CHEMISTRY

THE MOLECULAR SCIENCE

Second Edition

Olmsted & Williams

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Second Edition

John Olmsted III
California State University, Fullerton
Fullerton, California

Gregory M. Williams
California State University, Fullerton
Fullerton, California

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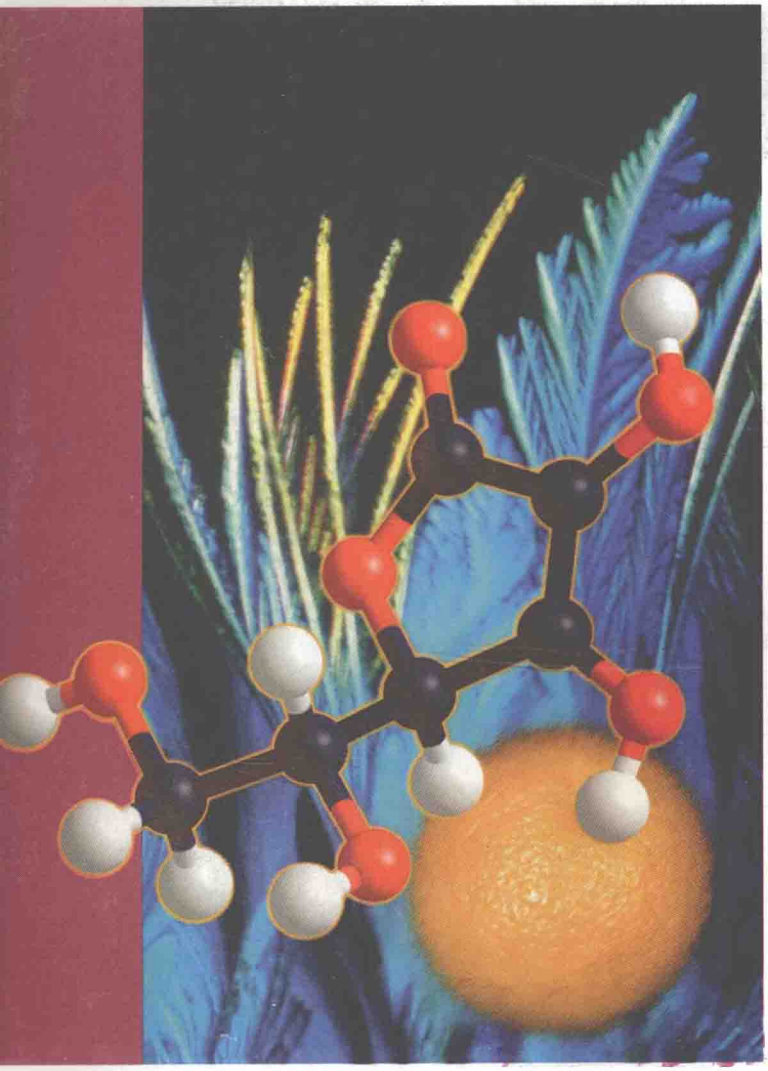

On the cover:
Our cover highlights one chemical substance, limestone ($CaCO_3$), at the macroscopic, microscopic, and molecular levels. Monumental sculpture such as the gargoyles that grace the Notre Dame Cathedral in Paris are made of limestone. Such sculpture shows damage caused by acid rain, a recent environmental problem. The background image shows the microscopic crystal structure of limestone as revealed by scanning electron microscopy. Materials scientists study this structure to determine methods for protecting sculptures from further damage. The molecular model shows calcium ions (large off-white balls) and carbonate ions (central carbon atoms, shown in black, each bonded to three oxygen atoms, shown in red) arranged in the layers that constitute the molecular architecture of limestone.

On the first edition:
The cover for the first edition of *Chemistry: The Molecular Science* highlighted ascorbic acid (vitamin C) at the macroscopic, microscopic, and molecular levels. Oranges are an important dietary source of this essential vitamin. The background image shows a photomicrograph of crystals of ascorbic acid. The ball-and-stick model shows how vitamin C is put together from six carbon atoms (black), six oxygen atoms (red), and eight hydrogen atoms (white).

