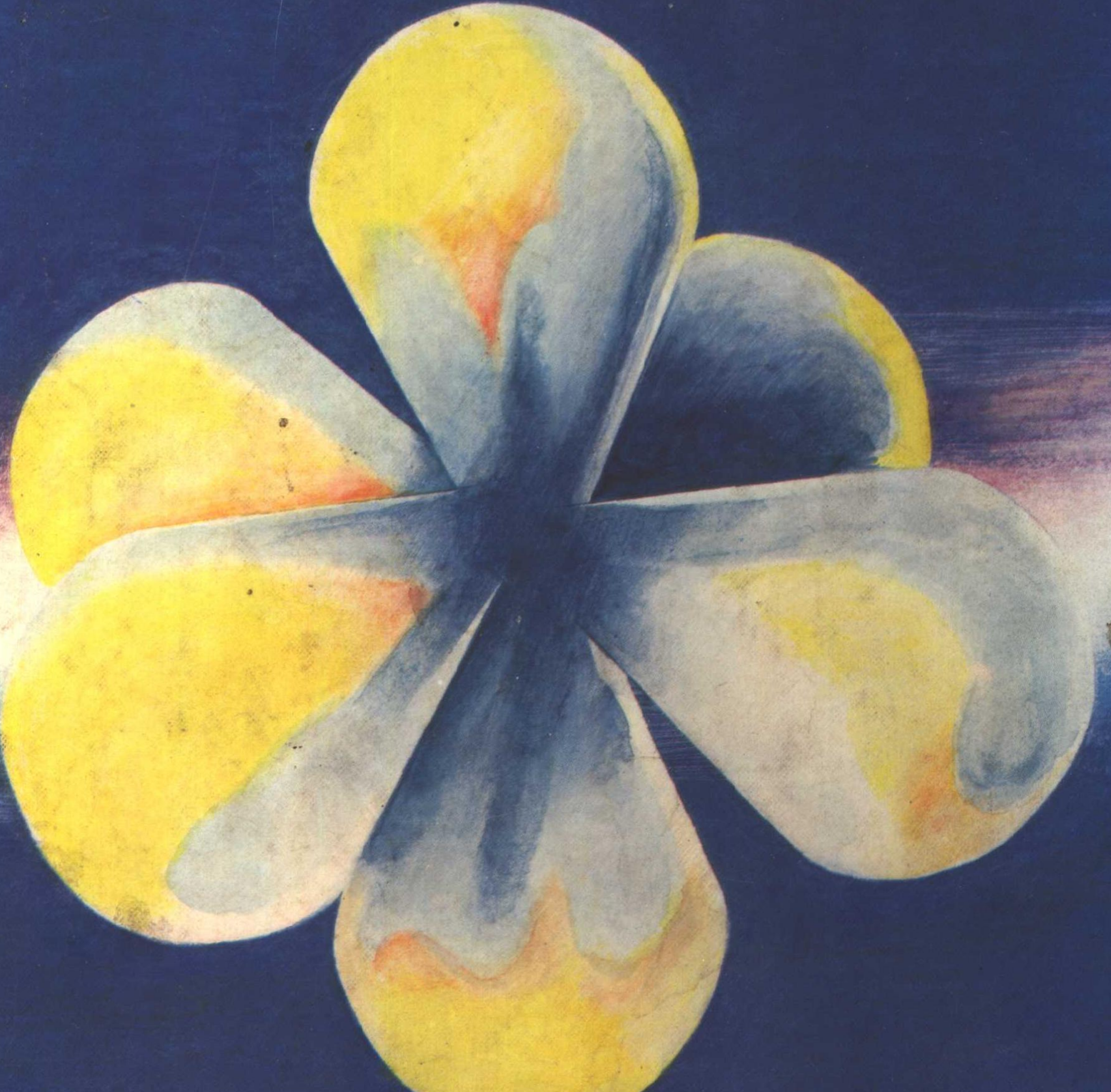
Brady Humiston

GENERAL CHEMISTRY
PRINCIPLES AND STRUCTURE
2ed.



GENERAL CHEMISTRY PRINCIPLES AND STRUCTURE

SECOND EDITION

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PREFACE

We were both pleased and encouraged by the enthusiastic reception that greeted the first edition of our book. Therefore, our goal in revising this text has been to strengthen and refine those features that attracted instructors to the book in the first place, while correcting weaknesses or deficiencies pointed out by our students and some reviewers.

