PRINCIPLES OF MODERN CHEMISTRY

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SAUNDERS GOLDEN SUNBURST SERIES
Saunders College Publishing
Philadelphia New York Chicago
San Francisco Montreal Toronto
London Sydney Tokyo Mexico City
Rio de Janeiro Madrid

Address orders to:
383 Madison Avenue
New York, NY 10017

Address editorial correspondence to:
West Washington Square
Philadelphia, PA 19105

Text Typeface: Times Roman
Compositor: Progressive Typographers, Inc.
Acquisitions Editor: John Vondeling
Project Editor: Sally Kusch
Copy Editor: Jay Freedman
Art Director: Carol Bleistine
Text Design: Edward A. Butler
Cover Design: Lawrence R. Didona
Text Artwork: Vantage Art
Production Manager: Tim Frelick
Assistant Production Manager: JoAnn Melody

Cover credit: Spectral light source. Don Carroll/The Image Bank

Library of Congress Cataloging-in-Publication Data

Oxtoby, David W.
Principles of modern chemistry.

(Saunders golden sunburst series)
Includes index.

1. Chemistry. I. Nachtrieb, Norman H. II. Title.
III. Series.
QD31.2.098 1985 540 85-14428

ISBN 0-03-070653-X

PRINCIPLES OF MODERN CHEMISTRY ISBN 0-03-070653-X

Library of Congress catalog card number 85-14428

6 32 98765432

CBS COLLEGE PUBLISHING
Saunders College Publishing
Holt, Rinehart and Winston
The Dryden Press

Preface

This is a general chemistry textbook that combines a full treatment of chemical principles with extensive emphasis on experimental and applied aspects of chemistry. Modern chemistry is a quantitative science, but "quantitative" does not necessarily mean "theoretical": we have based this text firmly in macroscopic experimental chemistry, and the mathematics that we introduce is guided throughout by chemical and physical principles. Chemistry comes to life through its applications to the real world. We hope to have conveyed some of the excitement of modern chemical research through this book.

ORGANIZATION

When we first conceived PRINCIPLES OF MODERN CHEMISTRY, our plan was to organize it in three parts. The first third of the book was to develop the vocabulary and a working knowledge of chemistry from a macroscopic, phenomenological point of view. The middle chapters were to seek an understanding of the causes of chemical behavior in terms of a microscopic, atomic and molecular, perspective. The balance of the book was to be an application of these principles to chemical processes we encounter in nature and in industry. We soon learned that chemistry is too vast and interconnected to lend itself to a hard and fast division of this sort, but the germ of this original plan is still discernible in the structure of the book.

The first two chapters are concerned with the principles of stoichiometry that grew out of the atomic theory of matter and with the vocabulary of chemistry. They may well serve as review for the student who has had a good chemistry course in high school, although we hope they may provide new insights. Chapters 3 through 10 develop chemistry from a largely macroscopic point of view, moving from a study of the states of matter (Chapters 3 and 4) to an examination of chemical equilibrium (Chapters 5 and 6) and its basis in thermodynamics (Chapters 7 and 8). This section closes with electrochemistry (Chapter 9) and chemical kinetics (Chapter 10). By emphasizing the macroscopic, experimental aspects of chemistry in these first chapters we hope to show that chemistry is not a series of theoretical models but is rather a discipline based on observations of the world around us, organized through the use of chemical principles.

The next five chapters have a different thrust. Their purpose is to search for an interpretation of the properties and chemical reactivity of substances at the atomic and molecular level. This section begins with elementary particles and nuclei (Chapter 11) and moves through atomic structure (Chapter 12) to an examination of chemical bonding (Chapter 13) and the properties of interacting atoms and molecules in liquids and solids (Chapters 14 and 15).

The last seven chapters then apply the principles developed earlier in the book to the chemistry of the periodic table. They reflect our conviction that descriptive chemistry is best taught not as a series of facts to be memorized but as an illustration of the general microscopic and macroscopic principles that underlie chemistry. We have therefore based these chapters not on a routine enumeration of the elements in each group of the periodic table, but rather in broader classes moving from the most electropositive to the most electronegative, giving greater emphasis to the more important elements. The heart of these chapters is the problems, which allow students to review, extend, and apply the principles developed earlier in the book.

