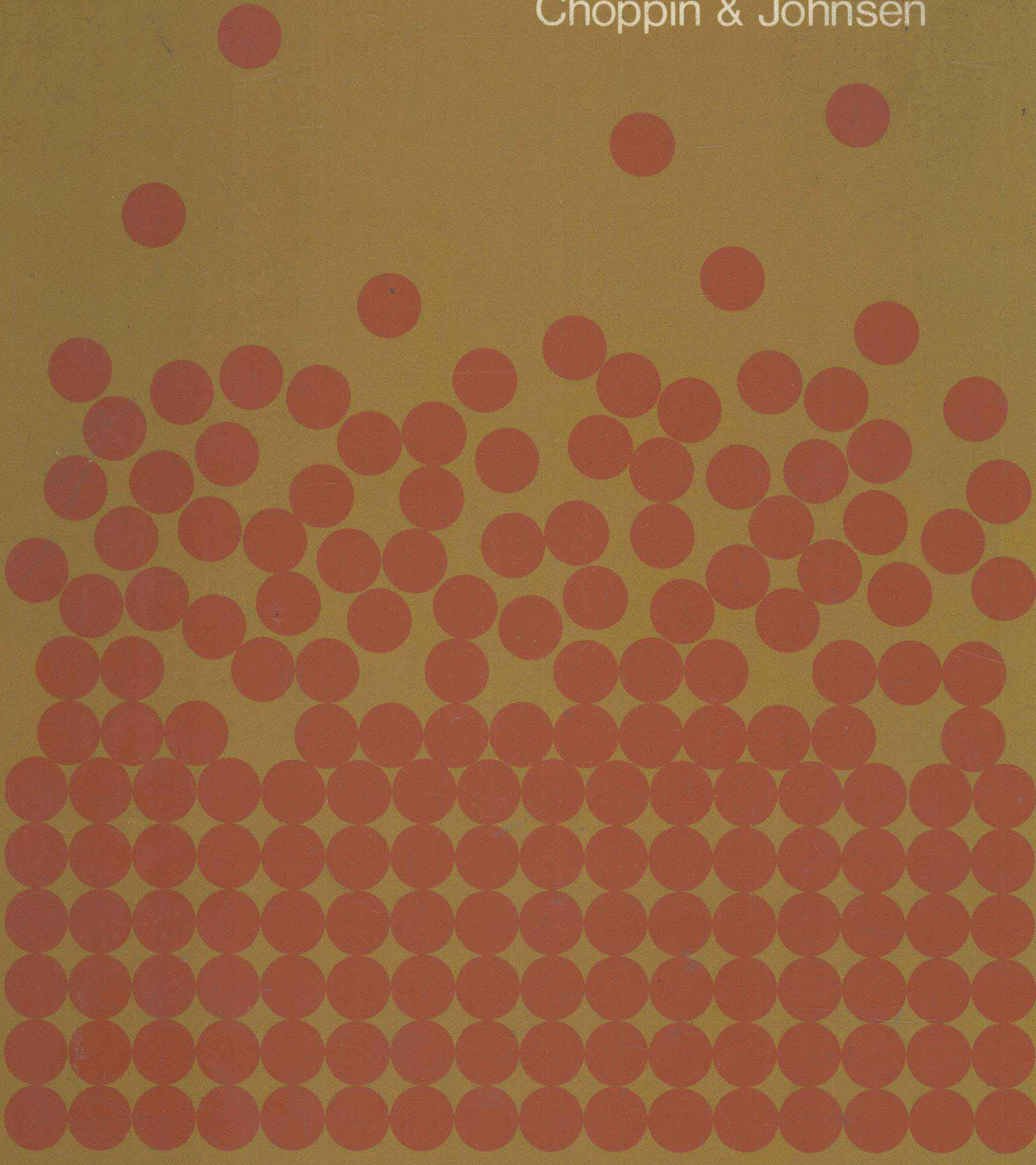
Introductory Chemistry

Choppin & Johnsen



INTRODUCTORY CHEMISTRY

GREGORY R. CHOPPIN
RUSSELL H. JOHNSEN
Florida State University

ADDISON-WESLEY PUBLISHING COMPANY, INC.
Reading, Massachusetts
Menlo Park, California • London • Don Mills, Ontario

This book is in the
ADDISON-WESLEY SERIES IN CHEMISTRY

Francis T. Bonner
Consulting Editor

 Printed in the United States of America. Published simultaneously in Canada. Library of Congress Catalog Card No. 77-140838.