In preparing this revision we have examined the first edition carefully, line by line, with an eye toward improving the overall readability of the text and the clarity of presentations. We have continued to choose simple language to develop concepts and have provided a liberal assortment of worked out example problems to assist the student. As before, no prior knowledge of chemistry is assumed, and new terms have been carefully defined before using them in subsequent discussions. As in the first edition, new terms are set in boldface type and are indexed; important definitions are italicized. In an effort to heighten student interest and to provide an increased awareness of the role of chemistry in our earthly existence, we have added many more examples of chemicals that enter our everyday lives as products of both nature and technology. These appear in discussions of concepts, in example problems, and in review questions and problems.

Although the theme and basic features of the book remain the same, several key changes have been made. At the suggestion of many users of the first edition, the end-of-chapter exercises have been considerably expanded. They have been divided into Review Questions and Review Problems. Among the problems a range of difficulty has been provided, and the most difficult problems are marked with an asterisk. At the end of each chapter there is an index of subject areas covered by the exercises to aid the instructor in assigning homework and to assist students in planning their study.

Pictorial illustrations continue to be used generously throughout the text. We have retained the use of stereoscopic illustrations to enrich discussions of the three-dimensional aspects of chemistry since, in the experience of many adopters of the first edition, they were a useful pedagogical device. At the suggestion of a number of users of the first edition, we have replaced line drawings of orbitals with stereophotographs of models, so that both the orientation of the orbitals and their space-filling character are depicted.

While refinements have been made throughout the book, several chapters were singled out for extensive revision. In the stoichiometry chapter the entire introduction to the mole concept has been drastically changed and, we feel, pedagogically improved. We have found the present approach very effective in the classroom. The material on ionic equilibrium has been entirely reorganized and divided into two chapters. The first deals with acid-base equilibria, the second with solubility and complex ion equilibria. The general approach to equilibrium problems has also been modified to make it easier for students to follow. The chapter on organic chemistry has also been completely rewritten to provide an overview of types of organic compounds with examples of where they are encountered in everyday situations. In this chapter we attempt to give the student a feel for the breadth of this important and fascinating area of chemistry.

Another new feature of the book, appearing on the viewer pocket inside the cover of the book, is an index to important reference tables. This handy reference guide permits the quick location of useful tables distributed throughout the various chapters in the text.

A difficult decision to reach in preparing a textbook of this kind is how many SI units to embrace. We have chosen to retain the atmosphere and torr as the units of pressure because of ease of measurement in the laboratory, although the relationship of these units to their SI counterparts is pointed out. With energy units, we have employed a dual approach. Tables include energies in both joules (or kJ) and calories (or kcal). Numerical problems are worked out sometimes in joules and other times in calories. We have selected this approach because energies appearing in all but the most recent literature have generally been expressed in calories. Therefore, we feel that students must develop an ability to handle both joules and calories.

As in the past, we have assumed a mathematical background sufficient to handle only simple algebra; calculus is avoided entirely. A review of some mathematical concepts, including the use of logarithms, is found in Appendix C. In developing concepts we have tried to limit the use of mathematics to that needed to impress on the student the importance of quantitative concepts and why these are necessary in the evolution of scientific thought.

In this edition the overall sequence of topics remains unchanged. Concepts have been developed in a logical order, beginning with quantitative relationships involving atomic weights, formulas, and chemical equations in Chapters 1 and 2; this order permits an early introduction of quantitative experiments in the laboratory. These are followed by a discussion of atomic structure and the periodic table. A historical approach is taken here to give some perspective to current notions about atomic structure.

The treatment of chemical bonding once again is divided into two chapters. Chapter 4 deals with elementary concepts of covalent and ionic bonding, sufficient we feel, to carry students through approximately two-thirds of the book. Modern theories of bonding are presented in Chapter 17, just prior to the need to use them in discussions of descriptive chemistry. This division provides students with the opportunity to gain some maturity in chemistry before the more sophisticated bonding concepts are presented, and obviates the need to reteach this material in the second half of the course when it is finally needed. Users of the book who have not agreed with this division of bonding concepts, however, have found no difficulty in teaching the material in Chapter 17 immediately following Chapter 4.

