Career

Senior Scientist

Dr. Barry Fanning is a Senior Scientist for a company that primarily focuses on agriculture, biomedical, concrete, inks, and other chemicals. He manages analytical teams and new product development research involving questions of product and process performance. The challenges are constant and engaging for him, as he has to continually learn more chemistry and engineering. Dr. Fanning's education included studies and degrees in chemistry, geochemistry, geology, solid state science, and organometallic synthesis and catalysis. But he feels he gained his most important insights through the laboratories and research tied to each course.

Dr. Fanning's advice to students is to "Get experience in your field, work in labs, talk to people and learn what they do." And most importantly, "Discover the things in the world that interest you and pursue them." Even projects that failed, gave him experience that led to greater success later. He says to "always choose optimism."

Dr. Barry Fanning



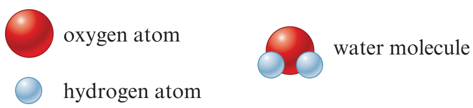
LLNL/Science Source

Figure 1.1 Scanning tunneling microscope image of DNA.

from a distance, it looks like a continuous solid substance. As you get closer, you see that the beach is really made up of individual grains of sand. As we examine these grains of sand, we find that they are composed of silicon and oxygen atoms connected to each other to form intricate shapes (Fig. 1.2). One of the main challenges of chemistry is to understand the connection between the macroscopic world that we experience and the *microscopic world* of atoms and molecules. To truly understand chemistry, you must learn to think on the atomic level. We will spend much time in this text helping you learn to do that.

Critical Thinking The scanning tunneling microscope allows us to visualize atoms. What if you were sent back in time before the invention of the scanning tunneling microscope? What evidence could you give to support the theory that all matter is made of atoms and molecules?

One of the amazing things about our universe is that the tremendous variety of substances we find there results from only about 100 different kinds of atoms. You can think of these approximately 100 atoms as the letters in an alphabet from which all the "words" in the universe are made. The way the atoms are organized in a given substance determines the properties of that substance. For example, water, one of the most common and important substances on the earth, is composed of two types of atoms: hydrogen and oxygen. Two hydrogen atoms and one oxygen atom are bound together to form the water molecule:



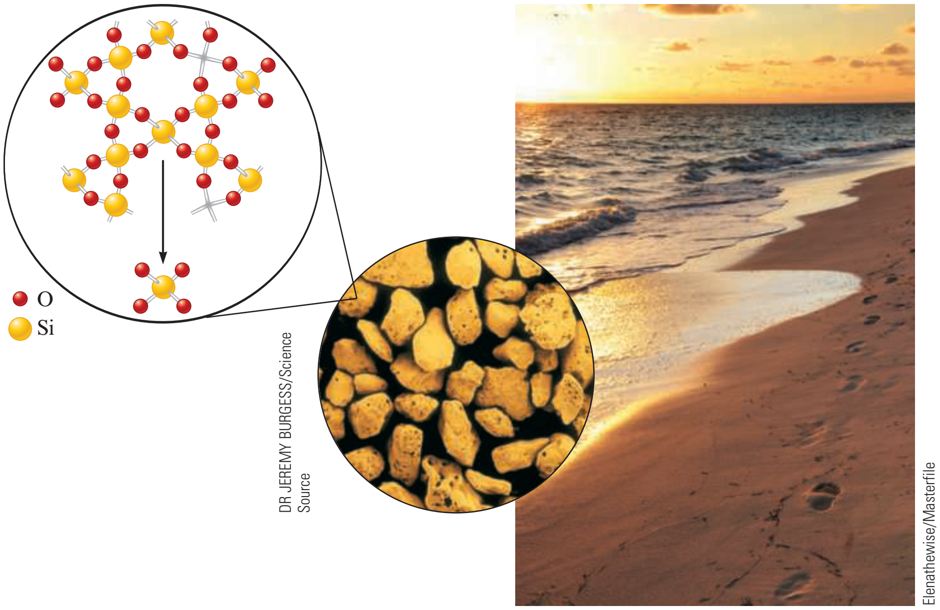
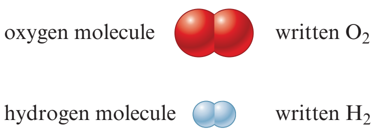
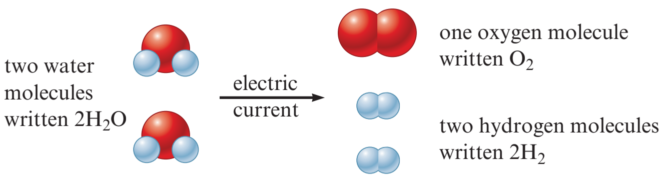


Figure 1.2 Sand on a beach looks uniform from a distance, but under a microscope the irregular sand grains are visible. At an atomic level, each grain is composed of molecules formed from atoms of oxygen and silicon.

