A TEXTBOOK OF PHYSICAL CHEMISTRY

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ACADEMIC PRESS New York San Francisco London
A Subsidiary of Harcourt Brace Jovanovich, Publishers

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 72-88328

PRINTED IN THE UNITED STATES OF AMERICA

Illustrations by Ana Hernandez

PREFACE

It might seem that there are only a limited number of ways in which the contents of the first course in physical chemistry can be presented to the student, and that all have already been tried. The pedagogical problem is a complex one, however; it is also one that shifts with time. We have seen the appearance of a great deal of traditional first year physical chemistry in beginning general chemistry texts, usually in curtailed form. At the same time, material which in the past was more commonly found in graduate courses is now appropriate for the undergraduate. The problem is that it is very easy to add new material to a course, and very difficult to avoid making it just an addition.

The older physical chemistry texts gradually evolved a coherent, integrated presentation in which the student progressed steadily through an accepted sequence of material, with each subject building on the previous one. The attempt here has been to achieve something comparable in the contemporary vein.

The traditional physical chemistry course performed a second function—one with which I think we dare not dispense. This was the function of indoctrinating the student, by practice as well as by precept, in scientific thinking. The student was asked to develop at least the beginnings of a critical understanding of the principle and of the approximations that go into each physical chemical relationship. He could be expected to know something about the limitations of a treatment and thus to have a real appreciation of its scope. The better student would acquire the ability to vary the principle or the assumptions to produce modified derivations. I have felt it to be essential that the newer material that is added be presented in reasonable depth so that the same demands can be made on the student as with the traditional topics. The effort has been to avoid letting physical chemistry become a descriptive course in which the student is asked to accept the results of advanced treatments but is not afforded the basis for being critical of them.

The order as well as the philosophy of presentation of material in this text deserves some explanation. An immediate problem is that which arises from the presence of two aspects of modern physical chemistry. One aspect is macroscopic and phenomenological in nature; it is exemplified by the topics of thermodynamics, phase equilibria, and electrochemistry. This is the classical aspect; the traditional textbook devoted itself almost exclusively to it. The second aspect is molecular and theoretical, exemplified by statistical thermodynamics and wave mechanics. The contemporary course gives about equal emphasis to these two main streams of physical chemistry, but there are differences of opinion as to their best order of presentation and the various existing texts differ noticeably in this respect. To be blunt, the choice has seemed to be whether to cover wave mechanics in the first or in the second half of the book. On the one hand, the theoretical approach provides great insight and it may therefore seem proper that it precede the classical material. On the other hand, phenomenology comprises that which we know as scientific, that is, experimental truth. It seems logical, for example, that the great concepts of thermodynamics precede theories about molecular details. An important practical point is that the macroscopic approach provides an entrée to physical chemistry which is easier on the student than is an initial burst of wave mechanics. The scientific maturity of students increases noticeably during the year course in physical chemistry and wave mechanics *is* a difficult subject.

I have adopted an order of presentation which attempts to be responsive to each of the above considerations. The first half of the book follows the general macroscopic stream, but with a great deal of the molecular approach presented at the same time. Thus Chapter 2 on kinetic molecular theory follows the opening one on gases; and Chapter 2 introduces the Boltzmann principle. Chapter 3 continues the emphasis of the molecular level with a discussion of polarizability, and of dipole and magnetic moments; it applies the Boltzmann principle to the treatment of molar polarization. (Chapter 3 includes the phenomonology of light absorption since this topic is too useful as a tool to be deferred to the much later chapter on molecular spectroscopy; the chapter also provides an early opportunity to discuss systems of units.)

The next group of chapters takes up thermodynamics. Classical and statistical thermodynamics are given almost equal emphasis—the two aspects *should* be together. The pedagogical problem of an early introduction of statistical thermodynamics is met as follows. First, the repeated use of the Boltzmann principle in the preceding chapters prepares the student for the formal development of partition functions. It is assumed that the modern student enters his physical chemistry course well aware that molecules have translational, rotational, and vibrational energy states, and it is straightforward to then derive the detailed statistical expressions for the various thermodynamic properties of ideal gases. The wave mechanical equations for the spacings of energy states must, of course, be used; however, their derivation (which comes later in the text) is not essential to the understanding of the thermodynamic concepts.

Chapters 7–13 complete the traditional sequence of chemical and phase equi-

libria, and electro-chemistry. The early introduction of statistical thermodynamics allows a good deal of reference to the molecular point of view.

Chapters 14 and 15 are innovative in that they divide chemical kinetics between gas phase and solution phase aspects. It seems to me that quite different emphases are involved and that such division is overdue. In gas kinetics, theory is concerned with the kinetic molecular treatment of collisions or, alternatively, with the statistical thermodynamics of the transition state (treated as an ideal gas). Solution kinetics seem better understood in terms of diffusional encounters, with the encounter complex generally requiring activation energy if reaction is to occur. The role of the solvent cannot be ignored. Also, of course, the mechanisms proposed for gas phase and for solution phase reactions often draw on rather different chemistries.

Surface chemistry is too often relegated to a dispensable chapter in the physical chemistry text. It seems better to spread surface chemical topics among various chapters, according to where their inclusion is most appropriate. For the same reason, the methods of colloid chemistry for molecular weight determination have been included in the chapter on colligative properties.