Our treatment of solutions is also divided between two chapters. Chapter 5 focuses on solutions (particularly aqueous solutions) as a medium for carrying out chemical reactions. Chapter 9, which follows a discussion of liquids (Chapter 8), deals with the physical properties of solutions as they are affected by the interactions between solute and solvent.

Chapter 5 introduces many important concepts that are developed in greater detail in later chapters (for example, chemical equilibrium and acid-base reactions). The stoichiometry of solutions, the concepts of ionic reactions, and acid-base and redox titrations are also discussed in Chapter 5. This chapter, at a relatively early stage, prepares students for a variety of quantitative and qualitative laboratory experiments that deal with reactions in solution. It also reflects our approach to descriptive chemistry. There is a certain body of factual descriptive chemistry that students "must know" because they need it in other courses. There are other aspects of descriptive chemistry that students should "know about." We have attempted to compile much of this "must know" chemistry in Chapter 5.

Students who have had a high-school chemistry course may be familiar with a good deal of the material in Chapter 5, and the instructor may assign portions of it for review. We think, however, that every student who has had a course in general chemistry should know this material thoroughly.

Thermodynamics (Chapter 10) and kinetics (Chapter 11) are included sequentially to relate the importance of these two factors in determining the outcome of a chemical reaction. The interplay between thermodynamics and kinetics is discussed later in connection with descriptive chemistry.

In Chapter 12, on equilibrium, the equilibrium law is discussed first as an experimental phenomenon, and then it is analyzed in terms of kinetics and thermodynamics. This general chapter on equilibrium concentrates on gaseous and heterogeneous systems and includes a thorough discussion of Le Chatelier's principle. After a chapter on acids and bases, the discussion of equilibrium is concluded with the two-chapter treatment of ionic equilibrium mentioned earlier.

Electrochemistry is considered in Chapter 16, which includes practical applications to electroplating, energy production, and the electrochemical measurement of concentrations.

As in the first edition, the intention of the descriptive chemistry chapters (Chapters 18 to 20) is to display trends and similarities in the structure and reactivity of the elements and their compounds. These chapters serve to illustrate chemical relationships; they are not intended to be memorized by the student. Their dominant theme is structure, and the stereoscopic illustrations serve well to illustrate a variety of three-dimensional shapes encountered here. In revising these chapters we have made more frequent reference to familiar chemicals and their practical applications.

Chapter 21 on organic chemistry is followed by a separate chapter on biochemistry. Here we show how complex biomolecules are composed of relatively simple building blocks and how their structures and biological functions are accounted for.

The final chapter is on nuclear chemistry. It includes, in addition to the usual topics, illustrations of how chemists can take advantage of nuclear phenomena to aid them in their understanding of chemical processes.

For completeness, more information has been included here than can usually be presented in a two-semester course. What, then, can be cut away? This decision must be made by the instructor. Since it is often the descriptive chemistry that is pruned, we have made each section, as nearly as possible, a self-contained unit. Thus the instructor can stress the areas that he or she feels are important.

The order of chapters reflects our own bias about the sequence of topics in a general chemistry course. We realize, however, that there are other pedagogically sound orders of presentation. Therefore, in our development of what we have found to be an effective topic sequence, we have also attempted to make units sufficiently independent so that their order of presentation can be easily modified. For example, if an instructor prefers not to divide the discussions on bonding between two semesters, the topics in Chapter 17 easily can be presented after Chapter 4. Similarly, a great deal of the material in Chapter 5 can, if the instructor wishes, be included in Chapter 9.

Supplements available to accompany this textbook include a student Study Guide, which is keyed section by section to the text and contains solutions to approximately two-thirds of the even-numbered numerical problems from the text, and a Laboratory Manual for General Chemistry, which contains 51 experiments, both quantitative and qualitative. For the instructor there is an Instructor's Manual listing chapter objectives with answers to questions and worked-out solutions to numerical problems not found in the Study Guide. Transparency masters of important illustrations and typical problem solutions from the text are also available.

