# The Development of Chemical Principles

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# Preface

If longer titles were convenient, this book might be accurately called *The Development of Structural Principles in Chemistry: An Introductory Study.* We like the term "development" because it suggests the two main things we are trying to do in this book.

We try to record experimental observations, identify creative insights, and pursue deductive consequences in the manner characteristic of the development of a scientific concept. For example, we quote the early data on conductance and colligative properties of electrolyte solutions, discuss Arrhenius' synthesis, and pursue the deductive consequences of his idea of partial ionization to identify its flaw and reveal the origins of the Debye-Hückel theory. We hope that the reader can participate in this development to "rediscover" the theory of ionization for himself and, at least vicariously, practice science. We also hope it will be apparent that the last word in the story has probably not been said.

We also try to follow the longer-range development of fruitful ideas to show that a good theoretical idea evolves. We try to show how the meaning of a term changes as the idea it represents is found to be applicable in more and more new areas. The evolution of the concept of molecule from the micro-billiard ball of Avogadro through the architectural notions of Kekulé, Le Bel, and Lewis to the complex of electron-nuclear interactions of Mulliken is a striking example of this type of development.

Obviously, both senses of the term "development" often commit us to examination of the history of our subject, including some of its false steps and discarded ideas. We do this mainly with science students in mind. Our conviction is that involving the student as a *critical* participant in the development of ideas should be given first priority. Science students, especially, should be encouraged early to practice science.

The topical focus of the book is structure. We follow the suggestion of the Westheimer report that chemistry is naturally divided by differences of intellectual style into study of structure, synthesis, and dynamics. A study of concept development implies a study of intellectual style. Historically, structural thinking matured first in chemistry and seems an appropriate emphasis for a first course. Clearly, a balanced treatment of modern structural theory cannot ignore some of dynamics and synthesis.

The plan of the book is to explore three lines of the development of contemporary chemical structural theory: the classical theory of bonding in molecules; the ionic interpretation of electrolyte solutions; and the physical theory of atomic structure. Important characteristics of each of these somewhat independent genetic strains are evident in our current hybrid. The first chapter reviews the foundations of atomic-molecular theory and stoichiometry. The next two chapters show how isomer relationships and reaction patterns lead to representation of molecules by geometrical diagrams with bond lines. Chapters 4 and 5 explore the properties of solutions and the origin of the concept of ion. Energetic relationships in chemistry are introduced in Chapter 6 on the basis of an "empirical" discovery of the Nernst equation. (This is intended to give concrete chemical foundation to a first contact with thermodynamic quantities and to make reasonable demands on the student's mathematical preparation.) The final three chapters treat the development of a theory of atomic structure and its significance for interpretation of the chemist's earlier theoretical entities, bonds and ions.

Accomplishments that are not strictly required for the development of the basic theme are treated in appendixes to several chapters. Such topics are kinetic theory of gases, a survey of organic functional group reactivity and nomenclature, and applied equilibrium calculations. The book as a whole has an appendix introducing the dynamics of chemical reaction from the new fundamental process (molecular-beam) viewpoint.* Only this appendix presumes a background in calculus.

*See R. Wolfgang, "The Revolution in Chemical Dynamics," *J. Chem. Ed.*, **45** (1968), 359.

Since the development of modern chemistry depends so much on concepts from mechanics, electricity, and wave physics, appendixes on these subjects are included. We are especially indebted to Professor A. B. Arons for permitting us to include his introductory chapter on waves as Appendix 3. The basic wave ideas are usually less familiar to the introductory chemistry student than are the elementary notions of mechanics.

If active participation in the development of ideas is the objective of the book, its problem and assignment materials bear a major responsibility for accomplishing this aim. We have placed problems in the body of the text at appropriate points, either to illustrate or to advance the argument. Probably the ideal procedure would be to solve these problems as they arise. We have also prepared some larger, more independent assignments, called "seminars" for lack of a better term. They present some specific experimental information as a challenge to theory building, usually after some outside reading. They provide an opportunity for articulation of extended critical arguments tied to specific results and for the development of a sense of the rules of scientific "debate." We have used them as assignments of the "term paper" type, which students have found rewarding. They might also serve as the basis for interesting discussion seminars.