INTRODUCTORY CHEMISTRY

PREFACE

In a period of growing chemical sophistication, it becomes increasingly difficult for the author and the teacher to make valid decisions concerning both the content and level of an introductory course in chemistry. On the one hand, we must give the student an introduction to our best and most useful ideas about the science of chemistry, and on the other hand we recognize that chemistry has become a very complex subject requiring a fairly high level of mathematical sophistication for complete understanding. Thus, to provide an appropriate introduction, one must tread a narrow line between comprehensibility and obscurity, keeping always in mind both the talents and limitations of the student.

We have tried to locate that thin line, and to meet the needs of the many students who need a reasonably sophisticated course in chemistry as a part of their professional training, but who do not bring to this course an extensive background of preparatory courses in science and mathematics. Thus we have dealt with the modern theories of chemical structure and reactivity, but usually on a descriptive, qualitative level. Atomic structure and molecular bonding are considered in terms of the quantum theory; the structure of metals is dealt with using the band theory as an extension of molecular orbital theory, while the properties of coordination complexes are handled in terms of ligand-field theory—but always without resorting to the mathematical trappings which most beginning students find so frustrating. We believe that the rigorous, exact treatment of these subjects can be left to later courses if the student is continuing in chemistry—or are not necessary if the student terminates his study of chemistry at this level.

We have given more consideration to the structure of chemistry and the interplay between experiment and theory, as well as the increasingly important role chemistry plays in the peripheral sciences. For example, organic chemistry and biochemistry are dealt with *not* by giving the usual systematic catalog of molecules and reactions, but instead by singling out and discussing in some depth a single topic: the origin of life. The unifying thread of the history of the development of chemical ideas replaces that of mathematical unity, which is often little appreciated by the beginning student.

Other topics are dealt with in more depth than is found in the typical introductory text. For example, we include a chapter on chemical dynamics and the theory of reaction rates; a chapter on the determination of physical properties, including microwave spectroscopy, nuclear magnetic resonance, and mass spectrometry; and a chapter on high-energy chemistry, which includes a discussion of the chemical effects of ionizing radiation and photochemistry as they relate to problems of environmental radiation hazards and atmospheric pollution.

Throughout the book we have tried to relate chemical knowledge and practice to contemporary social problems. However, this is *not* a book on the social implications of chemistry.

We realize that not all teachers will find the order of presentation or even the inclusion of all topics herein the most suitable for their purpose. Therefore, in writing this text, we planned it so that after the first 17 chapters the material is relatively independent of any set order, and the instructor can choose materials to suit his own individual needs.

Tallahassee, Florida G.R.C.
November 1971 R.H.J.

CONTENTS

1 The Scope of Modern Chemistry

2 Origins of the Atomic Theory

3 Chemical Reactions and Chemical Calculations

4 The States of Matter

5 Inside the Atom

6 Chemical Elements and the Periodic Law

7 The Quantum-Mechanical Model of the Hydrogen atom

8 Atoms More Complex than Hydrogen

14 Ionic Solutions

15 Molecular Orbital Theory

16 Structure and Bonding in Polyatomic Molecules

17 Carbon: The Stuff of Life

18 The Dynamics of Chemical Reactions

THE SCOPE OF MODERN CHEMISTRY

1

THE ORIGINS AND FUTURE OF CHEMISTRY

Chemistry has its remotest origins in the universal desire—which dates back to the dawn of civilization—to understand our environment. In the millennia that preceded the Christian era, there were no serious attempts to establish different branches of science; the problem of the physical world was viewed as a whole. Alchemy emerged as a separate field of study, combining practical chemical knowledge, derived from the practitioners of metallurgy, pottery, glass-making, etc., with speculative philosophies of the Greeks in the first century of the Christian period. It flourished well into the seventeenth century, although it became more and more the tool of the charlatan. Parallel to the alchemists' attempts to transmute metals, produce the philosopher's stone and the elixir of life, several important practical techniques were developed. For example, to a culture forced to make do with wine and beer, the technique of distillation brought such *aquae ardens* (strong waters) as brandy and whiskey, with their much higher alcohol contents.

Prior to the nineteenth century, science was practiced as an intellectual hobby and the great scientists earned their living in other ways, as doctors, clergymen, politicians. For example, it may be argued that Antoine Lavoisier initiated the age of modern chemistry when he explained the true nature of combustion and made clear the value of quantitative experimentation. Yet he earned his living by working in the tax-collection system of the French government under Louis XVI and, because of this association, was guillotined during the Reign of Terror in France.