To all those students
whose determination to learn chemistry
inspired us to write this book

Preface

You, our audience, are a diverse group because chemistry underlies fields extending from biology and geology through medicine and pharmacy to engineering and materials science. Consequently, a textbook must present general chemistry so that whatever your discipline, you can appreciate the elegance of chemistry and master its fundamental concepts. Regardless of where your interests lie, however, the important chemical properties and principles remain the same. These chemical properties and principles are the core of our presentation.

Chemistry is a mature science in the sense that the atomic theory, its primary unifying theme, is nearly 300 years old. Yet it is a surprisingly young science as well, bursting with the excitement of new discoveries such as buckminsterfullerene, taxol, and superconductivity as well as new challenges such as the causes and control of the ozone hole and new drugs to combat AIDS.

An introductory chemistry textbook must focus on basic concepts whose validity is well established, and we do this. At the same time, however, the vibrancy and excitement of chemistry centers on what is newly discovered and as yet imperfectly understood. We try to capture this ferment by introducing some of the cutting-edge developments that chemists were exploring while we were writing this textbook.

The vibrancy of contemporary chemistry is illustrated by items of chemical "news" that were reported as we finished our revisions for this second edition. The first set of Presidential Green Chemistry Challenge awards were announced in July 1996. These awards honor outstanding new applications that use fundamental chemical principles to reduce sources of pollution. Among the winners were a nonpolluting method to manufacture a biodegradable polymer (see Chapter 11) and a process that uses lime to convert agricultural waste into animal feed.

On other fronts, materials scientists in Mexico City discovered that Maya blue, a unique blue paint developed by the ancient Mayans, has a molecular structure remarkably like those of advanced modern materials such as superconductors (see Chapter 10). And among the many advances reported concerning the biological role of nitrogen monoxide (see Chapter 19) was the development of a new class of drugs called *diazeniumdiolates.* Despite their formidable name, these substances possess simple $(NO)_2$ structures that break down to release NO within the body. By modifying the portion of the drug to which the $(NO)_2$ structure is bound, researchers hope to produce drugs that will selectively provide NO to target organs, such as the blood vessels of sufferers of high blood pressure and the livers of patients with life-threatening infections.

Organization and Emphases

Our title, *Chemistry: The Molecular Science,* reveals the primary unifying theme of this book. Our presentation emphasizes the molecular view of chemical principles because practicing chemists visualize chemical processes at the molecular level. A chemist sees a pot of boiling water and thinks instinctively of water molecules moving from the liquid phase to the gas phase. In every chapter, you will find molecular descriptions and molecular pictures, and you will be asked to visualize how molecules behave and to draw molecular pictures.

Chemistry is molecular, but at the same time it is quantitative. For this reason, a second main thread running through our text is the presentation and use of the quantitative equations of basic chemistry. Qualitative concepts always underlie quantitative equations, so our presentation always seeks to buttress quantitative ideas with their conceptual foundations.

The power of quantitative relationships lies in their applications. Therefore in presenting equations, not only do we outline their underlying logic, but we also illustrate how they are applied to chemical problems. Sample Problems describe these applications and illuminate the conceptual approaches to problem solving as well as its mechanical aspects. Even though we set them off from the narrative text, we expect you to read the Sample Problems as part of the flow of the chapter.

The various topics within general chemistry present a rich tapestry in which each topic connects with many others. The linear presentation of a textbook cannot show the full richness of these connections, nor is there a sequence of topics that avoids cross-references, both forward and backward. Our sequence starts with the molecular composition of matter and a description of chemical reactions and builds an understanding of a variety of chemical topics on those fundamental ideas.

Throughout this development, we describe how substances behave in the context of the concepts that we are presenting. This interweaving of concepts and descriptions presents chemistry as chemists understand it, a blend of principles and properties that illuminate and reinforce each other. As we present chemical principles, we also describe some of their practical applications. Because instructors differ in their beliefs about the importance of the descriptive aspects of chemistry, your instructor may place greater or lesser emphasis on these descriptive features. We have tried to write the text in a way that supports both a strong emphasis on principles and a strong emphasis on practice.

General chemistry introduces principles and properties that are common to all facets of the subject. To emphasize this, we use examples from inorganic, organic, industrial, and biological chemistry to illustrate underlying principles. Rather than introduce these branches of chemistry as separate topics, we weave them into our discussion wherever it seems appropriate. We hope that this approach provides insights into the close relationships among all facets of chemistry.

