Principles of

PHYSICAL CHEMISTRY

With Applications to the Biological Sciences

Second Edition

David Freifelder

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PREFACE TO THE SECOND EDITION

From its conception *Principles of Physical Chemistry with Applications to the Biological Sciences* was written with the belief that it should be possible to make physical chemistry more meaningful and accessible to students in the life sciences. As explained in the Preface to the first edition, my *modus operandi* was to limit coverage to subjects of immediate value to such students, to minimize the mathematical derivations, and to include subjects that are of particular interest to biologists and not usually found in traditional physical chemistry textbooks.

In an effort to discover whether the goals of the first edition had been achieved, my publishers and I solicited information from instructors who used the book during the first years of publication. We asked for lists of typographical and textual errors, suggestions about topics to be eliminated or added, suggestions for improving clarity, and opinions about the appropriateness of the level of the mathematics. Many instructors responded to our request. Some offered the same suggestions; of course, there were also marked differences in opinion. Every response was noted, compared with others, and considered carefully. This new edition has been revised in accord with these comments.

Apart from corrections of numerous errors in the mathematics, the most significant change in *Principles of Physical Chemistry with Applications to the Biological Sciences* is the addition of a new chapter (Chapter 19) concerned with the structure of crystals, liquids, and liquid crystals, and the use of X-ray crystallography in determining molecular structure. X-ray diffraction as applied to macromolecules is, of course, a mathematically complex subject; a comprehensive treatment would be inconsistent with the level of presentation chosen for this book. Thus, I have merely attempted to explain some of the more elementary features of X-ray crystallography and provide a basic vocabulary; this knowledge should enable a student to study more advanced texts, if desired. Furthermore, a section on calorimetry has been added to supplement the treatment of thermodynamics, so the student will have some knowledge of the origin of the numbers found in thermodynamic tables. The topic of adiabatic expansion, omitted from the first edition, has also been added. For completeness, the concept of fugacity is now included in the treatment of real systems. A section on free energy and the significance of standard states has also been expanded and the relation between free energy changes and concentration has been clarified with several examples. The quantum mechanics section has been expanded slightly with a section describing tunneling. The phenomenon of independently folded domains in proteins is also an important addition to the chapter on macromolecules. Finally, summaries within chapters (*Comparison of Isothermal, Adiabatic, Reversible, and Irreversible Expansions*) and several appendices (*Exact and Inexact Differentials; Some Useful Thermodynamic Relations; Physical Properties of Water*) have been added.

In an attempt to reduce the mathematical complexity of discussions, derivations have been moved from within chapters and placed in appendices at the ends of those chapters. The student should now be able to understand the meaning and applications of the Debye-Hückel theory without resorting to advanced mathematics and physics that may not be part of his or her background. The section on C_0t analysis and several sections containing serious typographical errors have been corrected.

I hope that all users—professors and students alike—will find the second edition to be an improvement.

I wish to thank the numerous instructors, students, and reviewers who responded to my request for feedback. Special commendation must go to Arthur Bartlett and Donald Jones, my publishers, who were willing to have a second edition follow shortly after the first edition. Their faith and support reflect their commitment to maintaining the highest standards in their publications.

San Diego, Calif.
April, 1984

David Freifelder

PREFACE TO THE FIRST EDITION

Several years ago I was asked to revise a successful physical chemistry textbook so that it would be more useful to biology students and to chemistry students aiming for careers in the life sciences. Since I had been especially concerned about the deficient training in basic physical chemistry possessed by many students and researchers in the life sciences, I enthusiastically began the project. It did not take long for me to discover two great difficulties.

First, the needs of the researcher in the life sciences are, indeed, quite different from those of the chemist or the physicist—the traditional textbooks in physical chemistry include a great deal of material that will never be used by the life scientist yet omit subjects of considerable relevance.

Second, many students in the life sciences do not have the background in mathematics or the commitment to learn the mathematics needed to follow the derivations encountered in traditional physical chemistry textbooks.

Keeping the above two points in mind as I attempted my revision, I observed that by the time I had pared away the topics not useful to the life scientist, there was little left of the original manuscript. I then realized that if the book that had been requested were to exist, it would have to be written from scratch.

I decided to take this new task upon myself; so began a project that was to take me about 1500 hours and to consume reams and reams of paper. Through it all, I determined never to forget my own experiences in studying the material I was now writing about.

As a student of physical chemistry in 1956 I sat in class month after month watching derivations being developed on the blackboard and spent hundreds of hours solving problems that began with the words "Show that... " or "Derive.... " After having completed a year of physical chemistry, despite having received a good grade I found myself wondering what I had *truly* learned. This question seemed far more difficult to answer than any of the problems I had worked in the course; the course had seemed inordinately difficult whereas other courses in chemistry and physics had not seemed so. What was the reason for this? The answer to the latter question was simply that at no point had the practical usefulness of physical chemistry in the life sciences been made manifest. Physical chemistry has traditionally been taught as an abstract subject and is often unrelated to the kind of phenomena encountered in the laboratory and in real life, in part, I believe, because physical chemistry textbooks are usually written by persons whose expertise enables them not only to see the overall picture and the logical harmony of the subject easily but also to believe that these are obvious to all students, as well. Such authors most likely learned physical chemistry easily and spent little time probing the connection between physical chemistry and common experience—the very connection that is not at all obvious to the average student.

