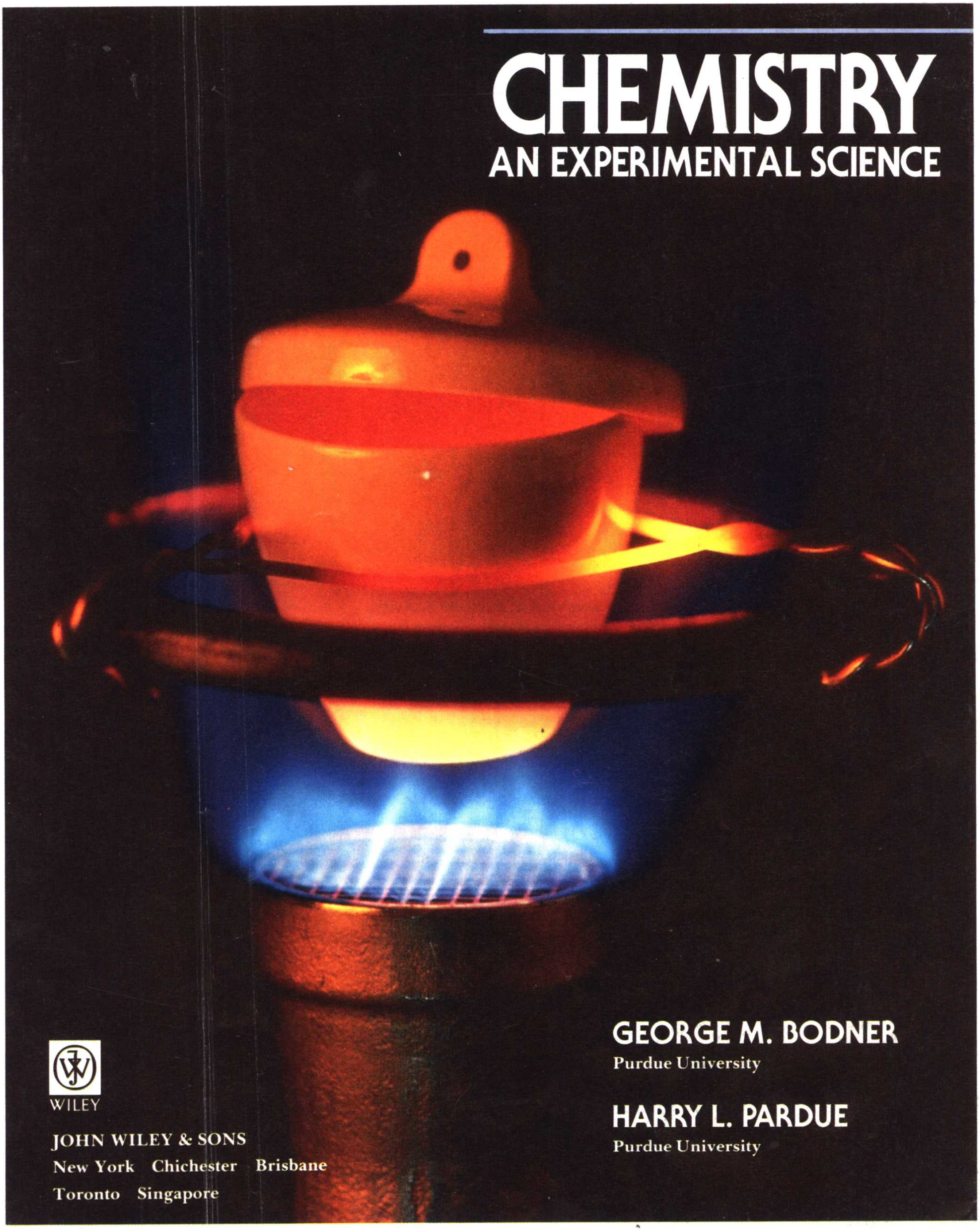
BODNER AND PARDUE

CHEMISTRY

AN EXPERIMENTAL SCIENCE



CHEMISTRY

AN EXPERIMENTAL SCIENCE

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HOW TO LOOK AT THE ILLUSTRATIONS

- Color is used to identify, associate, and relate items dealt with in various contexts. In drawings dealing with orbital theory, for instance, each category of orbital (s, 2p, sp, d) has its own identifying color. These colors appear not only in three-dimensional pictorial depictions of the orbitals but also in the diagrams and charts that deal with them on an abstract level.

