contemporary chemistry

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W. H. FREEMAN AND COMPANY
San Francisco

Frontispiece courtesy of Professor Ignacio Tinoco, Department of Chemistry, University of California, Berkeley. See p. 326 for an explanation of the presence of the cloud at the Matterhorn's peak.

Library of Congress Cataloging in Publication Data

Hearst, John E. 1935–
Contemporary chemistry.

Bibliography: p.
Includes index.
1. Chemistry. I. Ifft, James B., 1935– joint author. II. Title.
QD31.2.H4 540 75-28230
ISBN 0-7167-0172-3

Printed in the United States of America

9 8 7 6 5 4 3 2 1

preface

This is a textbook for an introductory, one-year college or university chemistry course. It is designed to accompany 60 to 80 one-hour lectures. The student is expected to have taken high-school algebra, geometry, trigonometry, and chemistry.

We wrote the book because of the widespread opinion that most high-quality chemistry textbooks are written by professional chemists for future professional chemists, whereas most students enrolled in elementary college chemistry courses are premedical students and life-science majors. This book is therefore directed more to the needs of these students, without compromising the principles that must be a part of every good, basic chemistry course. We have done this primarily by using examples from organic chemistry and biochemistry and eliminating most of the descriptive inorganic chemistry found in many introductory texts. We feel that descriptive chemistry is best learned in the laboratory with the chemicals in one's hands, and not just from the printed page. Extensive tables of data are presented in both the text and the appendixes to further acquaint the student with this subject. In addition, references are given to other sources of information.

We believe that the material in this book is suitable for all science majors. We also believe that the order of presentation of the material is superior to the more common chronological order. The book begins with atoms and ends with the genetic code.

We are pleased to express our appreciation to our friend and expert typist, Eleanor Scott, for her skill and patience in typing the several drafts of our manuscript.

October 1975

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1 introduction

This chapter is about science, particularly the science of chemistry – what it is, how it is practiced, and what it is "good for." Perhaps this material will help you formulate some questions for yourself about the nature of chemistry and why anyone should bother studying it. We hope you will be encouraged to seek the answers. Although we may never get to know you personally, we already know something about each other: you are beginning a course in chemistry and we have written a textbook about chemistry. Why are you taking chemistry? And why have we written this book? At least it can be said that we all have an interest in, a need for, or possibly an amazement at the subject of chemistry. Although we cannot get to know each other well through the pages of a book, we hope that, by reading this book, you will be able to learn something about us and why we are interested in chemistry.

1.1 WHAT IS CHEMISTRY?

Since the beginnings of history, science has been studied and practiced by only a small portion of humanity. The knowledge obtained by the practice of science has, however, played a dominant role in the history of civilization. The first "chemists" lived in the Stone Age and discovered how to control fire, then start it at will. To the Stone Age man, wood was changed to heat by fire. With the control of heat came the beginnings of the common chemistry of daily life, such as cooking, which altered the taste, color, and texture of food. The heating of clay made the production of bricks and pottery possible. The heating of the mineral kaolinite produced glazes and the heating of sand produced glass.

As early as 4000 B.C., man discovered that heating certain blue rocks produced droplets of copper. Thus began the science of metallurgy, which ushered in the Bronze Age and Iron Age. We see early in recorded history that those who made systematic observations of matter, its properties, and the changes it undergoes contributed enormously to the culture of man. The metal frying pan doubtless came into being simultaneously with metal spear heads and swords. Science served man's comfort and fostered his self-destruction. The amoral character of technical knowledge became apparent.

The origin of the word *chemistry* is obscure, but it comes to us via the Greek word *chēmeia*, meaning "the art of metalworking." In 900 B.C. the Egyptians were knowledgeable in metallurgy, in the production of pigments from minerals, and in the extraction of juices from plants. *Chēmeia* may be derived from the word *Kham*, the Egyptians' name for their land. It has also been suggested that *chēmeia* derives from the Greek word *chymos*, meaning "the juice of a plant," or from the Cantonese word *kem-mai*, meaning "gone astray in search of gold."

