FRANCIS MARION MILLER

CHEMISTRY

STRUCTURE AND DYNAMICS

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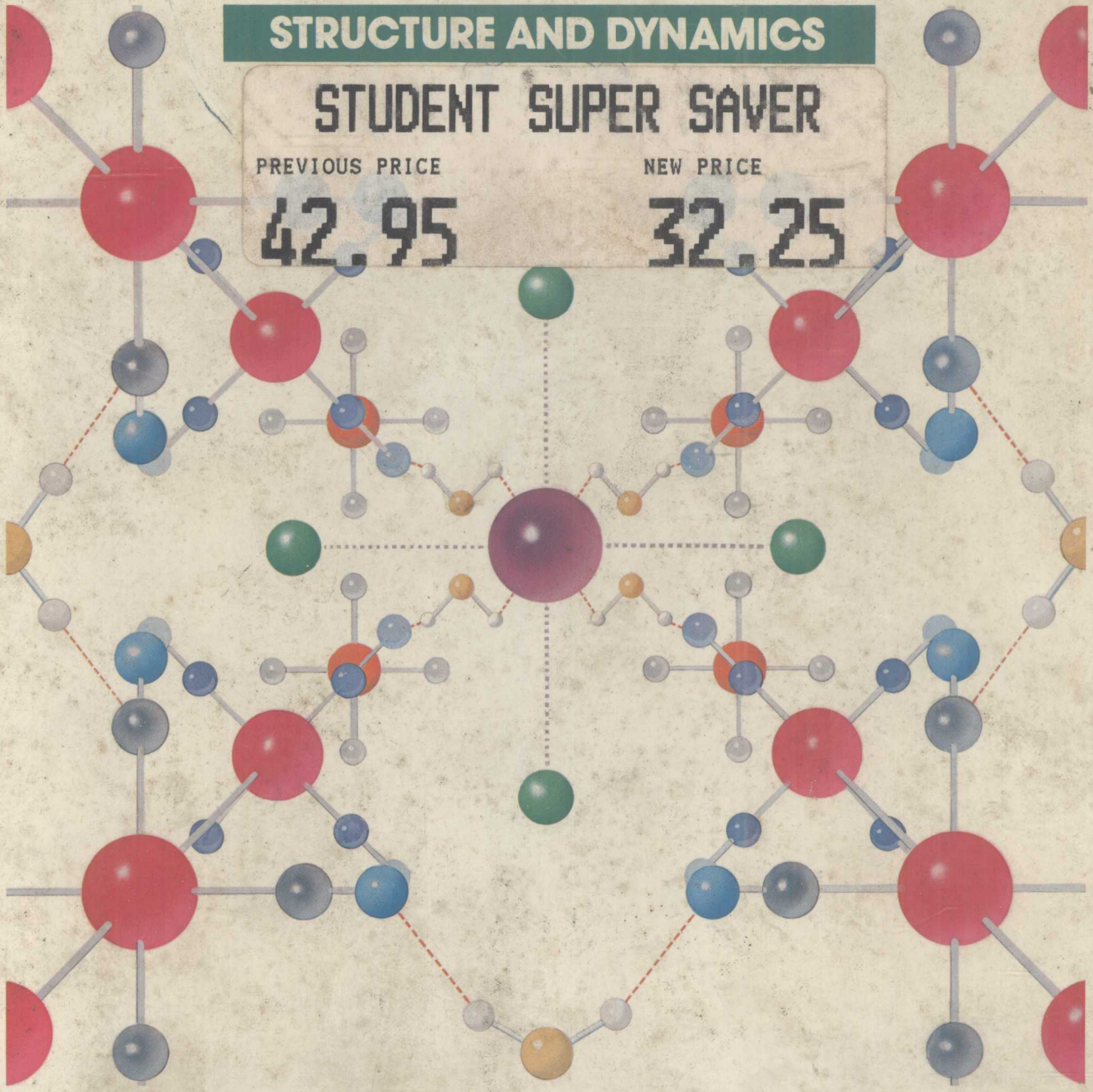

CHEMISTRY

STRUCTURE AND DYNAMICS

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TO C.W.M.

TO THE STUDENT

In producing this textbook, we have made every effort to provide you with a book that will assist your instructor in bringing the science of chemistry to you as smoothly and effectively as possible. As you begin your study, I want to point out some of the book's features, along with some suggestions about how to use it to the greatest advantage.

You should begin your study of each chapter by examining the *outline* to obtain an overview of the chapter's contents. A good approach then is to scan the chapter to gain a general grasp of the material. You should include the *chapter summary* in this first reading. Whenever possible, read the chapter as soon as it is assigned and before the material is discussed in the lecture.