With the introduction of the inductive, experimental approach, the body of scientific knowledge grew rapidly and scientists ceased attempting to learn the whole of science. Science became fragmented into many areas such as physics, chemistry, biology, and geology. This splintering continues with the establishment of newer disciplines; for example, meteorology and oceanography. However, a strong countercurrent of reintegration of the scientific body is also at work, and much exciting research is being done in areas covering several disciplines. Names like chemical physics and biochemistry illustrate the operation of this process of reestablishing the unity of science.

In this book, then, our primary interest is with this scientific discipline known as chemistry. We shall trace certain of the events which, beginning with the birth of modern chemistry in the middle of the eighteenth century, have led to our present knowledge. We shall see how chemistry emerged during the last two centuries as an extremely powerful tool for the understanding of the complex properties of matter.

As we begin this study, it is useful to define what chemistry is. As the breadth of man's study and the depth of his comprehension of nature increase, it becomes ever more difficult to define with any precision the province of any discipline of science. Nevertheless, some definition, however imperfect, can be valuable as a guide in the study of chemistry, and we might hope that chemists at least could agree on what chemistry is. In fact, that agreement, perhaps, provides the only good definition of chemistry: It is *what chemists do*. Thus the best way to describe the field of chemistry may be to consider the problems with which chemists are concerned. Some of these problems have been solved, some are near solution, and others continue to be sources of bafflement and fascination that keep new generations of chemists enmeshed in the search for understanding. Moreover, in science, there seems to operate a principle of continuous renewal, since the solution of any problem creates new problems to be solved in turn.

What the future of chemistry will be is not clear at this time, although there are abundant signs that a wide variety of new fields—in which chemistry merges with biology, neurology, and physics—are emerging. Within chemistry itself the trend seems to be toward studies of the properties of individual molecules rather than studies of very large numbers of molecules which can be treated only in terms of averages. Throughout this book we hope to point the way toward these new horizons as they appear to us.

BASIC PROBLEMS OF CHEMISTRY

Chemistry must be studied both as a basic science and as a technology. In the first instance, the concern is the search for a basic understanding of nature; the compulsion to study it derives from the deep thirst in man to use his intellect and imagination to increase his knowledge. Technology, by contrast, seeks to solve practical problems so that the quality of life may be enhanced. By definition, technology is the application of basic concepts to practical problems. This breakdown into two classifications, if taken too seriously, can be misleading. Clearly the solution to practical problems can be advanced only through expanding our understanding of the basic questions of chemistry. Conversely, the study of practical problems has frequently led to extremely important basic advances.

Chemistry is the science of matter, energy, and change. It is concerned with the nature of matter in the finest of detail, and with the kinds of transformation that matter undergoes, both spontaneously and under the prodding of the inquisitive chemist. Historically, a man interested in meteorological problems (John Dalton) was the first to successfully theorize about the nature of matter in terms of chemically unique atoms. The structure of atoms—and, more specifically, the structure of the nucleus of the atom—has become more commonly, but not exclusively, the province of the physicist. Much of what you will read in the early chapters of this book could thus be labeled *chemical physics*. Chemists share physicists' concern with the atom, but the concern is less with the internal structure of an individual atom than with the behavior of atoms in assemblies. These atomic assemblies, known as *molecules*, range from a very few to many millions of atoms in size, displaying a most fascinating variety of structures.

These molecules, furthermore, are frequently quite sensitive to change; they undergo reactions with other molecules to produce still other structures. Why should this be? Can we predict what kinds of structures can result from a given collection of atoms, and what *reactivity* (tendency to change) these structures will have? Can we explain and predict the speed at which these reactions will proceed? Can we predict that a given molecular structure will be biologically active, triggering various responses in a living organism either for benefit or detriment, depending on whether we consider that particular organism to be friendly and useful, or an enemy, such as a virus or bacterium? Can we learn enough about molecules and their reactions to understand the nature of life and the life process? This may, after all, be the ultimate question that can be put to the chemist.

These and related problems of the behavior and structure of molecules will be considered in some detail in the chapters that follow. We shall attempt to learn what the current status of each is, and perhaps gain some insight into the future course of chemistry.

CHEMISTRY AND TODAY'S PROBLEMS

What is the relevance of the basic problems of chemistry to the society of man? Are these problems just academic exercises designed to amuse a few people and provide hurdles for students? Or do they connect in an immediate way to our lives today, and more importantly to the lives of the inheritors of our society? In a world which seems to have a staggering array of problems, it is difficult to pinpoint the most important that beset society, but probably we can agree on a list of at least some of these problems. We then ask the question: What contribution can the science of chemistry make to the solutions of these pressing problems? Is chemistry just a means for making junk and plastic what-nots, or does it offer some hope of supplying some of the answers to the question of man's survival?