For those of us "going astray" today, chemistry is the observation and description of matter, its properties, and the changes it undergoes. Our knowledge is still amoral and is, unfortunately, still limited to a small portion of humanity. It remains a dominant influence upon human endeavors, however, and the quality of its use will ultimately determine how long the human race will survive on Mother Earth.

1.2 THE ADVANTAGES OF IGNORING HISTORY

People have been posing chemical questions—and answering some of them—for a very long time. In 2500 B.C. the Chinese postulated, in the *Shu-ching*, the Canonical Book of Records, that there were five elements. Progress in understanding matter was painfully slow from that time until about two centuries ago, when scientific knowledge began its present period of explosive growth.

The question raised by these thoughts is whether or not the arrangement of a general chemistry textbook should reflect the historical development of the subject. Apparently, many authors believe that it should. Most textbooks begin with a discussion of gases – one of the first areas of science to be treated quantitatively – and end with the most recent concepts in nuclear chemistry.

If you turn to the outline of this book, you will find a rather different approach. Our sequence of topics does not correspond to the historical development of science in general or chemistry in particular. We are not antihistory – not at all! The study of history provides invaluable insights into the development of man's understanding of everything that he has thought and written about: economics, government, philosophy, as well as science. However, two factors deter us from the historical approach. First, the progress of science has often been confusing at its best and illogical at its worst. To follow the actual, chronological progress of chemistry is an exercise in frustration. Second, we are writing a book about science, not the history of science. Many books have been written about the history of science and numerous courses in this fascinating field are available at our major universities. We encourage your pursuit of these studies as a supplement to the material presented here.

If we have rejected the traditional, historical approach to the presentation of general chemistry, what approach *have* we taken? One of our goals is that you learn enough basic chemistry from the earlier portions of this book to be able to understand some of the elementary aspects of molecular biology (that branch of biology in which the structure and development of biological systems are analyzed in terms of the physics and chemistry of their molecular constituents). The book builds up to and concludes with a discussion of the structure of proteins and nucleic acids and a description of the genetic code.

In order to achieve this goal, an elementary understanding of a number of areas of physical chemistry, such as thermodynamics, kinetics, and oxidation-reduction, is necessary. It is difficult to understand the structure and properties of a gigantic molecule without first understanding the structure and properties of the smallest molecules. It is impossible to understand a molecule without understanding the bonds that hold atoms together in a molecule. And finally, one cannot comprehend bonds between atoms without some appreciation of what atoms are really like.

And so our book begins – with atoms. The description of the atom is elementary but modern. Chapter 2 presents an introduction to the properties of waves and the associated concept of quantum states. In this way a rationale for atomic structure is provided. Chapter 3 presents a survey of some of the physical and chemical properties of the elements, as correlated by the periodic table of the elements. We believe that most of you are more interested in the biological implications of chemistry than in the descriptive inorganic chemistry that constitutes a large part of many general chemistry texts. Although the emphasis in this book is decidedly on such biological implications, Chapter 3 does give a brief introduction to the properties of inorganic compounds. If you wish to pursue inorganic chemistry further (and you should!), we refer you to such works as E. S. Gould's *Inorganic Reactions and Structure,* revised ed. (Holt, Rinehart and Winston, New York, 1962), R. T. Sanderson's *Inorganic Chemistry* (Reinhold, New York, 1967), or the monumental series by J. W. Mellor and G. D. Parkes, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Wiley, New York, 1922–), to which new volumes are added periodically.

Chapters 4 and 5 describe the bonds that hold atoms together to form molecules, and molecules to form liquids and solids. These intramolecular and intermolecular forces are very close to the heart of much of modern scientific research. Several theories of bond formation are included in Chapter 4, along with information about which theory does the better job of predicting bond energies or molecular geometries in various instances. A number of modern experimental techniques that are useful in the study of the properties of molecules are included in Chapter 5.

The chapter on the states of matter describes the properties of large collections of atoms or molecules in the gaseous, liquid, and solid states. It begins with the best understood state of matter, the gaseous, and presents and compares two descriptions, the experimental and the theoretical. Quantitative relations for the liquid and solid states are much more difficult to derive and understand, so the descriptions of these states are more qualitative.

