PHENOMENOLOGICAL THERMODYNAMICS

With Applications To Chemistry

JOSEPH de HEER

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PRENTICE-HALL, INC. / Englewood Cliffs NJ 07632

Library of Congress Cataloging in Publication Data

de Heer, Joseph (date)
Phenomenological thermodynamics with applications to chemistry.

Bibliography: p.
Includes index.
1. Thermodynamics. I. Title.
QD504.D4 1986 541.3'69 85-6516
ISBN 0-13-662172-4

Editorial/production supervision and interior design: Nicholas Romanelli
Cover design: Edsel Enterprises
Manufacturing buyer: John Hall

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 0-13-662172-4

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoameracana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Prentice-Hall of Southeast Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*
Whitehall Books Limited, *Wellington, New Zealand*

Preface

The most explicit title appropriate for this book would be *Lectures on Phenomenological Equilibrium Thermodynamics, with Special Emphasis on Applications to Chemistry*. Although this lengthy title does not appear on the cover, it serves as the proper heading under which to outline what the author of this monograph *does* and *does not* intend to accomplish.

First, this book is an outgrowth of the author's *lectures* on the subject, both on an introductory and on a more advanced level. Since these presentations were, in general, well received by the students involved, a continuous effort has been made to preserve the characteristics of lectures as much as possible. This has lead to some obvious, as well as to some unexpected, difficulties. Obviously, while frequent repetitions with a proper verbal emphasis are a powerful lecture tool, printing costs limit repetitions (in particular as far as mathematical formalisms are concerned), and the verbal emphasis can at best be substituted by an imaginative use of italics. The latter will not please those grammatical purists who consider themselves disciples of Fowler. It came as a surprise to the author that in a few instances the lecture style threatened to impart an undesirable flavor to the text. For example, a Socratic-type dialogue (in the derivation of the Phase Rule), which had proven to be very effective in the classroom, came across as "arrogant" to several helpful reviewers of the manuscript. Every effort has been made to eliminate such unintended effects.

Second, this is a book on *phenomenological* thermodynamics only. (In the first chapter the author explains why he prefers this adjective to *classical*, so frequently used in this context.) The argument as to whether the phenomenological and the statistical approaches should be combined will undoubtedly go on forever. Although the author sides with those who think they should *not* be combined, he wishes to avoid a "dogmatic" attitude regarding this matter; if an occasional corpuscular "picture" can make the phenomenological framework considerably easier to understand, it is included.

Of course, criteria for the occurrence of spontaneous (irreversible, "natural") processes are as important to likely readers as are the conditions for equilibrium (and stability). This book is restricted to *equilibrium* thermodynamics only insofar as it excludes the so-called "thermodynamics of irreversible processes," in the sense of Onsager, Prigogine, de Groot, and others.

This newer branch of thermodynamics will be alluded to occasionally but requires, in the author's opinion, a separate monograph.

Since the author is a physical chemist, and the book is an outgrowth of lectures given primarily, if not exclusively, to chemistry and chemical engineering students, problems in *chemistry* dominate the applications discussed in some detail. On the other hand, several sections have been added which traditionally have had more appeal to physicists than to chemists. These include sections 10.3 and 14.2 on the Joule–Kelvin effect, 14.3 on adiabatic demagnetization, as well as 17.1 and 17.2 on the equilibrium and stability of uniform and nonuniform gases. Beginning chemistry students may wish to skip these sections, although to many chemists a study of one or more of these subjects should be a rewarding experience.

Even with all the restrictions described above, the area of thermodynamics and its applications is so vast that it cannot possibly be contained in a single volume. Several opinions about this were expressed by editors and reviewers of the manuscript in its initial stages, but ultimately the author is solely responsible for the decisions regarding what to include and what to leave out, knowing full well that *any* such decisions would leave *some* potential readers dissatisfied. Throughout the book a special effort has been made to emphasize a *critical* discussion, in particular of the basic concepts on which the development of the subject is based. In the light of the fact that some consider phenomenological equilibrium thermodynamics a "closed" science. ("There is nothing in it that was not known already to Clausius and Gibbs" is the extreme expression of this viewpoint), it is incredible that many of the concepts are still highly controversial and sometimes definitely not yet understood. In some instances the author hopes to be able to shed some light on such topics, but in other cases he shall have to admit that the issues concerned are as yet unresolved. If admitting the latter status is to be interpreted as a weakness, so be it. The one thing the author does not wish to be accused of, in this context, is to sweep these intricate problems routinely under the proverbial rug.