TEACHING OPTIONS

While we chose the organization outlined above for what we feel are good pedagogical reasons, we recognize that other instructors may prefer to introduce topics in somewhat different sequences, and we have written the text to permit this kind of flexibility. For example, some instructors may choose to cover the material on atomic structure and chemical bonding earlier in their course. In this case, they can move directly to Section 11 – 1 and Chapters 12 through 15 after Chapter 6, or even after Chapter 2. Certain topics may be omitted without loss of continuity. For example, a principles-oriented course might cover the first 15 chapters thoroughly and then select only two or three of the last chapters for close attention, while a course with a more descriptive orientation might omit the Optional Topics and cover the last seven chapters more systematically. Further suggestions for ways of using this book in courses with different plans of organization are given in the Instructor's Manual.

MATHEMATICAL LEVEL

This book presupposes a solid high school background in algebra and coordinate geometry. We introduce the concepts of slope and area in the physical and chemical contexts in which they arise, and we use differential and integral notation only where necessary. The book is designed to be fully self-contained in its use of mathematical methods. In this context, Appendix C should prove particularly useful to the student and the instructor.

Key equations in the text are indicated by boldface numbers, and practice should be gained in using them for chemical calculations. Other equations, such as intermediate steps in mathematical derivations, are less central to the overall line of reasoning in the book.

WORKED EXAMPLES

This textbook includes worked examples, which help to show the methods of reasoning applied in solving chemical problems. The examples are inserted immediately after the corresponding principles have been presented, and in many cases can serve as models for working problems at the end of the chapter. Careful attention is given in the examples to the proper use of units and of significant figures and scientific notation.

KEY TERMS

Key terms appear in boldface where they are first introduced. In addition, definitions for most key terms are included in the Glossary for ready reference, with a notation of the section in which the term first appeared.

OPTIONAL TOPICS

A number of optional topics are indicated by boxed sections in the text. These are more advanced mathematically than the main part of the book, and can be omitted without loss of continuity. Their use allows the instructor considerable flexibility in the level of the course material taught.

CONCEPTS AND SKILLS

Each chapter concludes with a list of Concepts and Skills for review by the student. Included in this list are references back to the section in which the topic was covered, and forward to problems that help to test mastery of the particular skill involved. This feature is helpful for self-testing and review of material.

PROBLEMS

Problems are grouped into paired and unpaired categories. Answers to odd-numbered paired problems are collected at the end of the book, and permit the student to check the answer to the first problem in a pair before undertaking the second problem which is parallel to it. The unpaired problems provide further applications of the principles developed in the chapter. We have indicated the more challenging problems with a bullet (•).

APPENDICES

Appendices A, B, and C are important pedogogically. Appendix A discusses experimental error and scientific notation, while Appendix B introduces the SI system of units used throughout the book and describes the methods used for converting units. Appendix C provides a review of mathematics for general chemistry. Appendices D, E, and F are compilations of thermodynamic, electrochemical, and physical data, respectively. Students gain experience in using them through many of the problems in the book.

ANCILLARIES

Study and Problem-Solving Guide. The best way to master physical and chemical concepts is to solve problems; even students with outstanding mathematical skills can encounter difficulties with chemistry problems. Trouble usually arises in the conversion from the words of the problem through formal statements of concepts to manipulable mathematical equations. The *Study and Problem-Solving Guide* by Wade A. Freeman of the University of Illinois at Chicago helps students meet such difficulties head-on. It summarizes definitions, concepts, and equations, gives some additional insights into the material presented in the text, provides problem-solving hints, and, as a practical illustration, presents detailed solutions to all the odd-numbered problems in this book. We strongly recommend that each student purchase a copy of this book.

Instructor's Manual. The Instructor's Manual contains solutions to even-numbered problems as well as suggestions for ways to use this book in courses with different plans of organization.

ACKNOWLEDGMENTS

We gratefully acknowledge the many helpful suggestions given us by our colleagues at the University of Chicago, especially Edward Anders, R. Stephen Berry, Jeremy Burdett, Philip Eaton, John Light, Leon Stock, Nathan Sugarman, and Anthony Turkevich. Thanks are also due to our students, who used earlier versions of this textbook and whose questions and comments have helped to improve the final product.