Chapters 7 and 8 present introductions to two very important branches of physical chemistry, namely, thermodynamics and kinetics. These chapters are necessarily more mathematical than any others in the book. If this is a problem for you, we recommend that you spend extra time trying to understand the underlying concepts of these two disciplines rather than memorizing formulas. The *best* way to gain understanding is to practice solving problems, and then practice some more. After all, solving problems in order to understand nature is what science is all about.

The chapter on chemical equilibrium is one of the longest in the book. Many things chemists do concern systems at equilibrium; hence there is much information to assimilate. The mathematical level seldom ranges beyond algebra here. As is always true, an understanding of the underlying principles should be the primary goal of your study. So—solve problems! The chapter on oxidation-reduction reactions is concise, but it explains the methods for calculating electrochemical potentials of galvanic and electrolytic cells and the use of such potentials in determining equilibrium constants. The chapter ends with a description of the electrochemical processes in living cells.

The book concludes with an extensive discussion of biological molecules, both small and large. This chapter represents the climax of a year's study, in that nearly all the principles learned are applied in the description of the chemistry of life. The amino acid side chains are classified according to their acidity and polarity. The structures of monosaccharides and nucleotides are presented. The relation between molecular structure and optical properties, first introduced in Chapter 5, is a recurrent theme throughout Chapter 11. Polymerization and some general properties of polymers are then discussed, culminating in a description of the biopolymers: proteins, polysaccharides, and nucleic acids. The chapter concludes with a brief illustration of the central dogma of molecular biology, or molecular genetics. The final objective of the book is thus an explanation in molecular terms of the essential features of all life as we know it. It describes the molecular mechanism for the propagation and transfer of biological information.

1.3 THE SCIENTIFIC METHOD

What do you do when you are confronted with a refrigerator that doesn't work, a zipper that's stuck, or a jib sail that can't be raised? If you can stifle your anger or impatience for a few minutes, think about the probable source of the problem, postulate how the problem might be solved, and then try your solution, your life becomes somewhat less frustrating than it might otherwise be.

These are precisely the skills that the scientist must develop. If we replace the concept of a problem with the concept of a question, we have the first step in a scientific inquiry. A broken appliance is an obvious problem. "How can it be repaired?" is the obvious question. In scientific research it is easy to think of questions, but not all questions are likely to lead to productive lines of investigation. The formulation of a *good* question by a scientist is far more difficult. It requires a disciplined and highly trained mind as well as the crucial ingredient of curiosity. If people were not really interested in why nature behaves as it does, they would ask no questions and there would be no science.

Once a question is formulated, thereby defining a scientific problem, an experiment or set of experiments must be devised to provide data that will have a direct bearing on the question. Depending on the results of the initial experiments, further experiments may be indicated. If the question was perceived with sufficient insight and the initial experiments carried out with sufficient ingenuity and precision, the investigator may be able to proceed directly to the next step, which is the formulation of a hypothesis to explain his results, i.e., answer the question he originally asked. He can then devise further experiments to test this hypothesis and, if it seems valid, use it to provoke new, more sophisticated questions so that the cycle can start again.

Scientists seldom work within such a rigid framework of inquiry. The problems they work on are infinitely varied, and the kinds of insight and approach they use on these problems are often utterly different and highly personal in style. In one form or another, however, the elements of the scientific method described above enter every investigation.

1.4 WHY STUDY CHEMISTRY?

From our experience with several thousand students over the past decade, there are a number of answers to this question. Some of them are not very good: "Most people seem to take it," "My girlfriend is in the class," or "It's considered a snap course." Other answers are at least practical: "I've got to have it to get into medical school," "My engineering major requires it," or "I want to be a patent lawyer for a chemical company." The first group of students could benefit from some alternative answers, and the second group could also. In addition, there is a third group. These are the students who do not really know what chemistry is or what it is good for, but may suspect it has something to do with many of society's problems (e.g., problems of health, the environment, energy resources, and economics), and would like to find out. We are particularly interested in these students.

One reason for studying chemistry has already been provided in the preceding section: it gives experience in using the scientific method in solving problems or answering questions. This should considerably strengthen your ability to think carefully and analytically about the many problems you face daily.