We have not tried to write a comprehensive text. We are not sure what the content of introductory (general?) chemistry should be at present. However, we do enthusiastically endorse the conclusion of the report of the 1957 conference on "Improving the Quality of Introductory Physics Courses"* that the magnitude of the subject requires radical paring to allow time for deep exploration of principles and methods of reasoning. The detailed content of the introductory course should probably be adapted to the overall curricular situation in each institution. This procedure is certainly feasible since there are now

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available in inexpensive editions many good specialized monographs written for beginners.

We believe that emphasis on development is relevant to a wide variety of curricula, and we have used the materials of this book in several situations. The book originated in a one-semester course for well-prepared science and liberal arts students at Amherst College. That course was terminal for the liberal arts students but led to a second-semester course in thermodynamics and equilibrium for the science students. With some supplements, the material was used for the first-year course for science students at Carleton University. Parts of it have also been useful in a first-year course at Voorhees College, Denmark, South Carolina, and in a summer enrichment institute for secondary school students.

We owe unacknowledgeable debts to our predecessors; we have learned from many earlier texts and benefited from conversations with many teachers. However, a few of our most important debts can be acknowledged here. Professor Jay A. Young read the entire manuscript and gave us lively criticism and valuable encouragement. Parts of the manuscript were commented upon by Professors Francis Bonner, Robert H. Weightman, Richard D. Fink, Peter Kruus, James M. Holmes, and Paul M. Laughton. We owe a special debt to our teachers. Our scientific careers have a common "grandpaternity" (C. H. L.) and "paternity" (R. A. B.) in the inspiration engendered by Professor H. S. Taylor. Professor R. L. Burwell, Jr., a Taylor student, taught C. H. L. and in the process advocated a healthy skepticism toward excesses of pedagogic theory. (That lesson may not have been sufficiently well learned.) Both of us have been deeply interested in the universally required introductory "Science 1" course at Amherst College, and C. H. L. taught on its staff for several years. In the period that the course was directed by Professor A. B. Arons, it offered a lesson in the best science teaching. Our introductory chemistry course at Amherst was undoubtedly a response to the challenge of Science 1. We can only hope we have met the challenge.

We warmly acknowledge the expert contributions of Mrs. Madelaine deFriesse, Mrs. H. N. Stassen, Mrs. Ann Holt, and Mrs. Martha Langford in the preparation of the manuscript. We have to admit that the problems were checked by first-year students at Amherst and Carleton. We apologize to them and thank them. The patience of our wives in support of this project certainly must also be recognized.

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# Contents

CHAPTER 1

# The Atomic-Molecular Theory

## 1.1 THE DIFFERENTIATION BETWEEN SIMPLE SUBSTANCES AND MIXTURES; THE STARTING POINT FOR CHEMICAL SCIENCE

Consider a random assortment of natural phenomena: an apple falls, iron rusts, water boils, soda fizzes, a dye fades, a wheel rotates, a green leaf develops, a rocket soars, an electric bulb glows, silver is electroplated onto another metal. Which of these phenomena are the special province of chemical science? Which are within the domain of physics? Which are of concern to both?

Roughly speaking, physics is not primarily concerned with the kind of "stuff" under observation. The law of acceleration under gravitation is meant to apply equally well to a pound of lead or a pound of feathers, and does, provided air resistance is properly considered (e.g., eliminated by conducting experiments in a vacuum). In an event such as "falling," no new "stuff" is formed. Except for possible dents, the piece of lead seems pretty much the same after falling as it did before. On the other hand, the rusting of iron, the electrical deposition of silver, and the fading of a dye produce what would obviously be called changes in the sort of "stuff" present. These are chemical changes. It will be our task here to develop a systematic logical explanation* of the nature of such events.

To begin to develop an explanation of chemical change, it is first important to decide what are simple chemical materials and what are complicated ones. This is not an easy task. In Herbert Butterfield's important book, *The Origins of Modern Science*, the chapter on the origin of scientific chemistry is titled "The Postponed Scientific Revolution in Chemistry." Chemistry was late to bloom, largely because the most "common" materials are not necessarily simple.

* "Explanation" is a tricky concept. In this book we shall try to illustrate what counts as a scientific explanation and show something of the process by which some specific explanations arise. We shall not have occasion to attempt an analysis of the idea of explanation. The reader is urged to explore this fascinating question. A good starting point might be S. Toulmin's small book, *Foresight and Understanding*, Harper & Row, New York, 1963 (Harper Torchbook TB 564).