We have benefitted immensely from the thoughtful reviews provided to us by instructors at other colleges and universities. These include:

Mario Baur, UCLA

Francis Bonner, SUNY at Stony Brook

Lewis Brubacher, University of Waterloo

John DeKorte, Northern Arizona University

Leonard Fine, Columbia University

Wade Freeman, University of Illinois at Chicago

Robert Gavin, Macalester College

Graham Glass, Rice University

Anthony Haymet, University of California at Berkeley

Donald Jicha, University of North Carolina at Chapel Hill

William Masterton, University of Connecticut

Leonard Nash, Harvard University

Malcolm Nicol, UCLA

Ronald Ragsdale, University of Utah

Maurice Schwartz, Notre Dame University

Robert Sharp, University of Michigan
Conrad Stanitski, Randolph Macon College
J. C. Thompson, University of Toronto
Thomas Weaver, Northwestern University
Robert Yaris, Washington University

We would like in particular to acknowledge a debt to Eugene Rochow, who kept us on our toes both in our coverage of chemistry and in our use of the English language.

The staff at Saunders College Publishing has been extremely helpful and supportive through the entire process. In particular, we would like to single out Sally Kusch for her careful attention to detail in the production process, Jay Freedman for his expert work as developmental and copy editor, Margaret Mary Kerrigan for her counsel and sound advice, and above all, our editor, associate publisher John Vondeling, for his many suggestions and continuing support.

We would like to thank Eunice Phyfiher for her careful and cheerful typing and retyping of several versions of the manuscript, and Harriet Pearl for her help in typing the problems. Finally, we wish to acknowledge our deep gratitude to our wives for their understanding, encouragement, and support during the many evenings and weekends required for the completion of this project.

David W. Oxtoby
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"The search for truth is in one way hard and in another easy, for it is evident that no one can master it fully or miss it completely. But each adds a little to our knowledge of nature, and from all the facts assembled there arises a certain grandeur."

(Greek inscription, taken from Aristotle, on the facade of the National Academy of Sciences building in Washington, D.C.)

Contents Overview

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* Optional Topics

1 Stoichiometry and the Atomic Theory of Matter

1-1 CHEMISTRY AND THE NATURAL SCIENCES

What is chemistry? We can define it as the study of the properties of substances and of the reactions that transform them into other substances. But these are just words, words that fail to convey the range of problems studied by chemists and the excitement of the quest for knowledge in the field we call chemistry. An understanding of what chemistry is can only be gained by doing it: by carrying out chemical experiments in the laboratory and by applying the principles of chemistry to explain observations and make predictions. The discoveries that are made and the insights that are gained will begin to open up new and exciting vistas, and in turn will suggest further questions to be asked and challenges to be met.

If an eighteenth-century chemist were brought into a modern chemical laboratory, there are many things that he would recognize. Beakers and test tubes are still very much a part of the modern chemist's laboratory apparatus, and chemists continue to mix substances and watch the reactions that result. But the sophistication of the methods available for examining substances and reactions has increased dramatically, and more detailed and more fundamental questions can now be posed and answered. Many aspects of a modern chemical laboratory would be unfamiliar not only to an eighteenth-century chemist but even to one from the first part of the twentieth century.

One tool used in modern chemical research, for example, is the molecular beam spectrometer. This is a large piece of equipment in which two beams of atoms or molecules are prepared with well defined speeds and internal motions. The particles are allowed to collide, and the products are analyzed. Lasers, powerful and versatile sources of light, can be used to prepare the molecular beams going in and to analyze the product molecules coming out, with the whole experiment controlled by a small computer that has been programmed to analyze the results in terms of the forces between atoms and molecules. Such an experiment certainly fits into the tradition of classical chemistry (mixing chemicals and observing reactions), but it is a long way from the simple beaker-and-test-tube operations of the past.

In another laboratory, a chemist may be analyzing a product made by a small marine organism for use as a possible anti-cancer agent. The first step is to extract the product by adding a chemical solvent. The problem is then to separate the substance of interest from others that are present. In the past a lengthy series of mechanical separations using different solvents, or a series of distillations, might have been necessary. Now, a chemist may simply inject the mixture into a device called a gas chromatograph and obtain the separated fractions at the other end. The fraction of interest can then be analyzed using its light absorption properties to determine its molecular structure, and the chemist may then develop and test a procedure to synthesize the same product from commonly occurring substances.

These are just two examples of the type of research that modern chemists do; many more examples could be given. A common feature of twentieth-century natural science is that the traditional "compartments" used to identify scientific fields (physics, astronomy, chemistry, geology, biology) are no longer capable of holding separately all of modern scientific research. Instead, nature keeps spilling out of the various compartments into which we try to force it, and interdisciplinary research is necessary (see Fig. 1–1). Some of the most exciting areas of modern science lie at the interface between two fields that once were considered to be essentially distinct.