If you are at all curious about why things behave as they do, you have undoubtedly asked many questions about the world around you. The course of study you are about to begin will provide some immediate answers and enough background information that you can begin digging out other answers for yourself. Some questions you will soon be able to answer are: Why does a cake rise? Why is blood red and grass green? What is smog? Why can I see better several minutes after entering a dark room? How do those glasses that become darker in the sunlight work? Why do children tend to look like their parents? How does antifreeze keep a car radiator from freezing? How do you make wine? Why does a warm bottle of cola froth when it is opened? And on and on.

A third and very important reason for studying chemistry has to do with the quality of the environment in which you will spend the next half-century. Mercury poisoning, smog, overpopulation, water pollution, lead contamination, DDT, food shortages, radioactive wastes, thermal pollution. If you have read a newsmagazine or a newspaper or talked with a friend during the past year, you have undoubtedly heard of all these problems, and many more. Who is going to solve them?

Chemists will certainly not do it alone. These are extremely complex problems that will require the coordinated efforts of governmental agencies, scientists, engineers, sociologists, economists, etc. But the chemist will certainly play a major role because most of these problems are, at least in part, chemical. Smog consists of a variety of gaseous compounds and particulate matter generated in large part by the internal combustion engine. Chemists are playing a major role in identifying the components of smog, studying the microscopic atmospheric particles on which many chemical reactions occur, and working with automotive engineers to design cleaner-burning engines.

DDT is a chemical. It has virtually destroyed the osprey population of Long Island, found its way into the penguins of Antarctica, even though it has never been sprayed there, and accumulated sufficiently in the fat of some fish that they are unfit for humans to eat. Chemists made DDT; they must now make a safe substitute.

Mercury poisoning has eliminated the West Coast swordfish fleet. The reality of mercury poisoning has been demonstrated by the death and grotesque deformation of many of the residents of the tragic town of Minamata, Japan. A chemical plant discharged mercury into the bay, where it entered the fish that were caught by local fishermen and eaten by the townspeople. Chemists must find substitutes for certain mercury compounds and advise legislators how to prevent the further release of mercury into the environment.

To increase your interest in chemistry and keep you conscious of the relations between your studies and the world around you, we have included an *Interlude* at the end of each chapter except this one. Each Interlude is related to the chemistry you have learned from the preceding chapter. The Interludes may be divided into three classes. Four come under the heading of Ecology; they deal with resources and pollution, smog, energy sources for society, and the supersonic transport. Three we classify as Biology; they describe the chemical bases for smell and night vision and the scientific aspects of winemaking. The remaining three pertain to Technology, as represented by transistors, water softening, and fuel cells.

Many more Interludes could be written. We hope that the ones in this book will stimulate your desire to find out more about the role of chemistry in human endeavors, and that some of them will demonstrate to you that, in order for society to deal intelligently with many of its problems, we, the people, need as much technical knowledge as we can get. Furthermore, we need professional chemists who are willing to devote their time and energy to help clean up our befouled environment and keep it clean, and provide us with better health and a better understanding of what we are.

2 the fundamental properties of matter

2.1 THE ATOMIC HYPOTHESIS

The hypothesis that all matter consists of atoms is central to a modern scientific description of matter. For reasons that will become apparent throughout this book, the evidence in favor of this hypothesis is overwhelming. It is also very recent (less than two centuries old), considering that the atomic hypothesis was first propounded by the Greek philosopher Demokritos about 2400 years ago.

If we could magnify a drop of water about 50 million times, we would see clusters of three atoms in constant, rapid motion. Figure 2-1 is a two-dimensional representation of what magnified water might look like. Each group of three atoms is called a *molecule*. We will discuss the definition of a molecule in more detail later, but for now, a molecule can be thought of as a discrete group of atoms having a fixed, unvarying composition.

There are several noteworthy features of Figure 2-1. Not all atoms are the same size. There are, in fact, 105 known kinds of atoms having distinct values of physical properties such as radius and mass. Furthermore, the clusters of atoms (molecules) have a definite geometry. Each of the larger atoms (oxygen) has two smaller atoms (hydrogen) connected to it. The angle between the two center lines from hydrogen atom to oxygen atom is 104.5° and the distance between the center of each hydrogen and the center