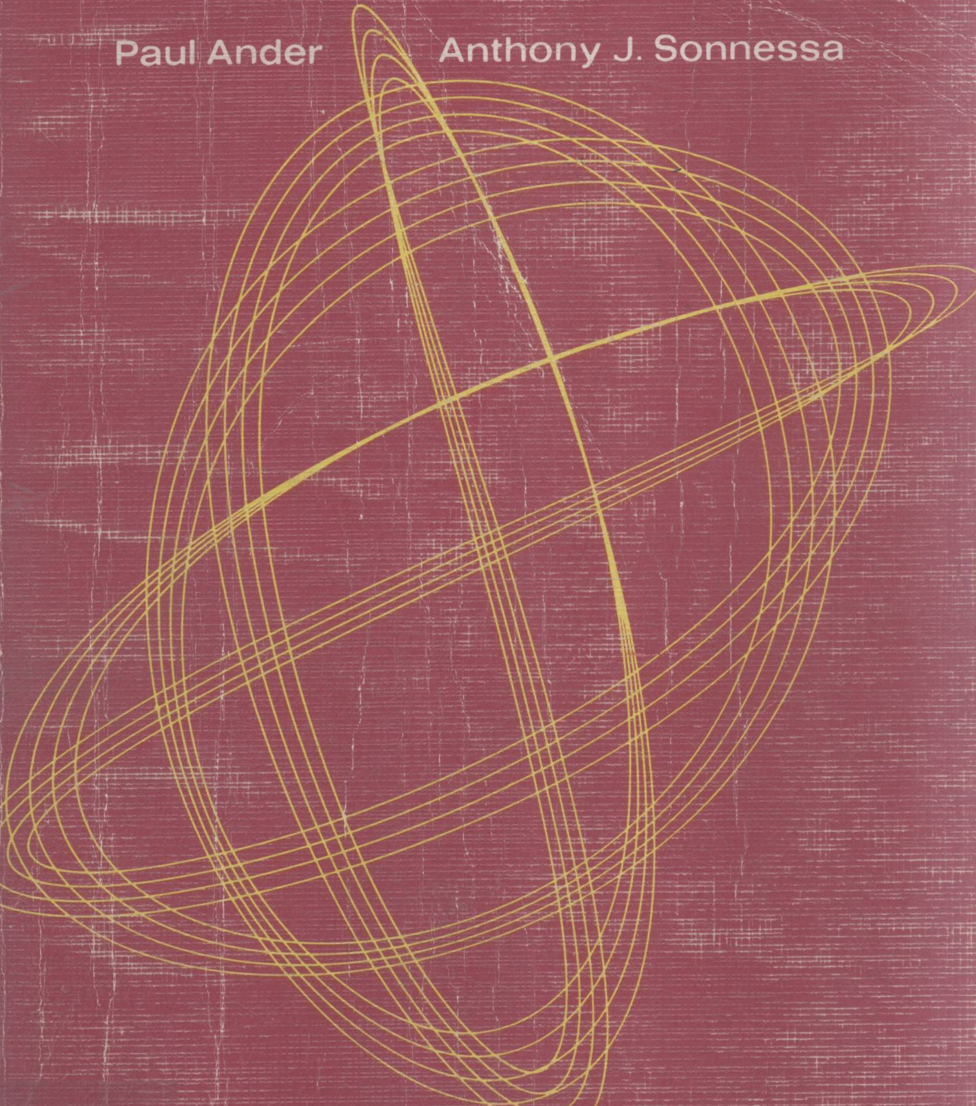
PRINCIPLES OF CHEMISTRY

AN INTRODUCTION TO THEORETICAL CONCEPTS

Paul Ander Anthony J. Sonnessa



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Preface

During the past few years it has been generally recognized that the initial college course in chemistry should employ a more quantitative approach to the subject matter. There are two principal reasons for this point of view. First, research today requires more rigorous training in the quantitative aspects of science. Second, high school graduates currently seem to exhibit great enthusiasm for the modern ideas in chemistry; they have heard or read about many exciting topics in chemistry, such as bonding theory, nuclear chemistry, and the structure of nucleic acids and proteins. To maintain and extend this interest, the rudiments of some modern topics should be presented in the freshman course.