Let us first consider what some of the problems are, and then try to relate them to the contributions that chemistry can make to their solution. Clearly many of these problems require social and political solutions as well as scientific ones, since new, modified social institutions must be developed to cope with them. But very frequently at the core of the problem there lies some aspect which is within the province of the natural sciences. For example, perhaps the most pressing problem that we shall have to face in the next 25 years is the population explosion, and the problems associated with it: uncontrolled urbanization, food shortages, environmental pollution, and the depersonalization of the individual that seems to accompany the formation of very large social units.

What role can chemistry play? Without too much intellectual chauvinism, one could agree that most certainly the prevention of food shortages and the control of environmental pollution will require major contributions from the chemist. The creation of new types of fertilizers, the conversion of materials that are at present nonedible into food, and the cultivation of the seas are partially chemical problems. The other side of the food-shortage coin—the control of population by acceptable, safe, and effective fertility-control measures—will also most certainly require new chemical knowledge.

Environmental pollution has become a major crisis almost overnight; the seemingly inexhaustible ability of the Earth to absorb our waste products has abruptly terminated. Perhaps one of the most important consequences of man's flight to the moon has been the dramatization of the finiteness of our planet. As the crew of the first lunar flight observed, "The Earth is a wonderful oasis in a very vast and inhospitable universe. We cannot afford to destroy its ability to support us, for there is no way of replenishing it from outside. We are truly a spaceship dependent upon our own ingenuity and foresight for survival." We must find new noncontaminating methods of transportation; we must generate power without polluting the air with combustion products or radioactive waste; we must manufacture needed goods without dumping the resulting waste products into streams, lakes, and even the oceans. Surely the chemistry of combustion, the chemistry of radioactive elements, and the largely chemical processes associated with heavy industry such as steel-making, sulfuric acid manufacturing, paper-making, etc., will require intensive study by the chemist in order for these processes to become noncontaminating. Major strides could be made today, using present technology, if appropriate changes were made in our political and social institutions; nevertheless, improved technology will make the problem simpler. For example, a very efficient battery of large power output and low weight would do much to solve the air pollution resulting from automobile exhaust.

The prevention and cure of disease, while generally considered to be a problem of the medical profession, has been advanced as well by the efforts of many chemists. These scientists have discovered and synthesized drugs which cure many previously fatal maladies and which someday soon will control cancer and circulatory diseases. Perhaps we can even look forward to a future when the transmission of inherited characteristics is sufficiently understood so that congenital maladies need no longer be passed from one generation to the next. Such a feat could come only through a very detailed knowledge of the molecules of which living cells are composed and the methods by which they duplicate themselves.

The pressure of great populations packed into cities seems to create almost unbearable emotional stresses on the inhabitants of these environments. With greater understanding of the chemistry of life may come an understanding of the origins of our responses to stress and some hope for modifying them beneficially. This could very well come about by chemical means.

Within the last few years it has been increasingly recognized that large sections of the cities of America are decaying into places almost unfit for humans. Yet an ever-increasing fraction of our population lives in or around these cities. The urban areas must be rescued from decay, and the trend reversed, so that the cities can again become desirable centers of human culture. Great rebuilding projects, the eradication of pests, the control of epidemic disease and epidemic despair, the provision of mobility within the city are urgent problems. Present-day chemical technology can do much to help win this battle, and we may hope that new techniques and materials growing out of chemical research will be able to provide new resources for the refinement of urban life.

Chemical technology—the child and companion of basic chemical research—also has an essential role to play in providing the artifacts of a complex civilization in a time of rapidly disappearing familiar natural resources. New sources of metals, from the more abundant rocks of the earth's surface, must be developed. New sources of organic materials, now largely obtained from petroleum and plant materials, must be developed from inorganic materials; for example, extracting carbon from limestone and hydrogen from water to manufacture hydrocarbons. Unquestionably, by the time we enter the twenty-first century, we shall be obtaining most of the materials of manufacture by means of new chemical processes, and obtaining them from sources quite untapped today.

THE RELATION BETWEEN BASIC SCIENCES AND TECHNOLOGY

Most of the above-mentioned problems and their solutions lie within the realm of technology; that is, the application of basic concepts to practical problems. In general, the technology sector draws on the area of basic science for ideas and guidance as though it were a bank. In the past, our basic ideal bank account was large, with deposits far exceeding withdrawals. But within the last several decades the situation has begun to change; the withdrawals are beginning to catch up with the deposits. A hundred years ago an idea, a theory, or a fact might lie fallow for many years before an application for it in industry or medicine or warfare was found. Today, this so-called "lag time" is a few years, and sometimes even months. The space program, for example, has depleted our account of basic ideas completely in some areas and is operating on current income. This has led to a situation which is quite