You are now ready for a careful reading of the chapter, taking time to study the worked-out *examples*, which provide further illustration of the ideas explained in the text. A worthwhile tactic is to attempt to answer the question in the example before looking at the solution. When you have worked through the chapter thoroughly, again read the summary, because in many cases the ideas and relationships of the chapter are stated there in a slightly different way, providing you with another perspective of the material.

To check your mastery of the material in the chapter, make certain that you are able to satisfy each item in the *chapter mastery checklist*. Do this in an active way by carrying out each operation and verifying your answer. This can be done both with the examples in the chapter and with the *exercises* at the end of the chapter. These exercises are grouped by topic, and those with colored numbers have answers in the appendix. You can best acquire a thorough competence in the topic by working a number of these exercises.

Also included at the end of each chapter is a list of *suggested readings*. These articles were chosen to provide you with interesting and informative supplementary material related to the discussions in the chapter.

A useful feature of this text is the *glossary*. Where possible, terms here are defined with somewhat different words from those used in the chapters. The glossary items include reference to the section of the book where a term is introduced. Therefore, if at a later point in your study you find that you are uncertain about the meaning of a word or the statement of a law, the glossary will provide a ready source of the definition and a reference to the more complete explanation in the body of the book.

Your study of chemistry with this text does not require a high level of mathematics. However, mathematics is part of the language of chemistry, and a lack of familiarity with that language can become a barrier to success in understanding chemistry. Appendix A is a *review of mathematics*, included to assist you in your recollection of the operations of algebra, exponential numbers, logarithms, and graphing. Examine it now, and then refer to it any time you are not completely certain of a mathematical operation.

I hope that you are eager to begin your study of chemistry and that this course is an enjoyable and rewarding experience for you.

Francis Marion Miller

TO THE INSTRUCTOR

Chemistry: Structure and Dynamics is a text for a two-semester general chemistry course for science majors. The book assumes no previous knowledge of chemistry or of calculus. Nevertheless, it is designed to provide students whose background includes a year or more of high school chemistry with stimulation and some new material.

The objective of a general chemistry course for science majors is preparation for such advanced courses as organic chemistry, analytical chemistry, physical chemistry, and biochemistry. Students emerging from the course should have firm ideas of molecular structure, acids and bases, equilibrium, the energetics of physical and chemical changes, and fundamental descriptive chemistry. At the same time, the course should enhance the student's ability to analyze a problem and proceed logically toward a solution; the student should develop an understanding of scientific methodology.

The decision to write this text was based on the conviction that the most coherent and unified presentation of the subject matter usually considered in the general chemistry course for science majors is based on two principles:

1 The topic of energy and enthalpy changes must be introduced early and the energy changes accompanying physical and chemical changes emphasized wherever possible.

2 The physical and chemical properties of elements and compounds must be correlated thoroughly with the structure and polarity of the substances under consideration.

Following the first principle, I have examined energy rather thoroughly in Chapter 4 in terms of the first law of thermodynamics, thermochemistry, enthalpy changes, radiant energy, and electrical energy. Students are thus prepared for the ideas of molecular energies in gas behavior (Chapter 5), electron energy levels (Chapter 6), ionization energies and electron affinities (Chapter 7), bond energies (Chapter 9), the energy changes associated with phase changes (Chapters 10 and 12), enthalpy cycles and the dissociation of acids and bases (Chapter 13), activation energies (Chapter 14), the second and third laws of thermodynamics (Chapter 18), electrochemical energy changes (Chapter 19), radiant energy changes (Chapter 20), and a variety of energy considerations associated with descriptive chemistry (Chapter 21 *et seq.*).

In agreement with the second principle, after the introduction of the basic ideas of molecular geometry (Chapter 8), the consequences of molecular shape and polarity are invoked at every appropriate opportunity: structure and physical properties (Chapter 10), solubilities and properties of solutions (Chapter 12), structure and chemical reactivity (Chapter 13), and throughout the discussions of descriptive chemistry in the last third of the book.

An objective constantly in mind during the writing of this book was to produce a text that would be of maximum usefulness to the student reader. I have made every effort to achieve the highest possible degree of readability, to avoid jargon while introducing the vocabulary of chemistry, and to provide clear, precise, and meaningful definitions of new terms. The illustrations have been planned and executed with care. To make troublesome concepts as accessible as possible I have chosen to present the development of the foundations

of chemistry as it actually occurred. I have made a consistent effort to show how chemistry is done, rather than to hand down facts. Where feasible, experimental methods are discussed. To show that the ideas of chemistry are reasonable and have developed in a logical manner, I have examined how scientific models relate to observed facts. Practical applications with which the student is likely to be familiar have been included wherever possible.