Coverage

Although there is a common core to a 1-year course in general chemistry, beyond that core are a number of topics from which each instructor makes a selection. Consequently, we present somewhat more material in this book than is likely to be covered in the usual course. Your instructor will choose to emphasize some topics beyond the core while omitting others. Several chapters contain sections that can be omitted without a loss of continuity. In addition, Chapter 11, Macromolecules, and Chapter 20, Nuclear Chemistry and Radiochemistry, cover topics that, although central to the interface between chemistry and modern society, lie somewhat outside the mainstream of coverage in traditional general chemistry.

Each chapter begins with an introduction that establishes the context for the subject matter to be covered. This is followed by sequential developments of major concepts and techniques; these developments use practical examples and are illustrated as much as possible through molecular pictures. Many chapters end with sections that discuss some important practical consequences of abstract chemical concepts. Examples are The Earth's Atmosphere (Section 5.7), Band Theory of Solids (Section 9.6), Bioenergetics (Section 13.6), Catalysis (Section 14.7), and Transition Metals in Biology (Section 18.6).

The Second Edition

When a textbook is finished, it becomes fixed in print; yet the field of chemistry is far from static. Furthermore, as students and professors use a textbook, they find not only its strengths but also where it might be improved. In this second edition we

have retained the features described but have revised and added material in light of new developments in chemistry and users' experience with the first edition.

The second edition incorporates three major organizational changes. First, every chapter opens with an Introduction that places the material of the chapter in a contemporary context. These Introductions are designed to help you understand why the topics of the chapter are important. Second, the bulk of the chapter Problems are "paired" so that each even-numbered problem is similar to its preceding odd-numbered problem. This allows you to consult the answer (in the back of the text) or detailed solution (in the Study Guide/Solutions Manual) for an odd-numbered problem and then test your understanding by working a different but related problem. Third, what was Chapter 18 in the first edition is reorganized and expanded into two new chapters, 18 and 19, in the second edition. This change allows us to describe in greater detail the chemistry of transition metals and main group elements.

In addition to these organizational changes, the presentations of several key concepts have been revised. The procedure for constructing Lewis structures (see Chapter 8) is slightly modified, making it easier to apply. Our description of delocalized orbitals (see Chapter 9) is streamlined in a way that retains essential features while omitting less important details. Thermodynamic definitions and derivations (see Chapter 12 and 13) are refined to improve their clarity. Our treatment of equilibrium (see Chapter 15) includes greater emphasis on qualitative reasoning and presents equilibrium constants as dimensionless numbers. In describing aqueous equilibria (see Chapter 16), we pay greater attention to the common ion effect and reduce the quantitative coverage of buffer capacity.

Mastering Chemistry

Success in general chemistry requires a blend of ingredients. It requires a clearly presented body of information; we hope you will find that in this textbook. It requires lucid instruction from a committed teacher; we hope that our text facilitates such instruction. Finally, success in chemistry requires commitment and hard work from the student. We have tried to structure the text so that it encourages this commitment and directs the work along productive lines.

Although no single formula is guaranteed to work for every type of student, there are strategies that successful students consistently recommend. Foremost among these is a focus on the understanding of concepts, because memorization without understanding leads to frustration, not to success. We explain principles using logical underpinnings that can make them easier to understand.

Much of chemistry is concerned with the applications of concepts to practical problems. Our text is laced with Sample Problems, Section Exercises, and Problems designed to help you learn such applications. Each Sample Problem includes a brief explanation of the method by which the problem should be approached. Then it provides a step-by-step description of the solution. Section Exercises appear at the end of each section and are designed to give you immediate practice in applying the concepts presented in the section. So that you can know whether you are reasoning correctly, we provide the answers to all Section Exercises at the end of each chapter.

At the end of each chapter, we provide material designed to engage you in active learning. For greatest effectiveness, use this material to guide the manner in which you study. A list of Key Terms flags the terms with which you must be familiar, and a Chapter Summary of key concepts provides a brief overview of the major themes of the chapter. Skills to Master reminds you what problem-solving techniques require your attention, and the Learning Exercises are qualitative questions designed to help you organize your ideas about the material in the chapter.