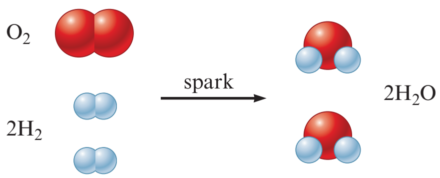
When an electric current passes through it, water is broken apart into hydrogen and oxygen. These *chemical elements* themselves exist naturally as diatomic (two-atom) molecules:



We can represent the decomposition of water to its component elements, hydrogen and oxygen, as follows:



Notice that it takes two molecules of water to furnish the right number of oxygen and hydrogen atoms to allow for the formation of the two-atom molecules. This reaction explains why the battery in your car can explode if you jump-start it improperly. When you hook up the jumper cables, current flows through the dead battery, which contains water (and other things), and causes hydrogen and oxygen to form by decomposition of some of the water. A spark can cause this accumulated hydrogen and oxygen to explode, forming water again.



This example illustrates two of the fundamental concepts of chemistry:

1. Matter is composed of various types of atoms.
2. One substance changes to another by reorganizing the way the atoms are attached to each other.

These are core ideas of chemistry, and we will have much more to say about them.

1.2 Science: A Process for Understanding Nature and Its Changes

How do you tackle the problems that confront you in real life? Imagine, for example, that your phone is dying when you are out of the house during the day, and you have no easy way to charge it between classes and work. How would you go about solving this problem? First, you need to collect some information. You might do some research online to identify common causes of shortened battery life. Second, you need a specific idea about what might be going wrong. Maybe there is something wrong with your charger, or maybe it's a problem with your phone's software. Third, you need to test those ideas to find out whether you were right. You could try a different charger, and if that doesn't help, you could do a software update. If neither of those fixes your problem, you will have to go back to the first step and do more research. What you are doing in solving this everyday problem is applying the same process that scientists use to study nature. The first thing you did was collect relevant data. Then you made a prediction, and then you tested it by trying it out. This process contains the fundamental elements of science:

1. Making observations (collecting data)
2. Suggesting a possible explanation (formulating a hypothesis)
3. Doing experiments to test the possible explanation (testing the hypothesis)

Scientists call this process the *scientific method*. One of life's most important activities is solving problems—not routine exercises, but real problems—problems that have new facets to them, that involve things you may have never confronted before.

The more creative you are at solving problems, the more effective you will be in your career and your personal life. Part of the reason for learning chemistry, therefore, is to become a better problem solver. Chemists are usually excellent problem solvers because to master chemistry, you have to master the scientific approach. Chemical problems are frequently very complicated—there is usually no neat and tidy solution. Often, it is difficult to know where to begin.

The Scientific Method

Science is a framework for gaining and organizing knowledge. Science is not simply a set of facts but also a plan of action—a *procedure* for processing and understanding certain types of information. Scientific thinking is useful in all aspects of life, but in this text, we will use it to understand how the chemical world operates. As we said in our previous discussion, the process that lies at the center of scientific inquiry is called the **scientific method**. There are actually many scientific methods, depending on the nature of the specific problem under study and the particular investigator involved. However, it is useful to consider the following general framework for a generic scientific method:

Steps in the Scientific Method

1. **Making observations.** Observations may be *qualitative* (the sky is blue; water is a liquid) or *quantitative* (water boils at 100°C; a certain chemistry book weighs 2 kg). A qualitative observation does not involve a number. A quantitative observation (called a **measurement**) involves both a number and a unit.
2. **Formulating hypotheses.** A **hypothesis** is a *possible* explanation for an observation.
3. **Performing experiments.** An experiment is carried out to test a hypothesis. This involves gathering new information that enables a scientist to decide whether the hypothesis is valid—that is, whether it is supported by the new information learned from the experiment. Experiments always produce new observations, and this brings the process back to the beginning again.