Throughout the book, a large number of paragraphs (usually rather brief, but occasionally of considerable length), appear in small print. These contain clarifications for, elaborations upon, or digressions from the main body of the text. It is left up to the individual readers to decide which of these comments are helpful to them and which ones do not reflect their primary interests.

The contents of this book divides logically into four parts. Part I presents the basic concepts, definitions, and mathematical techniques. For the beginning student, these eight chapters may be too much to swallow. Consequently, on an introductory level, parts of many chapters could be dealt with more superficially. Chapter 7 may be skipped in its entirety (if one has no intention to study Carathéodory's approach to the Second Law), and some of the material in Chapter 8 could be postponed. On the other hand, the better we master the mathematical techniques, the greater the reward in the sense of a preparation for the study of the main subject as it will be presented in the rest of the book.

In Part II the laws of thermodynamics are developed. This is one of the very few treatises on thermodynamics which gives *both* the "traditional" *and* the "axiomatic" (Carathéodory) approach. Readers who wish to confine themselves to the former can skip section 9.3 as well as all of Chapter 13. Chapters 10 and 14 are entirely devoted to some basic applications. Those primarily interested in applications to chemistry may wish to skip sections 10.3 and 14.2 on the Joule–Kelvin effect, as well as section 14.3 on adiabatic demagnetization.

Part III, on equilibrium and stability, contains the major features involved in the applications to chemistry. Again there is considerable flexibility in what one should, or should not, include at various levels of study. In introductory courses, some obvious candidates for omission are Chapter 17, sections 18.3 and 18.4, 20.3, and 21.4, and selected parts of Chapter 22. In choosing the subject matter for this part of the book, the author's strong affinity for the thermodynamics of phase equilibria is very apparent. The sections concerned attempt to give both a rather novel discussion of many features that have been "hidden" in the literature for a long time, as well as an initial presentation (as far as textbooks are concerned) of a number of recently published new ideas.

Part IV, dealing with some of the most important model systems, is obviously even more "open ended" than any of the preceding parts. The subject matter covers a wide range, from the derivation of the familiar equations for the colligative properties in dilute solutions (section 26.3) to a discussion of such esoteric topics as retrograde and barotropic phenomena (section 27.3). Obviously, one more time, readers and teachers can make a selection commensurate with their special interests. It is the fervent hope of the author that a study of the material *presented* will make the vast literature on topics *omitted* in this book much more accessible to readers.

In the appropriate chapters, readers will find some Exercises and Problems. The former contain primarily derivations and questions of a qualitative nature, which are woven into the text. The latter are mostly numerical applications and are given at the end of the relevant chapters. In both categories, some assignments are brief and very simple, others are much more challenging. Teachers "adopting" this book will undoubtedly wish to augment the various types of assignments with their own favorite examples. In selecting *units*, the author strongly feels that we should use those with which most of us are comfortable and which best express the magnitude they are trying to convey. There is no reason why we should not use an SI unit such as the joule, in lieu of the "rival" calorie, throughout most of this book. On the other hand, the author does not use SI units dogmatically; e.g., he balks at replacing atmospheres by pascals. Some relevant tables of units and conversion factors appear at the end of this book. Several other decisions had to be made regarding controversial issues involving notations and sign conventions. These are justified as they are encountered for the first time in the text.

In acknowledging all the help the author has received, directly and indirectly, he should first give credit to his teachers. As a sophomore chemical engineering student at Delft Institute of Technology, he had to take his first course on the subject in the *physics* department. This course was extremely hard to follow, and so was the textbook used, *De Beide Hoofdwetten der Thermodynamika*, by G. L. de Haas-Lorentz. It took many years to appreciate fully the approach taken, which was stimulated primarily by the writings of T. Ehrenfest-Afanassjewa. A few years later, this initial exposure was followed by a series of lectures on *chemical* thermodynamics by F. E. C. Scheffer, a brilliant classroom teacher. As a former pupil of Bakhuis-Roozeboom and van der Waals, Scheffer's interest was concentrated first and foremost in the area of chemical phase theory. This is reflected in some of the preferences of the present author, already referred to above.

In the summer of 1967, after having taught thermodynamics for fifteen years at various levels of sophistication, the author had the opportunity to attend a set of illuminating lectures on the subject by G. E. Uhlenbeck. These followed largely the methodology of *his* teacher, H. A. Lorentz, but were strongly flavored by Uhlenbeck's own penetrating insights. The present book has profited from the writings of many others, in the form of both articles and monographs. The indebtedness concerned is acknowledged in the relevant sections. At the end of several chapters, an annotated list of references is provided.

