WILEY

SEVENTH EDITION

CHEMICAL THERMODYNAMICS

BASIC CONCEPTS AND METHODS

IRVING M. KLOTZ
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CARNOT KELVIN
Gibbs Helmholtz Clausius
Lewis Joule PLANCK

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Seventh Edition

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A JOHN WILEY & SONS, INC., PUBLICATION

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

Library of Congress Cataloging-in-Publication Data is available.

ISBN: 978-0-471-78015-1

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

CHEMICAL THERMODYNAMICS

Dedicated to the Memory of
Irving Myron Klotz
January 22, 1916–April 27, 2005
Distinguished scientist, master teacher, dedicated mentor, and colleague

PREFACE

This is the seventh edition of a book that was first published by Professor Klotz in 1950. He died while we were preparing this edition, and it is dedicated to his memory.

Many friends have asked why a new edition of a thermodynamics text is necessary, because the subject has not changed basically since the work of J. Willard Gibbs. One answer is given by the statement of Lord Rayleigh in a letter to Gibbs*,

> The original version, though now attracting the attention it deserves, is too condensed and too difficult for most, I might say all, readers.

This statement follows a request for Gibbs to prepare a new edition of, or a treatise founded on, the original. Those of us who still have difficulty with Gibbs are in good company. Planck wrote his famous textbook on thermodynamics independently of Gibbs, but subsequent authors were trying to make the work of Gibbs more easily understood than the Gibbs original. Similarly, each new edition of an established text tries to improve its pedagogical methods and bring itself up to date with recent developments or applications. This is the case with this edition.

One hundred fifty years ago, the two classic laws of thermodynamics were formulated independently by Kelvin and by Clausius, essentially by making the Carnot theorem and the Joule–Mayer–Helmholtz principle of conservation of energy concordant with each other. At first the physicists of the middle 1800s focused primarily on heat engines, in part because of the pressing need for efficient sources of power. At that time, chemists, who are rarely at ease with the calculus, shied away from

*Quoted in E. B. Wilson, *Proc. Natl. Acad. Sci., U. S. A.* **31**, 34–38 (1945).

thermodynamics. In fact, most of them probably found the comment of the distinguished philosopher and mathematician August Comte very congenial:

> Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational. If mathematical analysis should ever hold a prominent place in chemistry-an aberration which is happily impossible-it would occasion a rapid and widespread degradation of that science.
> —A. Comte, Cours de philosophie positive, Bachelier, Paris, 1838, Vol. 3, pp. 28–29

By the turn of the nineteenth into the twentieth century, the work of Gibbs, Helmholtz, Planck, van't Hoff, and others showed that the scope of thermodynamic concepts could be expanded into chemical systems and transformations. Consequently, during the first 50 years of the twentieth century, thermodynamics progressively pervaded all aspects of chemistry and flourished as a recognizable entity on its own—chemical thermodynamics.

By the middle of the twentieth century, biochemistry became increasingly understood in molecular and energetic terms, so thermodynamic concepts were extended into disciplines in the basic life sciences and their use has expanded progressively. During this same period, geology and materials science have adapted thermodynamics to their needs. Consequently, the successive revisions of this text incorporated examples and exercises representative of these fields.

In general, the spirit and format of the previous editions of this text have been maintained. The fundamental objective of the book remains unchanged: to present to the student the logical foundations and interrelationships of thermodynamics and to teach the student the methods by which the basic concepts may be applied to practical problems. In the treatment of basic concepts, we have adopted the classic, or phenomenological, approach to thermodynamics and have excluded the statistical viewpoint. This attitude has several pedagogical advantages. First, it permits the maintenance of a logical unity throughout the book. In addition, it offers an opportunity to stress the "operational" approach to abstract concepts. Furthermore, it makes some contribution toward freeing the student from a perpetual yearning for a mechanical analog for every new concept that is introduced.

A great deal of attention is paid in this text to training the student in the application of the basic concepts to problems that are commonly encountered by the chemist, the biologist, the geologist, and the materials scientist. The mathematical tools that are necessary for this purpose are considered in more detail than is usual. In addition, computational techniques, graphical, numerical, and analytical, are described fully and are used frequently, both in illustrative and in assigned problems. Furthermore, exercises have been designed to simulate more than in most texts the type of problem that may be encountered by the practicing scientist. Short, unrelated exercises are thus kept to a minimum, whereas series of computations or derivations, which illustrate a technique or principle of general applicability, are emphasized.

We have also made a definite effort to keep this volume to a manageable size. Too often, a textbook that attempts to be exhaustive in its coverage merely serves to overwhelm the student. On the other hand, if a student can be guided to a sound grasp of the fundamental principles and be shown how these can be applied to a few typical problems, that individual will be capable of examining other special topics independently or with the aid of one of the excellent comprehensive treatises that are available.

Another feature of this book is the extensive use of subheadings in outline form to indicate the position of a given topic in the general sequence of presentation. In using this method of presentation, we have been influenced strongly by the viewpoint expressed so aptly by Poincare:

> The order in which these elements are placed is much more important than the elements themselves. If I have the feeling . . . of this order, so as to perceive at a glance the reasoning as a whole, I need no longer fear lest I forget one of the elements, for each of them will take its allotted place in the array, and that without any effort of memory on my part.
> —H. Poincare, The Foundations of Science, translated by G. B. Halsted, Science Press, 1913.

It is a universal experience of teachers, that students can to retain a body of information much more effectively if they are aware of the place of the parts in the whole.

Although thermodynamics has not changed fundamentally since the first edition was published, conventions and pedagogical approaches have changed, and new applications continue to appear. A new edition prompts us to take note of the progressive expansion in range of areas in science and engineering that have been illuminated by thermodynamic concepts and principles. We have taken the opportunity, therefore, to revise our approach to some topics and to add problems that reflect new applications. We have continued to take advantage of the resources available on the World Wide Web so that students can gain access to databases available online.

We are indebted to the staff of Seeley-Mudd Science and Engineering Library for their assistance in obtaining resource materials. R.M.R. is grateful to the Chemistry Department of Northwestern University for its hospitality during his extended visiting appointment. We thank Warren Peticolas for his comments on several chapters and for his helpful suggestions on Henry's law. We are grateful to E. Virginia Hobbs for the index and to Sheree Van Vreede for her copyediting. We thank Rubin Battino for his careful reading of the entire manuscript.

A solutions manual that contains solutions to most exercises in the text is available.

While this edition was being prepared, the senior author, Irving M. Klotz, died. He will be sorely missed by colleagues, students, and the scientific community. This edition is dedicated to his memory.

ROBERT M. ROSENBERG

Evanston, Illinois

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