To understand a given phenomenon, these steps are repeated many times, gradually accumulating the knowledge necessary to provide a possible explanation of the phenomenon.

Scientific Models

Once a set of hypotheses that agrees with the various observations is obtained, the hypotheses are assembled into a theory. A **theory**, which is often called a **model**, is a set of tested hypotheses that gives an overall explanation of some natural phenomenon.

It is very important to distinguish between observations and theories. An observation is something that is witnessed and can be recorded. A theory is an *interpretation*—a possible explanation of why nature behaves in a particular way. Theories inevitably change as more information becomes available. For example, the motions of the sun and stars have remained virtually the same over the thousands of years during which humans have been observing them, but our explanations—our theories—for these motions have changed greatly since ancient times.

Scientists do not stop asking questions just because a given theory seems to account satisfactorily for some aspect of natural behavior. They continue doing experiments to refine or replace the existing theories. This is generally done by using the currently accepted theory to make a prediction and then performing an experiment (making a new observation) to see whether the results bear out this prediction.

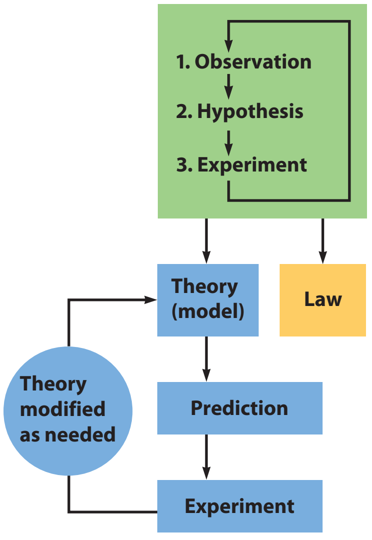


Figure 1.3 The various parts of the scientific method.

Always remember that theories (models) are human inventions. They represent attempts to explain observed natural behavior in terms of human experiences. A theory is actually an educated guess. We must continue to do experiments and to refine our theories (making them consistent with new knowledge) if we hope to approach a more complete understanding of nature.

As scientists observe nature, they often see that the same observation applies to many different systems. For example, studies of innumerable chemical changes have shown that the total observed mass of the materials involved is the same before and after the change. Such generally observed behavior is formulated into a statement called a **natural law** (Fig. 1.3).

Note the difference between a natural law and a theory. A natural law is a summary of observed (measurable) behavior, whereas a theory is an explanation of behavior. **A law summarizes what happens; a theory (model) is an attempt to explain why it happens.**

Human Limitations on Science

In this section, we have described the scientific method as it might ideally be applied. However, it is important to remember that science does not always progress smoothly and efficiently. For one thing, hypotheses and observations are not totally independent of each other, as we have assumed in the description of the idealized scientific method. The coupling of observations and hypotheses occurs because once we begin to proceed down a given theoretical path, our hypotheses are unavoidably couched in the language of that theory. In other words, we tend to see what we expect to see and often fail to notice things that we do not expect. Thus, the theory we are testing helps us because it focuses our questions. However, at the same time, this focusing process may limit our ability to see other possible explanations.

It is also important to keep in mind that scientists are human. They have prejudices; they misinterpret data; they become emotionally attached to their theories and thus lose objectivity; and they play politics. Science is affected by profit motives, budgets, fads, wars, and religious beliefs. Galileo, for example, was forced to recant his astronomical observations in the face of strong religious resistance. Lavoisier, the father of modern chemistry, was beheaded because of his political affiliations. Great progress in the chemistry of nitrogen fertilizers resulted from the desire to produce explosives to

Chemical Connections

A Note-able Achievement

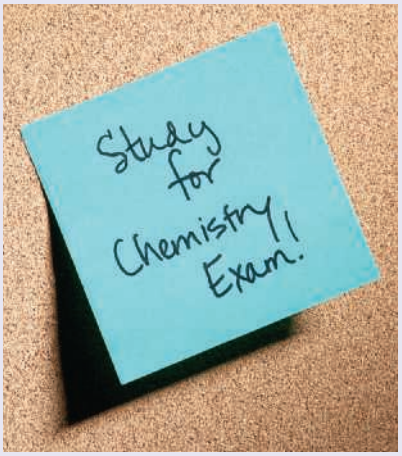
Post-it Notes, a product of the 3M Corporation, revolutionized casual written communications and personal reminders. Introduced in the United States in 1980, these sticky-but-not-too-sticky notes have now found countless uses in offices, cars, and homes throughout the world.

