A TEXTBOOK OF PHYSICAL CHEMISTRY

third edition

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Preface

A Textbook of Physical Chemistry serves as an intermediate-level textbook for the standard year-long course in physical chemistry, usually taken by chemistry and engineering majors in their junior year. Shorter texts are available, in which the presentation is kept to a fairly elementary level. Longer books try for considerable mathematical and conceptual elegance. I have tried here to steer a middle course. The book can be made more or less demanding, however, by suitable inclusion or omission of sections (including those in small print) in the various chapters. Care has been taken that otherwise easier sections do not rely on some previous, more advanced material.

I have held to the precept that physical chemistry is not a descriptive subject but a quantitative one epitomizing the scientific method. With a few inevitable exceptions, all equations and relationships have been derived from first principles and in sufficient detail that the student should not be left mystified. No mathematical preparation beyond calculus is required. Partial differentiation is explained in detail so that the student need not have prior exposure to it, and the same is true of such topics as matrix multiplication (which appears in the chapter on group theory and symmetry).

I have written in as plain and straightforward a manner as I know how. The student audience that I am addressing has always been in my mind.

It is appropriate to make some comparisons with the previous, second edition. The sequence of topics is about the same. The same general structure is retained, namely that of a main section to each chapter, followed by a section called "Commentary and Notes" and a "Special Topics" section. The Commentary and Notes sections are intended to add qualitative insight to topics covered in the main portion of the chapter and to provide interesting descriptive material. Biographies of outstanding scientists and such topics as the thermochemistry of nutrition are included. In general, no problems are written on the material of these sections. The Special Topics sections treat certain subjects that can be covered at the instructor's option but that are not essential to the main body of material. The presentation in the Special Topics sections is rigorous, and problems on them are included. Several sections that were Special Topics in the second edition have been moved into the main body of the text, however, in order to improve the continuity of presentation.

As in the second edition, the statistical mechanical treatment of the first and second laws of thermodynamics follows the phenomenological presentation of these laws. Instructors preferring to treat statistical thermodynamics as a single unit may do so by setting aside Sections 4-11 and 6-11 for later presentation.

There is some 20 percent turnover of material to allow the inclusion of such new subjects as Fourier transform spectroscopy, more detail on the RRKM treatment of reaction rates, and some discussion of oscillatory reactions. The Carathéodory theorem is included as an alternative to the standard Carnot cycle development of the entropy concept. The postulates of wave mechanics are now treated explicitly and in some detail. Contemporary data have replaced older material in many instances, and there are many new figures, including some computer graphics where they have appeared useful.

There is some 80 percent turnover in the Exercises and Problems sections (exercises and problems are now numbered in a single sequence). As before, answers are given to the exercises. A manual of worked-out answers to both exercises and problems, prepared by Edwin Joseph Bohač, Jr., of the Georgia Institute of Technology, is available from the publisher on request.

Both the traditional cgs/esu and the newer SI systems of units are used, often in parallel. (Table 3-3 gives a useful set of factors that allows conversion from cgs/esu to SI equations and vice versa.) After all, the chemist or engineer who is unacquainted with *both* systems is seriously handicapped. Some current literature, especially from overseas, is in SI units, but much appears mostly in cgs or a mixture of cgs and SI quantities; and, of course, the vast store of past literature and data compilations is in the older system. I add that I am not enamored of the SI system, considering it to be neither particularly relevant nor convenient to physical chemistry [see *J. Chem. Ed.*, *55*, 634 (1978)].

The preparation of this edition was carried out in part while I was a guest at the University of Hawaii and would have been completed while I was a guest at the University of Canterbury in Christchurch, New Zealand, except for the intervention of a change in personal plans. I am very grateful to both chemistry departments for their hospitality, both institutionally and as individual faculty members. My secretary, Kay Siu, has been indispensable in many aspects; and, as before, I thank my wife for her help in proofreading—help that makes the book (if not the subject) partly hers. My special thanks go to the several reviewers who provided valuable suggestions for improvements in the second edition, and to those who helped greatly with suggestions and corrections at the manuscript stage.

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