At the beginning of this preface we mentioned that this book is an outgrowth of the author's lectures on the subject. Thus he is indebted in the first place to many students, for their general encouragement as well as for their criticism of specific items. Good students are often the best teachers! The completion of this project owes much to Dr. Arlan D. Norman, who, as Chairman of the Chemistry Department of the University of Colorado at Boulder, lived up to his expressed conviction that writing a book of this nature is a valuable scholarly activity, which justifies *some* relief of teaching duties. Many colleagues, inside as well as outside this department, have offered advice on specific points. Their input is acknowledged in the appropriate chapters. In this context, a special word of thanks goes out to J. T. Hynes and S. J. Strickler, whose frequent counsel was invaluable.

This manuscript has been reviewed, and "rereviewed," by more peers than the author is able to recount. All this started with the critical reading of several "sample chapters" at the request of six potential publishers, and it finally ended with a third set of reviews on behalf of Prentice-Hall. Since most of the persons involved have remained anonymous (occasionally, the names of those who reviewed the same section of the manuscript at the same

time were released as a group*), it is only possible to convey to them a feeling of "collective gratitude." William E. Palke and John S. Winn deserve a special word of thanks for having read the *entire* manuscript *twice*. Since his services were solicited by the author, Bill Palke was the only reviewer who never had the opportunity to hide under the cloak of anonymity. By leveling more valuable criticism at the manuscript than all other reviewers taken together, he proved that lack of anonymity need not be a liability to being effective as a critic! Finally, a special word of thanks to Ellsworth G. Mason for his advice on problems of style and grammar.

From the above it should be crystal clear that the author has had the benefit of much advice and help. Writing this book has not only confirmed to him the controversial nature and intricate complexity of phenomenological equilibrium thermodynamics, but also his fallibility in mastering this subject. The latter condition alone should be held responsible for any remaining errors.

The author expresses his gratitude to the editors of Prentice-Hall, in particular Elizabeth G. Perry, the former chemistry editor, who showed enough confidence in him to offer a publication contract against the background of a highly competitive market. Her successor, Nancy L. Forsyth, coordinated the final phases of the reviewing process in a most efficient manner, and "launched" the manuscript into production.

Gail Maxwell typed the "sample" chapters for the initial reviews, and the first version of Part I of the manuscript. She also deserves credit for all the illustrations, in the sense that the professional draftsperson, later engaged by Prentice-Hall, had to do little but retrace her drawings. Vicky Nelson did a superb job in typing the rest of the manuscript, and bore with me through the tedious chore of making revisions and corrections.

Last, but not least, a special word of thanks to Nicholas Romanelli, who supervised the entire production process for Prentice-Hall. Thanks to his expertise, a very complex manuscript has been transformed into a book with a far better aesthetic appearance than the author ever thought possible.

Boulder, Colorado, April 1, 1985 Joseph de Heer

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* The following anecdotal point may give the teachers among the readers some food for thought. One of the scientists, whose name was revealed as one of those who was asked to evaluate the sample chapters, got his first instruction in thermodynamics from . . . the author!

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Part I

Basic Concepts and Definitions; Mathematical Techniques

Chapter 1

Thermodynamics as a Phenomenological Theory

This chapter introduces the essence of the author's approach to the subject. Alternative points of view are possible, depending on one's opinions about the structure of scientific theories.

1.1 A Few Remarks about the Philosophy of Science

According to one point of view, the philosophy of science addresses four topics: *location, structure, validation, and assessment.** In analyzing the *location* issue, one raises questions of domain, such as: Is mathematics (or sociology) a science? Or, with special reference to the topic of this book, one may ask whether the laws of thermodynamics can be applied to, e.g., biology or economics. The *structure* of thermodynamics constitutes the main topic of section 1.2. *Validation* deals with the justification of the methods used in science, the "inductive approach" in particular. This often leads one into what is frequently called "metaphysics," although the usage of the latter term is ambiguous. An elaboration would fall entirely outside the scope of this introduction. *Assessment* goes beyond these "logical" aspects of science; in stressing its "relevance" one is concerned with what Philip Frank has called its "sociological" aspects. To give a contemporary example, Berry has linked the need for waste recycling to thermodynamic concepts.† It should come as no surprise that questions of *assessment* are frequently tangled up with those of *location*. (See also section 1.3.)

* Peter J. Caws, *Scientific Research*, September 1967, p. 81.

† R. Stephen Berry, "The Option for Survival," *Bulletin of the Atomic Scientists*, May 1971, p. 22.