- Elements by themselves or as components of ball-and-stick and space-filling molecular models are identified by conventional colors throughout the book. Thus hydrogen is white, oxygen red, chlorine green, sulfur yellow, and so on.

- Various rays such as infrared rays, alpha, beta and gamma rays, ultraviolet rays and x-rays are shown in their characteristic colors. This is the case in illustrations of laboratory equipment generating these rays as well as in charts and diagrams expressing data about them.

- The relative sizes and configurations of the various orbitals are drawn to scale in accordance with their known mathematical data to ensure an authentic and consistent appearance.

- The space-filling molecular models are drawn to scale. Thus the relative diameters of the atomic elements comprising the molecules reflect their known mathematical data. In figures of the water molecule, for instance, the diameters of the component hydrogen and oxygen atoms are drawn in the ratio of 0.37 to 0.66.

- Figures of ball-and-stick and space-filling models show the bonding angles drawn to accurately reflect their known divergences. Thus in the water molecule the angle between the hydrogen atoms is shown at a true 104°5′. The result is an authentic depiction and not a casual impression.

- Three-dimensional formula structures are drawn to emphasize their spatial geometry with clarity.

- Laboratory equipment (flasks, beakers, bunsen burners, etc.) has been drawn with reference to lab equipment catalogues to ensure accuracy in appearance.

- Classic experiments are depicted with careful attention to key aspects concerning the physical equipment used and its set-up.

- Crystal molecular structures are drawn to ensure that the positions of the atoms in space relative to each other and thus the geometry of the structures is unequivocally clear.

- Various items that repeat throughout the book are identified by their own unique colors: energy level diagrams; various diagrams and periodic tables that deal with the concept of the states of matter wherein gas, solid and liquid each have their own color; orbit diagrams; diagrams which deal with the concepts of metals, nonmetals and metalloids; symbols for the concepts of attraction and repulsion; and so on.

PREFACE

TO THE INSTRUCTOR

Those of us who teach chemistry argue about what topics should be emphasized and about the best order for presenting these topics, but chemists at widely differing institutions are in remarkable agreement about the material that should be covered in a given course.

This does not mean that the consensus is stable—there is abundant evidence to show that it changes with time. At one time, introductory chemistry courses focused on the preparation and properties of elements and compounds. More than half of a typical textbook at that time was devoted to topics such as the chemistry of the halogens, the Frasch process for mining sulfur, the preparation of phosphine, the manufacture of nitric acid, the production of pig iron in blast furnaces, and so on.

Courses based on these texts were inevitably displaced by those that focused on the principles of chemistry. These courses introduced discussions of the photoelectric effect, the Schrödinger model of the hydrogen atom, wave–particle duality, molecular orbitals, entropy, and free energy. They spent less time talking about the chemistry of the transition metals, and more time using atomic orbitals to explain this chemistry.

The title of this text—*Chemistry: An Experimental Science*—reflects our beliefs about the direction in which general chemistry courses should evolve. We agree with the Committee on Professional Training of the American Chemical Society, which recommends putting the "chemistry" back into introductory chemistry courses. But to us, this means more than just adding additional inorganic chemistry. It means returning to an experimental perspective, in which observations are made before they are explained.

Many texts, for example, place the descriptive chemistry at the end. This assumes that we have to introduce the students to all of the principles of chemistry—from the structure of the atom, to equilibria and free energy—before we can talk about the chemistry of the elements. We think this is a mistake, and have integrated the descriptive chemistry throughout the book. As much as possible, we start by noting what happens when chemical systems are observed. Once the observations are made, we then try to develop explanations for this behavior.