The invention of sticky notes occurred over a period of about 10 years and involved a great deal of serendipity. The adhesive for Post-it Notes was discovered by Dr. Spencer F. Silver of 3M in 1968. Silver found that when an acrylate polymer material was made in a particular way, it formed cross-linked microspheres. When suspended in a solvent and sprayed on a sheet of paper, this substance formed a "sparse monolayer" of adhesive after the solvent evaporated. Scanning electron microscope images of the adhesive show that it has an irregular surface, a little like the surface of a gravel road. In contrast, the adhesive on cellophane tape looks smooth and uniform, like a superhighway. The bumpy surface of Silver's adhesive caused it to be sticky but not so sticky to produce permanent adhesion, because the number of contact points between the binding surfaces was limited.

When he invented this adhesive, Silver had no specific ideas for its use, so he spread the word of his discovery to his fellow employees at 3M to see if anyone had an application for it. In addition, over the next several years, development was carried out to improve the adhesive's properties. It was not until 1974 that the idea for Post-it Notes popped up. One Sunday, Art Fry, a chemical engineer for 3M, was singing in his church choir when he became annoyed that the bookmark in his hymnal kept falling out. He thought to himself that it would be nice if the bookmark were sticky enough to stay in place but not so sticky that it couldn't be moved. Luckily, he remembered Silver's glue—and the Post-it Note was born.

For the next three years, Fry worked to overcome the manufacturing obstacles associated with the product. By 1977, enough Post-it Notes were being produced to supply 3M's corporate headquarters, where the employees quickly became addicted to their many uses.

In the years since the introduction of Post-it Notes, 3M has heard some remarkable stories connected to the use of these notes. For example, a Post-it Note was applied to the nose of a corporate jet, where it was intended



to be read by the plane's Las Vegas ground crew. Someone forgot to remove it, however. The note was still on the nose of the plane when it landed in Minneapolis, having survived a takeoff, a landing, and speeds of 500 miles per hour at temperatures as low as −56°F. Stories describe how a Post-it Note on the front door of a home survived the 140-mile-per-hour winds of Hurricane Hugo and how a foreign official accepted Post-it Notes in lieu of cash when a small bribe was needed to cut through bureaucratic hassles.

Post-it Notes have definitely changed the way we communicate and remember things.

fight wars. The progress of science is often affected more by the frailties of humans and their institutions than by the limitations of scientific measuring devices. The scientific methods are only as effective as the humans using them. They do not automatically lead to progress.

Critical Thinking What if everyone in the government used the scientific method to analyze and solve society's problems, and politics were never involved in the solutions? How would this be different from the present situation, and would it be better or worse?

Pioneers in Chemistry

Robert Boyle (1627–1691)

Robert Boyle was born in Ireland. He became especially interested in experiments involving air and developed an air pump with which he produced evacuated cylinders. He used these cylinders to show that a feather and a lump of lead fall at the same rate in the absence of air resistance and that sound cannot be produced in a vacuum. His most famous experiments involved careful measurements of the volume of a gas as a function of pressure. In his book, Boyle urged that the ancient view of elements as mystical substances should be abandoned and that an element should instead be defined as anything that cannot be broken down into simpler substances. This concept was an important step in the development of modern chemistry.

Bridgeman Images

1.3 Units of Measurement

Making observations is fundamental to all science. A quantitative observation, or *measurement,* always consists of two parts: a *number* and a scale (called a *unit*). Both parts must be present for the measurement to be meaningful.

In this textbook, we will use measurements of mass, length, time, temperature, electric current, and the amount of a substance, among others. Scientists recognized long ago that standard systems of units had to be adopted if measurements were to be useful. If every scientist had a different set of units, complete chaos would result. Unfortunately, different standards were adopted in different parts of the world. The two major systems are the *English system* used in the United States and the *metric system* used by most of the rest of the industrialized world. This duality causes a good deal of trouble; for example, parts as simple as bolts are not interchangeable between machines built using the two systems. As a result, the United States has begun to adopt the metric system.