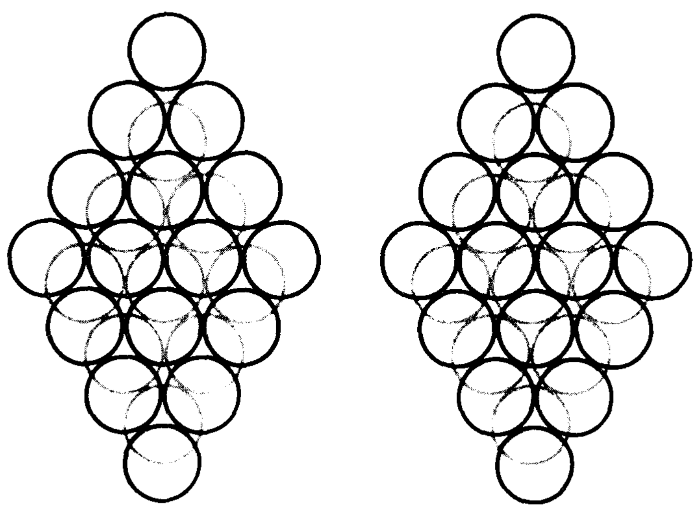
Finally, we wish to thank the reviewers who have contributed to this revision. Professors Charles Barr and Michael Imhoff of Austin College; Jo Beran, Texas A & I University; Philip Fuchs, Purdue University; Floyd Kelly, Casper College; Philip Lamprey, Lowell Technological Institute; Michael Peterson, North Seattle Community College; Jack Powell, Iowa State University; Don Roach, Miami-Dade Community College; Ted Sottery, University of Maine, Portland-Gorham; and Michael Wartell, Metropolitan State College have all helped us to develop a framework for the revision through their suggestions and criticisms of the first edition. We also thank Professors John Alexander, University of Cincinnati; I. C. Hisatsune, Pennsylvania State University; Delwin Johnson, St. Louis Community College at Forest Park; Joseph Long, Broome Community College; Ruth Sime, Sacramento City College; and Kenneth Watkins, Colorado State University all of whom provided many detailed suggestions for even further refinement of the final draft of this revision. We are particularly grateful to our colleagues and students for their suggestions, especially Drs. Ernest Birnbaum, Eugene Holleran, Eugene Kupchik, William Pasfield, John Skarulis, and Siao Sun, who served as sounding boards for our ideas and helped us to assess student reaction to the various modes of presentation in the text. Our continued appreciation is extended to Drs. Don Cromer and Carroll Johnson, who provided us with copies of some of the stereo illustrations. Special praise goes to the staff at Wiley, particularly our editor and friend, Gary Carlson, whose guidance, sound decisions, and sense of humor have made our task enjoyable. And, most important, we must thank our wives and children, who continue to be our inspiration.

James E. Brady

Gerard E. Humiston

TO THE STUDENT

This textbook contains a substantial number of stereo (three-dimensional) illustrations that are intended to help you visualize some of the 3-D aspects of chemistry. Each stereo illustration, like the one below, consists of a pair of drawings that, at first glance, appear to be identical; actually they are slightly different. When viewed in such a way that the left eye focuses on the left drawing and the right eye focuses on the right drawing, your mind brings them together and creates a three-dimensional image.



A viewer is included inside the back cover of the book to help you obtain a 3-D illusion. To get accustomed to using the viewer, assemble it according to the directions printed on the viewer and locate the bottom edge along the solid line under the drawing above. The viewer should be placed so that the folded support panel is placed between the two drawings. Now look through the lenses of the viewer, keeping both eyes open. Start with your eyes a few inches above the viewer. At first you may find that it takes a moment for the stereo image to fuse. You may have to move the viewer slightly if a double image persists. The drawing should appear to be two layers of tangent circles, one above the other.

In your study of chemistry you will encounter many new terms whose meaning you will need to know to understand the discussions that follow. These are set in **boldface** type the first time that they appear in the text. Each of these is also included in the index for later reference. Important definitions have been set in *italics* to call your attention to them.

SUPPLEMENTARY MATERIALS

A **study guide** including worked-out problems, important terms, answers to problems, review material and detailed solutions to approximately one third of the numerical problems in this book is available for student use.

Brady and Sottery, Study Guide and Selected Problem Solutions to Accompany General Chemistry:
Principles and Structure. ISBN: 0-471-03498-3.