As early as Chapter 2, we describe the differences between the chemical and physical properties of metals and nonmetals and between ionic and covalent compounds. When the periodic properties of the elements are discussed in Chapter 6, they are immediately used to explain the existence of semimetals and to discuss the reactivity of the active metals. The chemistry of the main-group metals is introduced in Chapter 7 as a basis for discussions of oxidation-reduction reactions and ionic compounds, rather than vice versa. Ionic bonds are then contrasted with covalent bonds, thermochemistry is introduced, and the chemistry of the nonmetals is described in Chapter 10. Chapter 11 then focuses on the qualitative chemistry of acids, bases, and salts.

To us, descriptive chemistry is more than inorganic reaction chemistry. It includes an understanding of the chemistry of aqueous solutions, particularly acid–base, solubility, and complex-ion equilibria. We also believe that one of the best ways of learning this chemistry is through the qualitative analysis scheme. We have therefore included a truncated "qual" scheme that can be covered in four or perhaps five three-hour laboratory periods.

Most general chemistry texts introduce kinetics before equilibria, because we can explain why reactions come to equilibrium from a kinetic perspective. But you don't need to understand first-order and second-order reactions, rate constants, instantaneous rates of reaction, reaction mechanisms, activation energies, and so on, to understand equilibrium. We therefore begin the equilibrium chapters with a discussion of the collision-theory model of chemical reactions. The various tricks that are needed to handle equilibrium calculations are then introduced in terms of relatively simple, gas-phase reactions. (We find that when students understand how these techniques can be applied to reactions in which the solvent plays no role, they are much better at reactions in

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aqueous solution.) In a later chapter, we then return to chemical kinetics — after the student has achieved some facility with simpler calculations.

Our belief that observations should precede explanations also influenced our placement of the chapters on electrochemistry and thermodynamics. Many texts develop the concept of free energy and then relate it to electrochemical cells. We start with the system that can be observed — the electrochemical cell — and then develop the theoretical explanation for this behavior.

Many instructors who adopt this text will disagree with some of our ideas about order. We have therefore tried to write each section so that it could stand alone. The chapters on gases and thermochemistry, for example, can be taught at almost any time after the basics of stoichiometry have been introduced. Chapter 6 (the periodic table) builds on the discussion of the structure of the atom in Chapter 5. However, Chapter 7, on main-group metals and their salts, can be grouped with the material in Chapter 10 on nonmetals at almost any time during the year.

The chapter on electrochemistry builds on the preceding discussion of oxidation-reduction reactions, but these two chapters can be covered at essentially any point in the second-half of the course. Chapters 20 through 25, on thermodynamics, kinetics, transition-metal chemistry, nuclear chemistry, organic chemistry, and polymer chemistry were written so that they could be used at any point, in essentially any order.

The following supplements to this textbook are available:

1. SOLUTIONS MANUAL: Contains solutions to all end-of-chapter problems.
2. STUDY GUIDE: Contains statements of objectives, a review of significant topics, additional worked examples, self-test questions and problems, and a list of new terms for each chapter.
3. TRANSPARENCIES: A package of full-color transparencies that reproduce key illustrations from the text.
4. INSTRUCTOR'S MANUAL: Discusses the objectives and rationale for each chapter, possible course outlines, and suggestions for exams.
5. TEST BANK: A printed test bank with answers that includes a variety of test formats.
6. MICROTEST: A computerized version of the test bank available for use with IBM PC or Apple Macintosh computers.
7. LECTURE DEMONSTRATION MANUAL: Contains short, simple lecture demonstrations keyed to the text material.

TO THE STUDENT

Students enroll in general chemistry courses for many reasons. For some, it is a direct result of the major they select, because the language and critical thinking skills chemists use has been judged to be a valuable tool for success in that field. Some students choose chemistry to fulfill a science elective; others take it because it is a required course for professional schools in medicine, dentistry, or veterinary medicine. Some of you might even be considering a career in chemistry.