For these and other reasons, chemistry curricula are in the process of revision. Course content has been updated for analytical, inorganic, organic, and physical chemistry. In each of these courses, stress has been placed upon *principles* rather than upon descriptive aspects. One need only look at recently published textbooks in these areas to become aware of this trend. The movement toward presenting material of a more advanced nature in these courses creates two basic needs which must be satisfied in the introductory course. First, it is essential that the freshman course prepare the student for the advanced material presented in these upper-level courses by introducing him to the language used; and second, freshman course should include those topics that are either omitted or treated superficially in the later courses to provide more time for the advanced material.

The nature of the work performed today in physics, biology, and engineering requires an understanding of chemical principles, and the freshman chemistry course taken by students in these areas should provide them with the necessary background. This book has been written to meet the needs of such students, as well as the chemistry major. Most of the material has been presented to a select group of science majors at Seton Hall University in a course that has been most stimulating to both the instructor (P. A.) and the students.

Wherever possible, the research approach has been employed: First, the experimental facts are presented, then a theory is advanced to explain the facts. For thorough understanding of the later chapters, the student must be familiar with certain basic physical and mathematical terms. These are therefore reviewed in Chapter 1 as an integral part of the text, rather than being relegated to an appendix. Chapter 2 deals with the experimental foundations of the quantum theory. The application of this theory to atomic structure is discussed, and the theory is correlated with the properties of atoms and molecules. In Chapter 3, the quantum theory is extended to the bonding of atoms in molecules. The student is introduced to the qualitative ideas of the bonding theories and to the results derived from these theories. Descriptive inorganic and organic chemistry has not been discussed systematically in this book because the authors feel that it is covered more adequately in the upper-level courses. However, the principles described in the book are applied to the chemistry of the elements whenever possible, and it is hoped that later courses will extend this application.

Chapter 4 extends the application of the principles to the formation of ionic compounds and to their properties in the solid state and in solution. The importance of understanding the arrangement of atoms and ions in the solid state cannot be denied. The elementary presentation of this material in the second part of the chapter should enable the student to better grasp the more advanced presentation given in physical chemistry courses.

Chapter 5 treats the properties of gases. The approach, once again, is to start with the experimental facts, then to explain the facts by using a theoretical model. The modifications in the model of an ideal gas necessary to explain the observed properties of real gases illustrate for the beginning student the need for reviewing theories in the light of new experimental findings.

The empirical and theoretical aspects of chemical equilibrium are treated separately in Sections I and II of Chapter 8. The student is first given a firm feeling for equilibrium by treating many types of equilibria empirically, in order to enable him to understand more readily the more abstract and difficult theoretical aspects of the subject. The breakdown is also for the convenience of those instructors who desire to omit the theoretical aspects entirely because of time limitations.

There is great interest today in biological macromolecules, which are usually discussed in elementary biochemistry and biology courses. Accordingly, an introduction to the nature of macromolecules has been presented in Chapter 10. Also presented are the mechanisms for the formation of polymers which provide the student with excellent, simple examples of reaction mechanisms.

Although nuclear chemistry is usually included in physical chemistry texts, it is rarely presented in physical chemistry courses and the principles of this subject are generally not provided for in the undergraduate curriculum. Since the principles of nuclear chemistry can be presented using only algebra, it can be part of a freshman course.

The authors have tried to arrange the material in this book so that certain topics can be omitted if the teacher desires. This material, however, is there for the more interested student. Hopefully, the student will find the problems challenging. The authors have tried to include some problems which illustrate important principles not fully developed in the text, so that the student can deduce them for himself.

A minimum knowledge of calculus is required for Chapters 8 (Section II), 9, and 10 only. The other chapters require only knowledge of algebra.