Many new books have appeared recently that have been designed to teach physical chemistry to potential biologists or to prepare chemistry students for subsequent courses related to the life sciences. The publication of these books might have suggested to me that I should not expend any time in writing my own, but reading each has reinforced my feeling that today's student, completing a course designed by a physical chemist possessing traditional expertise, will still be left with the feeling of confusion that confronted me 25 years ago. I continue to believe that the student heading for a career in the life sciences needs a physical chemistry textbook written by an experimental biologist who did not find the learning of physical chemistry to be a trivial task. This is the book that has resulted from that belief.

The book is not exclusively for biology majors—this should be emphasized. At present, a student planning to enter a graduate program in the life sciences or to apply to medical school may, as an undergraduate, major in a biological field, in chemistry, or in physics (or even in the classics, economics, or history, which is true of some of my own students). This book is for all of these people. Furthermore, the strong practical orientation of the book makes it one that should not be ignored for chemistry programs designed to train experimental chemists.

The reader who compares this book with other books about physical chemistry and also with those specifically meant for the student in the life sciences will discover that this book differs in several ways.

First, this book relies less on mathematics than traditional texts do. I appreciate the fact that physical chemistry has a firm mathematical basis, yet this is often beyond the training of the student and can become intimidating. Mathematics is useful if it provides deeper understanding of the material. If an author's major requirement is that the student understand how equation 6 mathematically becomes equation 7, then the emphasis on mathematics may impede learning. In this book, no mathematics more advanced than elementary calculus and simple probability theory is used and even these subjects are reviewed in appendices given at the end of the book.

A second important difference is that thermodynamics is given a molecular foundation. Thermodynamics is a marvelously logical subject that does not require molecular explanation. If the two basic postulates, the First and Second Laws of Thermodynamics, are accepted, all else follows logically; it is unnecessary to think about the fact that matter consists of atoms and molecules. To approach thermodynamics as a logical system enables one to use thermodynamics as an elegant tool for deriving numerous valuable equations. Yet such an approach ignores the fact that the systems being discussed do indeed consist of molecules. It has been my experience that to ignore this fact is not satisfying to experimental scientists or to biochemists and molecular biologists, who spend their professional lives trying to unravel the molecular basis of living phenomena and who prefer to know how molecules behave in a given system. Thus, I have presented thermodynamics by combining its postulates with the physical notions of molecular motion and probability. Thermodynamics loses some of its logical beauty in this treatment but the student will benefit by knowing what one actually means by such concepts as internal energy, free energy, entropy, and so forth. Furthermore, the molecular viewpoint used in this book also makes the theory of solutions clearer because, with this viewpoint, one is not hesitant to discuss cohesive forces early in the theory.

A third difference that should be noticeable in this book is the extensive discussion of macromolecules, such as proteins and nucleic acids, in the examples that are part of each chapter. The reason for this emphasis is simple. Most biologists devote more time to the properties of macromolecules than to smaller molecules. Furthermore, in the life sciences physical chemistry can be applied more directly to the study of macromolecules than to smaller molecules.

A fourth difference is the inclusion of lengthy discussions — a chapter for each — of properties of macromolecules and photochemistry, subjects of importance to all endeavoring to study the life sciences, whether approaching from backgrounds in chemistry or biology. Furthermore, quantum mechanics is introduced primarily as a means of understanding spectroscopy, which reflects the practical needs of many experimental scientists.

A fifth difference appears in the problems listed at the end of each chapter. Many problems of a variety of types are provided. Most of these tend to be either very experimental in nature or to require molecular explanations and are designed to give practice in solving the problems that will be encountered when doing laboratory work. Derivations and theoretical notions, which are the mainstay of problem lists in traditional books, have only occasionally been included in this book. Answers to all problems are given, often in detail, at the end of the book.

Once the manuscript for this book was finished, many people helped me to doublecheck the accuracy and soundness of every aspect of it. I received expert advice from Professors Robert Abeles, Irving Epstein, Tom Hollocher, William Jencks, Chris Miller, and Serge Timasheff, all of Brandeis University. In order to obtain the viewpoints of students who had already successfully learned physical chemistry within the past few years, I enlisted the aid of Mike White, who read the entire manuscript, and of Bruce Breit, Alec Cheung, Bruce Gomes, Jon Greene, Les Lang, and Rob Rottapel. To be useful, a textbook must be understandable to the novice. Thus various chapters were read by several undergraduates; Gil Drozdow, Jeff Friedman, and Drew Weissman explained to me any parts that gave them difficulty, and these were reexamined and revised when this was necessary. Finally, when the revised manuscript was completed, another beginning biochemist, Gregg Bannett, read most of it, and further adjustments were made where these were needed. For help in convincing a publisher that the finished manuscript should be published, I thank Peter von Hippel of the University of Oregon, who read early drafts and gave them his stamp of approval. My final thanks must go to Mildred Kravitz, who hates typing but who faithfully joined me in typing about 3000 pages of manuscript. And to my children, Rachel and Joshua, who hope some day to write their own books and who tolerated my typewriter on the dining room table for about a year.

Lexington, Massachusetts David Freifelder

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