No matter why you are taking general chemistry, this course is designed to meet some of the following objectives: to introduce you to some of the language that chemists use to describe the world around us, a language that has been adopted by professionals in such diverse fields as political science and astronomy; to introduce you to concepts and skills that are needed in later courses in your major; to foster problem solving skills that can be transferred to your profession or to life in general.

Developing problem solving skills is such an important component of chemistry courses that it is useful to summarize some of the differences research has found between good and poor problem solvers.

Good Problem Solvers:

1. Believe they can solve almost any problem if they work long enough.
2. Are persistent; they don't give up easily.
3. Read carefully, and reread a problem, until they understand what information is given and what they are asked to solve for.
4. Break problems into small steps, which they solve one at a time.
5. Organize their work so that don't lose sight of what they've accomplished, and can follow the steps they've taken so far.
6. Check their work, not only at the end of the problem but at various points along the way.

7. Build models, or representations, of the problem, which can take the form of a list of relevant information, a picture of the system under consideration, or a concrete example.
8. Try to solve a simpler, related problem when faced with a problem they can't solve.
9. Guess and test; they try out several approaches to a problem until they are successful.

Poor Problem Solvers:

1. Don't believe they can solve problems; they believe that you either know the answer or you don't.
2. Give up easily if they don't seem to get the answer.
3. Are careless readers, who often misread what is written. They tend to jump into the problem before they understand what it asks for.
4. Seldom check their work to see if it makes sense.
5. Organize their work carelessly.
6. Have only one approach to a given problem. When they can't recall a formula, for example, they give up.

This text contains worked examples designed to help you: (1) determine what the problem asks for, (2) select relevant information, (3) keep track of this information, (4) check the results of calculations, (5) work problems that contain too much information, (6) work problems that don't seem to contain enough information, (7) work backwards, and (8) make assumptions or approximations that turn complex problems into simpler ones.

It might be useful to distinguish between two closely related concepts: *problems* and *exercises*. Hayes defined a problem as follows.

> Whenever there is a gap between where you are now and where you want to be, and you don't know how to find a way to cross that gap, you have a problem.[1]

If you know what to do when you read a question, it's an exercise not a problem. Status as a problem is not an innate characteristic of a question, it is a subtle interaction between the question and the individual trying to answer the question. It reflects experience with that type of question more than intellectual ability.

When you go to class, you may find that your instructor has developed an impressive repertoire of techniques that can be used to turn problems into exercises. We like to call these techniques "algorithms", which are defined as "rules for calculating something, especially by machine." Algorithms are useful for solving routine questions or exercises. In fact, the existence of an algorithm constructed from prior experience may be what turns a question from a problem into an exercise.

Students who have not built algorithms for at least some of the steps in a problem will have difficulty solving the problem. There is more to working problems, however, than applying algorithms in the correct order. Problem solving has been defined as "What you do, when you don't know what to do." By definition, there is no clear cut answer to what you should do when faced with a novel problem. We believe, however, that successful problem solvers, when faced with a problem,

1. Read the problem.
2. Read the problem again.
3. Write down what they hope is the relevant information.
4. Read the problem again.
5. Draw a picture or make a list to help build a model, or representation, of the problem.
6. Try something.
7. Try something else.
8. See where this gets them.
9. Read the problem again.
10. Try something else.
11. See where that gets them.
12. Test an intermediate result.
13. Repeat this process until they get an answer that might be correct.
14. Test the answer to see if it makes sense.
15. Start over if they have to, celebrate if they don't.

We have two suggestions for improving your problem-solving skills. First, recognize the importance of practice. The more problems you work, the better you will become at solving problems. Second, recognize the importance of working with other students. Take turns working problems out loud, explaining each step in the problem to the others in your group. While you do this, they should listen carefully to make sure they understand each step you take, to check each step to make sure that you aren't making any errors, to identify errors when they perceive them (without giving any hints about what they believe is the correct answer), and to insure that you vocalize each of the major steps in the problem. Research has shown that this approach can significantly improve the problem solving skills of each member of the group.