Proficiency in using chemical concepts comes only with practice. The Problems are designed to give you the opportunity for such practice. About half the Problems are identified by the section to which they relate. One of the skills of problem solving, however, is the ability to identify the concepts underlying the problem. For this reason, we have included many problems that are not identified by section. These problems, which appear as Additional Paired Problems and Additional Unpaired Problems, are not necessarily more difficult than those identified by section, but by placing them randomly, we give you the opportunity to learn how to recognize problem types.

Two axioms characterize successful students, in our experience. The first is an attitude: ***Be an active learner.*** *Ask* questions, *seek* help from many sources, *form* study groups, *work* extra problems, *prepare* chapter outlines. Try a combination of these and additional strategies until you find a set that works best for you. The second is a perspective: ***Think molecules.*** Every phenomenon in chemistry has an atomic/molecular basis that can make the phenomenon easier to understand. Ask yourself *what* the molecules are doing and *why.* Imagine yourself to be the size of a molecule and ask what you would see. Learn how to draw pictures showing what goes on at the molecular level. When you have mastered this perspective, you will have learned how to think like a chemist and will appreciate the unity of chemistry. You may even decide that you are a chemist.

Acknowledgments

A textbook in general chemistry does not just happen. It is painstakingly developed over several years. Moreover, it is a team effort that consumes the attention and talents of many individuals. The first edition of *Chemistry: The Molecular Science* came to fruition over a 5-year span, during which time many individuals made essential contributions. The revisions for the second edition required an equally intense cooperative effort over a much shorter time span.

Our textbook began with our interactions with several generations of general chemistry students with whom we had shared the frustrations of imperfect explanations and on whom we had tried out diverse methods of presenting elusive concepts. We were encouraged, time and again, by students asking us when our book would appear. We are grateful to them for serving as the educational laboratory in which we improved our instructional skills. Equally, we are grateful to users of the first edition who provided us with constructive comments to which we responded as we prepared the second edition.

Support and criticism from our talented editors shaped the scope, content, level, and language of our text throughout its development. Jim Smith, vice president and publisher, provided unerring guidance as the text moved from a proposal through initial drafts to published first edition. His guidance has been equally astute and invaluable during the preparation of the second edition. As revisions began on the second edition, Lloyd Black, executive editor, joined the editorial team and added his special talents to our efforts. John Murdzek, developmental editor for both editions, kept our attention on the important details, including accuracy, continuity, and relevance. Carol Sullivan Weis was the project manager and Pat Joiner was the production editor for both editions; they converted our manuscript into the book you now hold in your hands, and the beauty and readability of the page layouts are entirely due to their editing and production skills. Nancy McDonald, design manager, created a design for the second edition that enhances the text without overpowering its purpose, which is to help you learn chemistry.

Illustrations can powerfully assist learning, and we hope that the illustrations in this text make it easier for you to grasp chemical concepts. Several talented individuals are responsible for the quality of our illustrations. We are particularly indebted to Greg and Carolyn Duffy, who are ArtScribe, Inc., for creating elegant colored artwork from our crude black-and-white sketches. Donata Dettbarn, assistant editor, is responsible for many new photographs in the second edition. All the illustrations throughout the book have been immeasurably enhanced by John Murdzek's discerning eye and attention to detail.

Our writing has been tempered in the crucible of peer review and criticism. A legion of professors agreed to assist in this role, and they provided us with a wealth of insights that far surpassed our own. All of those in the list that follows contributed to our endeavor, but we wish particularly to thank first edition reviewers Alan Burkett, Donald Campbell, John Rund, Paul Hunter, Glenn Kuehn, and Larry Peck. These individuals reviewed our work repeatedly and in detail and always told us explicitly what they thought we were doing wrong while at the same time encouraging us to make things right.

Every student knows that writing is time intensive and that good writing requires focused concentration for blocks of time. In the regard, writing a textbook is no different from other writing. We owe an immense debt to those who permitted us to devote to this project the time required for its completion. Above all, we are indebted to our wives, Eileen and Trudy, who did not realize at the outset how extensive our time commitments would become but who remained supportive and understanding despite several years of long evenings and lost weekends. That they were willing to put up with more of the same during revisions for the second edition was more than we have any right to expect.

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