CONTENTS

1 INTRODUCTION

Never before in history have people found themselves so able to influence their physical environment, for good or bad, as today. This has come about as a result of scientific discoveries. This book deals with a branch of physical science called chemistry, which concerns itself with the composition of substances, the ways in which their properties are related to their composition, and the interaction of these substances with one another to produce new materials.

The degree to which chemistry has changed civilization is evident everywhere. A good part of the clothing we wear, the automobiles we drive, and other products we encounter daily are composed of materials that simply did not exist at the turn of the century. In recent years the realization that a living organism is a complex chemical "factory" has generated a strong interest in the study of biochemistry and has brought great advances in our knowledge of the nature of life. Medicines created in the laboratory have made us healthier and, through the cure of disease, have prolonged our lives. It has been only recently, however, that we have also become painfully aware of a host of problems arising from this growth of technology. It is the solution of such problems that poses much of the challenge for chemistry in the future.

In this first chapter we consider how science operates, see the materials and concepts with which chemists work and about which they are concerned, and see how the concept of the atom became firmly established. We shall also introduce you to some of the jargon used by chemists. It is important to become familiar with chemical terminology (which will undoubtedly require some memorization), because many of the difficulties that students encounter in the study of chemistry can be traced to their inability to "speak the language."

1.1 THE SCIENTIFIC METHOD

Many of the most important advances in science, such as the discoveries of radioactivity by Henri Becquerel and penicillin by Alexander Fleming, have come about by accident. These discoveries were really only partly accidental, however, because the people involved had learned to think "scientifically" and were aware that they had observed something new and exciting.

Progress in chemistry, as well as in other sciences such as biology, physics, and psychology, is accomplished by applying a procedure called the **scientific method.** It can be divided into a series of steps that are followed, often unconsciously, in answering scientific questions. The first step can be called **observation.** The experiments that you, or any other scientist, perform in the laboratory are designed to observe nature under controlled conditions, and the bits of information that you gather are called **data.** For example, you might observe that when hydrogen gas and oxygen gas are heated together, a violent explosion results and water vapor is produced. This type of observation, which is devoid of numerical information, is said to be **qualitative.** A different chemist might make some measurements and find that, under the same conditions of temperature and pressure, one cubic foot of hydrogen gas will completely consume only one-half cubic foot of oxygen gas to produce one cubic foot of water vapor. This is a quantitative observation because it results in numerical data. We will see that quantitative measurements are generally more useful to a scientist than are qualitative observations because the former provide more information.

After a large amount of data has been collected, it is desirable to find a way to summarize the information in a concise way. Statements that accomplish this goal are called **laws** and, in a sense, simply serve as a convenient means of storage for vast quantities of experimental facts. They also provide a means of predicting the results of some as yet untried experiment. For instance, after a series of measurements regarding the relative quantities of hydrogen and oxygen that will react with one another, a chemist would conclude that when these two substances interact at the same temperature and pressure to form water, one volume of oxygen gas consumes two volumes of hydrogen gas. This simple statement is a law dealing with the reaction of hydrogen with oxygen. If we had five cubic feet of oxygen gas, we would predict that the optimum production of water would require 10 cubic feet of hydrogen.

A law may be expressed in a simple verbal statement, such as the law we just discussed regarding the reaction of hydrogen with oxygen. However, it is often more useful to have a law stated in the form of an equation. For instance, it is observed that the force of attraction between oppositely charged particles decreases as their distance of separation increases. This is more accurately stated by Coulomb's equation, or law,

$$F = \frac{q_1 q_2}{r^2}$$

in which F is the force of attraction between two oppositely charged particles, q_1 and q_2 are the charges on the particles, and r is their distance of separation. Laws quite commonly are expressed in equation form.

As we have noted, a law simply correlates large quantities of information. Laws in themselves do not explain why nature behaves as it does. Scientists, being human (despite what you may have heard to the contrary), are not satisfied with simple statements of fact and seek to explain their observations. Thus the second step in the scientific method is to propose tentative explanations, or **hypotheses,** that may be tested by experiment. If they are not disproven by repeated experiment, they develop into **theories.** Theories themselves always serve as guides to new experiments and are constantly being tested. When a theory is proven incorrect by experiment, it must either be discarded in favor of a new one or, as is often the case, modified so that all of the experimental observations may be accounted for. Science develops, then, through a constant interplay between theory and experiment.

It should be remembered that theories can seldom be *proven* to be cor-