---

[1] J. Hayes, "The Complete Problem Solver", Franklin Institute Press, Philadelphia, PA 1980.

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CHAPTER 1

THE FUNDAMENTALS OF MEASUREMENT

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1.1 CHEMISTRY AS AN EXPERIMENTAL SCIENCE

Chemistry is easy to define:

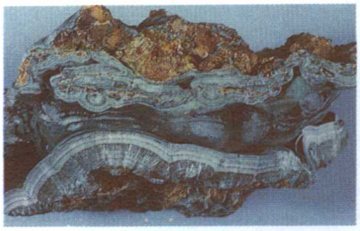
> **Chemistry is the science that deals with the composition and properties of substances and the reactions by which one substance is converted into another.**

But it is harder to appreciate what this definition means. It can be argued that the purpose of this text is to provide the background necessary to fully understand this definition and its implications.

One of the best ways of teaching a new word or concept is to provide both examples and non-examples of the concept. Perhaps the best way to begin defining chemistry is to provide you with examples of what it is not.

In 1921, a group from the American Museum of Natural History began excavations at an archaeological site on Dragon-Bone Hill, near the town of Chou-k'ou-tien (Zhoukoudian), 34 miles southwest of Beijing, China. Fossils found at this site were assigned to a new species, *Homo erectus pekinensis,* commonly known as Peking man. These excavations suggest that for at least 500,000 years, people have known enough about the properties of stone to make tools, and they have been able to take advantage of the chemical reactions involved in combustion in order to cook food. But even the most liberal interpretation would not allow us to call this chemistry, because of the absence of any control over these reactions or processes.

The ability to control the transformation of one substance into another can be traced back to the origin of two different technologies: brewing and metallurgy. There is ample evidence that people have been brewing beer for at least 12,000 years, since the time when the first cereal grains were cultivated. Metallurgy, the process of extracting metals from their ores, has been practiced for at least 6000 years, since copper was first produced by heating the ore malachite.



A sample of the ore malachite from the Campbell Cole Shaft in Bisbee, Arizona.

But brewing beer by burying barley until it germinates and then allowing the barley to ferment in the open air was not chemistry. Nor was extracting copper metal from one of its ores. People carried out both processes in the same fashion time after time without any understanding of what was happening or why. Even the discovery around 3500 B.C. that copper mixed with 10% to 12% tin gave a new metal that was harder than copper, and yet easier to melt and cast, was not chemistry. The preparation of bronze was a major technical breakthrough in metallurgy, but it did not provide people with an understanding of how to make other metals.

Between the sixth century B.C. and the third century B.C., the Greek philosophers (literally, lovers of wisdom) tried to build a theoretical model for the behavior of the natural world. They argued that the world was made up of four primary, or *elementary,* substances: fire, air, earth, and water (see Figure 1.1). These substances differed in two properties: hot versus cold and dry versus wet.

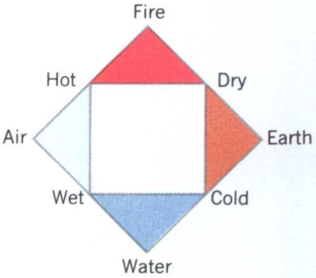


FIG. 1.1 The ancient Greeks assumed the world was composed of four elements—fire, air, earth, and water—that differed in two properties—hot versus cold and dry versus wet.

Fire:	**hot and dry**
Air:	**hot and wet**
Earth:	**cold and dry**
Water:	**cold and wet**

Their model was able to explain some common observations. Water (cold and wet) evaporates or turns into air (hot and wet) when it is heated. A piece of wood, which contains a great deal of earth (cold and dry), bursts into flame (hot and dry) when it is heated.

This model was the first step toward the goal of understanding the properties and compositions of different substances and the reactions that convert one sub-

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