Chemistry is no exception in this regard. Because it occupies a central role in the natural sciences, its overlap with other fields provides a fruitful source for new discoveries. For example, both chemistry and physics gain from each other: chemistry advances through an incorporation of physical laws and techniques, while physics is enriched through the discovery by chemists of new substances with interesting physical properties. Astronomers now use results from chemical laboratories to search for new compounds in distant galaxies, and from them to learn about the origins of the universe. Geologists analyze the structures of minerals and the transformations between different forms of matter in the earth's crust by using principles from chemical bonding and chemical thermodynamics. Biologists in recent years have turned increasingly toward a detailed study of the chemical basis for life processes. These contacts between chemistry and other fields are by no means peripheral. Indeed, they form the basis and impetus for much modern chemical research.

The Methods of Science

Progress in chemistry, and indeed in all of the sciences, occurs through a balance between two complementary aspects: **theory** (predictions and conclusions) and **experiment** (discovery of facts). There are periods in the development of science when one may lag behind the other, but when the gap becomes too great, scientific progress slows down.

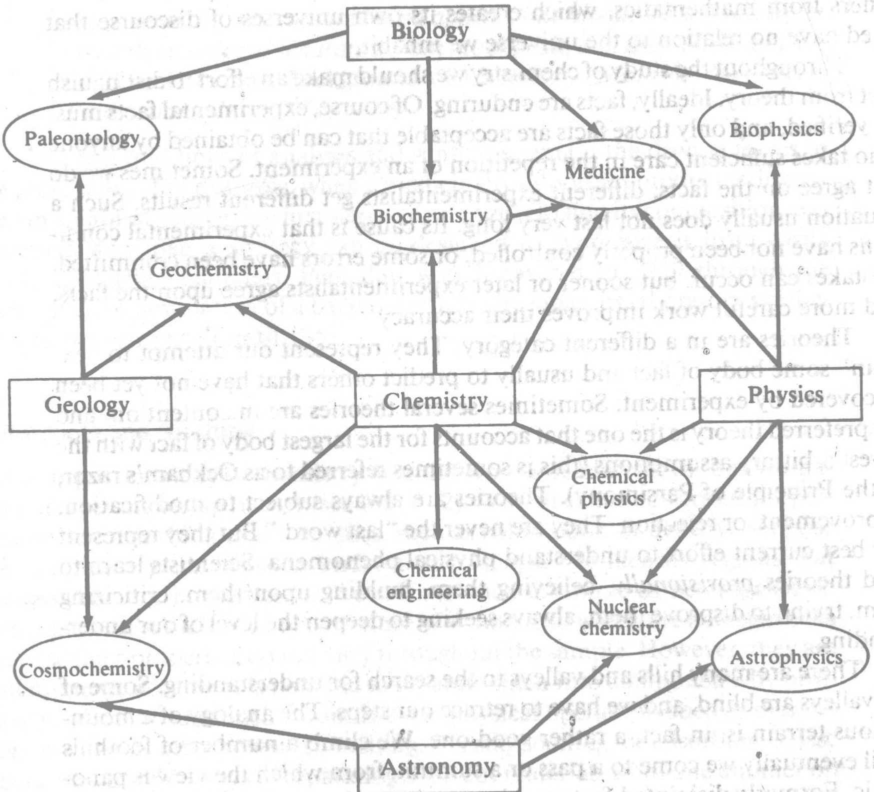

FIGURE 1-1 Interrelations among the natural sciences.

Experimentation without the guidance of theory (or hypothesis or "hunch") does not proceed very far. Because innumerable experiments can be performed, the problem for the scientist is to choose which experiments are important, and then to carry them out in a carefully controlled fashion. Asking intelligent questions of nature is essentially what experiment is about. Sometimes the answers that come back fit in with other pieces of information and a correlation emerges, suggesting in turn further questions (experiments). Other times an apparent contradiction appears, and additional experiments are needed before a more comprehensive picture emerges.

Just as experiment requires guidance from theory, so theories need to be tested constantly against the real world of nature; the ultimate test of every theory is that it must agree with experiment. Predictions of Albert Einstein's general theory of relativity, for example, continue to be verified many years after they were first made. On the other hand, his efforts during the last years of his life to develop a generalized field theory that would encompass all known interactions of matter did not succeed. The physicist Enrico Fermi said of Einstein's effort, "Beautiful theory, wrong universe." In this sense science