The authors thank those who have aided them, both directly and indirectly, in this project. We are indebted to Professors Kenneth Wiberg of Yale University and Jack Halpern of The University of Chicago for their helpful comments on the manuscript. We are further indebted to Professor Eugene Kupchik of St. John's University for his perusal of the entire manuscript. We are grateful to Professor Charles Erickson of Rutgers, The State University for making sets of problems available to us for inclusion in the book. We gratefully acknowledge the support and encouragement given us during this project by several of our colleagues at Seton Hall University. Special thanks are due Mrs. Sally Kynor Johnson, whose excellent typing of the manuscript was of great aid, and Miss Lynn Ebbets, who assisted with the typing. We are particularly indebted to our past teachers and to our students, who have been, and remain, sources of stimulation.

We will be grateful for any constructive criticism of this book.

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1 REVIEW OF MATHEMATICAL AND PHYSICAL TERMS

1-1 SCIENCE

Man has shown an interest in the natural world about him from the beginning of history. This interest is understandable since the forces in nature affect our lives in a very direct way: lightning, earthquakes, tides, rain and the lack of it, to name a few, all can have drastic effects on human life. Primitive man, through his ignorance of the causes of these natural phenomena, feared them and was completely at their mercy. Superstition and magic, both detrimental to the progress of civilization, were the result of these fears.

It was not until man began carefully and dispassionately to study the causes of natural phenomena that he was able to progress to a high degree of civilization. These studies led to the accumulation of a large body of information which was eventually embodied in quantitative laws and theories, which, in turn, led to further discoveries. From these scientific discoveries, the inventive mind of man developed the machines and industrial processes which are in direct proportion to the degree of civilization.

The process of systematizing experimental facts into theories or laws upon which predictions of future studies and events can be based can be considered the essence of science.

The vast body of knowledge arising from centuries of experimental studies led to broad divisions of science, each of them closely allied to the others. One classification of these divisions could be physical, biological, behavioral, and social sciences. They all attempt to apply the scientific method to the study of their fields; they differ only in that they focus attention on different aspects of science. However, a good scientist should, in the last analysis, be aware of the important discoveries arising from closely allied fields. This is especially true in the physical sciences, which include physics, chemistry, geology, astronomy, and meteorology. Inasmuch as physics is concerned with a fundamental study of matter and energy, all of the other physical sciences look to physics for basic relationships with which to aid in the interpretation of phenomena in their respective fields.

Chemistry is concerned with the changes that occur when atoms and molecules interact and undergo transformation from one form to another. These changes involve atoms and molecules in motion, and it is found that the laws of physics concerning forces between bodies in motion are essential to a quantitative study of atoms and molecules. The science of mathematics, in turn, is of importance to all sciences, since its application to the analysis of experimental results makes it possible to formulate these results in an exact, quantitative manner.

1-1.1 Observations and Measurements

The first step in the study of natural phenomena is the observation of the phenomena. These observables are our only contact with the physical world, and they are conveyed to us by our senses. Thus the experimental data we obtain consists of observables which are only as good as our method of detection. Man has learned through experience that his own senses are limited in many ways and has invented ingenious instruments to aid in his observations (telescope, microscope, photoelectric cell, and so on). However, no primary distinction is made between the observations obtained using instruments and those using the unaided senses, since the interposition of an instrument does not affect the reality of the observation.

The ultimate goal is to obtain quantitative relations between observables. Thus, it is known that when a body is released from the hand it will fall to the ground. What is of greater importance is to know the relationship between the distance it falls and the time of fall. Before this result can be obtained, the process of measurement must be applied to the observation. Measurement is the assignment, to the observable, of a number which tells the size or magnitude of this observable.

The choice of observables is purely arbitrary and is based on experience and expediency. The fundamental observables, from which all others can be derived, are length, mass, and time. Once the observables have been chosen, the units of measurement for the three must be assigned. In the physical sciences, the universally accepted system of units is the metric system. In