Chapters 16–18 carry the student through wave mechanics and its applications. The subject presents the problem that all but the very simplest results require so extensive a mathematical approach that their presentation could easily transform the course into one on mathematical methods. Fortunately, these simpler results do in fact provide the basis for the great majority of applications outside of serious chemical physics. Thus the solutions for the hydrogen atom supply the language of chemical bonding as well as the basis functions for many first order calculations. Hydrogen-like wave functions are, accordingly, discussed in considerable quantitative detail. Further, the treatment of chemical bonding rests to a high degree on the use of the symmetry properties of molecules. The central role that group theory plays in this respect makes it an appropriate and again overdue subject in the physical chemistry course. I have found that group theory used in conjunction with hydrogen-like wave functions provides students with a better appreciation of chemical bonding than does the usual approach. Knowledge of some formal group theory is also necessary to the treatment of electronic and vibrational excited states. Finally, much time is lost in certain senior courses if the student is not reasonably well acquainted with group theoretical methods. For these various reasons, the topic receives the attention of a full chapter.

The chapter on molecular spectroscopy and photochemistry takes a somewhat broader view than is usual. The excited state is presented as a chemical species which differs from the ground state in structure as well as in energy, and which can undergo various chemical and physical processes. Vibrational spectra can be discussed in terms of normal modes because of the group theoretical background supplied by the preceding chapter.

Crystal structure, colloid and polymer chemistry, and radio and nuclear chemistry are placed at the end. The material is not terminal with respect to any pedagogical scheme, of course. The situation is simply that these three subjects are not

prerequisite to any others in the text and therefore have no unique logical positioning.

An explanation should also be given of the manner in which the text is structured. As usual, there is more material than can be covered in the normal year course in physical chemistry. I have felt that some distinction is needed between that which is essential, that which is important, and that which is interesting but merely descriptive. To assist both the instructor and the student in making such distinction, each chapter is divided into three parts.

The first portion of every chapter is deemed essential to the topic; collectively, these portions comprise a coherent core. The second part of each chapter is called Commentary and Notes. In this section we look back over the chapter in terms of commentaries on one aspect or another; also, additional material may be presented, but generally without detailed derivation. The Commentary and Notes sections are intended to be descriptive in nature and to be helpful, rather than a burden to the student. With a few exceptions, no problems are written on these sections.

The last part of each chapter is called Special Topics. As the name suggests, various specific topics are presented; these are given in the same detail as is material in the core. Certain topics are placed in this section because, although they are standard, they are judged to be of lower priority than core material, and not to be prerequisite to it. Examples are: magnetochemistry, the Joule–Thomson effect, the Hittorf method in transference measurements, heterogeneous catalysis, and blackbody radiation. Other special topics cover advanced material whose study should be valuable, time permitting. Examples are: use of the Lennard–Jones potential function in the treatment of nonideal gases, the statistical thermodynamic treatment of equilibrium constants, first order perturbation theory, ligand field theory, the Hückel method. The core does not draw appreciably on any special topic; assignment of a special topic is therefore entirely optional (occasionally a special topic will refer to a preceding one).

The problems at the end of each chapter consist of Exercises (with answers given), Problems, and Special Topics Problems. Some are in the style of those in my study-aid book, "Understanding Physical Chemistry," Benjamin, 1969; others are of the longer, calculational type. Especially long ones are marked as requiring the use of a calculator or desk type computer. I do feel that many aspects of physical chemistry cannot properly be appreciated unless the relevant calculations are actually made in detail.

Some acknowledgments are in order. Much of this book was written while the author was a guest at the University of Western Australia. I am greatly indebted to the hospitality extended by Professor N. Bayliss as Chairman of the Department of Chemistry, and by all members of the department individually. My thanks go to D. W. Watts both as a friendly critic and for his many special efforts on our behalf. I sincerely appreciate the assistance of E. Leffler, whose proofreading included reworking many problems, and the efforts of colleagues at the University of Southern California and elsewhere, who helped greatly in their reviewing of various chapters. I should mention J. Aklonis, R. Bau, T. Dunn, and G. Segal,

among others. The physical chemistry class of 1970–1971 was unmerciful in its discovery of errors (at 50¢ a piece), as were my graduate students; their contribution was a major one. My daughter Jean spent an Australian summer typing much of the manuscript; M. Beverly and S. Cutri, secretaries, and the late M. Reinecke, draftswoman, were indispensable. C. Bruce proofread the entire book, as did Vida Slawson, whose overall contributions I deeply appreciate. Last and not least the many hours spent by Virginia my wife, from reading galleys to indexing, has made the book (if not the subject) partly hers. Finally, I wish to acknowledge my appreciation of a "can do" publisher and of the competence and efficiency of its editorial staff.

I know from experience that errors and maladroit passages inevitably remain in spite of all efforts. I sincerely hope that readers will freely call such to my attention.

A Note to the Reader

Many of the topics are sufficiently involved that I have used a spiral approach to them. By this I mean that the initial presentations sometimes are made on the most direct basis, with certain sidelights or elegancies deferred until later in the chapter. I suggest that the core portion of each chapter be read in its entirety before detailed study is undertaken. Because of this aspect and also because of the structuring of the chapters into divisions, I have tried to make the Index unusually complete. It is intended to be used routinely.

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