Most scientists in all countries have used the metric system for many years. In 1960, an international agreement set up a system of units called the *International System* (*le Système International* in French), which uses **SI units**. This system is based on the metric system and units derived from the metric system. The fundamental SI units are listed in Table 1.1. We will discuss how to manipulate these units later in this chapter.

▲ Soda is commonly sold in 2-L bottles—an example of the use of SI units in everyday life.

Table 1.1 | Fundamental SI Units

Physical Quantity	Name of Unit	Abbreviation
Mass	Kilogram	kg
Length	Meter	m
Time	Second	s
Temperature	Kelvin	K
Electric current	Ampere	A
Amount of substance	Mole	mol
Luminous intensity	Candela	cd

Table 1.2 | Prefixes Used in the SI System

Prefix	Symbol	Meaning	Exponential Notation*
exa	E	1,000,000,000,000,000,000	10^{18}
peta	P	1,000,000,000,000,000	10^{15}
tera	T	1,000,000,000,000	10^{12}
giga	G	1,000,000,000	10^{9}
mega	M	1,000,000	10^{6}
kilo	k	1,000	10^{3}
hecto	h	100	10^{2}
deka	da	10	10^{1}
—	—	1	10^{0}
deci	d	0.1	10^{-1}
centi	c	0.01	10^{-2}
milli	m	0.001	10^{-3}
micro	μ	0.000001	10^{-6}
nano	n	0.000000001	10^{-9}
pico	p	0.000000000001	10^{-12}
femto	f	0.000000000000001	10^{-15}
atto	a	0.000000000000000001	10^{-18}

*See Appendix 1.1 if you need a review of exponential notation.

Table 1.3 | Some Examples of Commonly Used Units

Length	A dime is 1-mm thick. A quarter is 2.5 cm in diameter. The average height of an adult man is 1.8 m.
Mass	A nickel has a mass of about 5 g. A 120-lb person has a mass of about 55 kg.
Volume	A 12-oz can of soda has a volume of about 360 mL.

Because the fundamental units are not always convenient (expressing the mass of a pin in kilograms is awkward), prefixes are used to change the size of the unit. These are listed in Table 1.2. Some common objects and their measurements in SI units are listed in Table 1.3.

One physical quantity that is very important in chemistry is *volume,* which is the amount of three-dimensional space something occupies. Volume is not a fundamental SI unit but is derived from length. A cube that measures 1 meter (m) on each edge is represented in Fig. 1.4. This cube has a volume of $(1\ \text{m})^3 = 1\ \text{m}^3$. There are 10 decimeters (dm) in a meter, so the volume of this cube is $(1\ \text{m})^3 = (10\ \text{dm})^3 = 1000\ \text{dm}^3$. A cubic decimeter, that is, $(1\ \text{dm})^3$, is commonly called a *liter (L),* which is a unit of volume slightly larger than a quart. As shown in Fig. 1.5, 1000 L is contained in a cube with a volume of 1 cubic meter. Similarly, since 1 decimeter equals

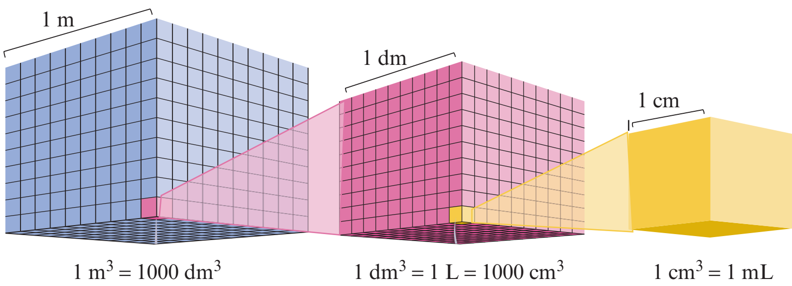


Figure 1.4 The largest cube has sides 1 m in length and a volume of 1 m^3. The middle-sized cube has sides 1 dm in length and a volume of 1 dm^3, or 1 L. The smallest cube has sides 1 cm in length and a volume of 1 cm^3, or 1 mL.