I have paid particular attention to the development of topics with which students often have difficulty gaining an effective level of understanding. Believing that repetition is one helpful technique, I have introduced troublesome ideas early and considered them frequently to achieve maximum familiarity. Equilibrium, including LeChatelier's principle, and entropy are first examined in relation to changes of state (Chapters 10 and 12). The factors affecting acid-base strength are discussed in detail in Chapter 13 as background for the quantitative consideration of aqueous acid-base equilibria in Chapter 16. Oxidation-reduction is first encountered in Chapter 8, where oxidation states are examined, and is reconsidered briefly in Chapter 13 along with other reaction types. In the electrochemistry chapter (Chapter 19), the student uses the ion-electron method for balancing redox equations in connection with half-cell reactions.

Many years of teaching chemistry have provided me with convincing evidence that students gain a functional comprehension of a new idea more quickly if the concept is developed logically from first principles than if the topic is summarized in a superficial manner. I believe that I have attained the proper balance between telling students more than they need to know in an introductory course and presenting an idea or equation without an explanation of its origin. As the result, students can at least appreciate the way in which the idea or equation was developed, and not simply be told "it can be shown that. . . ."

As the title indicates, I have divided the book on a general basis into an initial development of chemical structure followed by a consideration of chemical dynamics. However, keeping the needs of laboratory programs in mind, stoichiometry, molar concentration, and reactions in solution are covered in Chapter 3, and the behavior of gases in Chapter 5. This organization permits a logical development of the subject matter, as well as the use of a wide variety of laboratory experiments during the first half of the semester.

The book employs several approaches not generally found in general chemistry texts. In Chapter 2 the foundation for discussing the mole concept and stoichiometry is developed on the basis of Dalton's atomic theory and Gay-Lussac's law of combining volumes, prior to considering the ideal gas law. Bond dissociation energies are examined in the coverage of covalent bonds (Chapter 9) rather than in the thermodynamics chapter. I have introduced the essential features of descriptive chemistry in Chapter 13, immediately following the discussions of bonding and physical properties. Here the types of chemical reactions, acids and bases, and reactivity trends are surveyed as preparation for the consideration of kinetics, equilibrium, and thermodynamics and for elaboration in later chapters.

The goal of the science of chemistry is to explain the behavior of matter and, on a more immediate level, to correlate descriptive chemistry. I have attempted to provide a theoretical background adequate to permit maximum correlation and minimum student distress in the coverage of descriptive chemistry. The detailed chemistry of the nonmetals (Chapters 22 and 23), metals (Chapter 25), and coordination complexes (Chapter 26) is delayed until a solid foundation has been established in the areas of kinetics, equilibrium, thermodynamics, and electrochemistry. The coverage of the behavior of metals and nonmetals is more extensive than can be handled in some courses, permitting the selection and presentation of the topics desired. Consistent with the effort to present a nonfragmented picture of chemistry, I have included carbon chemistry with that of the other nonmetals, while taking due note of the importance of the field of organic chemistry.

The book's scope is comprehensive, allowing the selection and presentation of material most suitable for the course and the students. Beyond the core of subject matter usually covered in two semesters, the text includes several topics that can be treated completely or partially on an optional basis: radiant energy and spectroscopy (Chapter 20), atmospheric chemistry (Chapter 21), geochemistry and metallurgy (Chapter 24), and nuclear chemistry (Chapter 27). These topics can also be presented at earlier points in the course if desired. The *Instructor's Manual* includes alternate topic sequences.

I have attempted to handle the use of SI units on a rational basis. To unify the ideas of energy changes and interconvertibility, enthalpy changes, ionization energies, electron affinities, bond energies, etc., are all expressed in units of joules. I use nanometers as the unit for bond length and ultraviolet and visible radiation wavelength. However, I have retained the traditional units of atmospheres, liters, and milliliters, since these units currently provide a more significant description of quantities than do pascals or cubic meters.

To assist student achievement in the course, all important mathematical operations and nonquantitative evaluations are illustrated and explained in step-by-step solutions of in-chapter examples. A summary, including key terms, appears at the end of each chapter, along with a checklist to determine chapter mastery. A complete glossary is located at the end of the book. Exercises at the ends of chapters are abundant and cover a range of difficulty. The appendixes contain a review of mathematical operations, units, physical constants, and the more involved derivations of equations. Answers to selected exercises (those whose numbers appear in color in the exercise sets) are provided at the end of the book. The *Instructor's Manual* contains answers to the remaining exercises, and the *Solutions Manual* provides solutions to all the exercises.

A valuable aid to students seeking another perspective and additional practice with problem solving will be found in *Coping with Chemistry*, the study guide prepared by Carl Trindle of the University of Virginia for use with this volume.

An effort of this magnitude requires the assistance and cooperation of many people. My colleagues Gordon Kresheck, Roy Mason, Morley Russell, Joe Vaughn, and Malcolm Weiss graciously provided comments and sugges-

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I hope that you will find this text well-suited to your needs and that it will be of significant assistance to your students in their study of chemistry. Your comments regarding its features and your recommendations for its improvement will be most welcome.

Francis Marion Miller

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