

THERMODYNAMICS

THIRD EDITION

Principles Characterizing
Physical and Chemical
Processes

J. M. Honig



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West Lafayette, Indiana



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Preface

The present volume involves several alterations in the presentation of thermodynamic topics covered in the previous editions. Obviously, it is not a trivial exercise to present in a novel fashion any material that covers a period of more than 160 years. However, as best as I can determine the treatment of irreversible phenomena in Sections 1.13, 1.14, and 1.20 appears not to be widely known. Following much indecision, and with encouragement by the editors, I have dropped the various exercises requiring numerical evaluation of formulae developed in the text. After much thought I have also relegated the Carathéodory formulation of the Second Law of Thermodynamics (and a derivation of the Debye–Hückel equation) as a separate chapter to the end of the book. This permitted me to concentrate on a simpler exposition that directly links entropy to the reversible transfer of heat. It also provides a neat parallelism with the First Law that directly connects energy to work performance in an adiabatic process. A more careful discussion of the basic mechanism that forces electrochemical phenomena has been provided. I have also added material on the effects of curved interfaces and self assembly, and presented a more systematic formulation of the basics of irreversible processes. A discussion of critical phenomena is now included as a separate chapter. Lastly, the treatment of binary solutions has been expanded to deal with asymmetric properties of such systems.

The aim, as before, has been to avoid as much as possible a presentation that is simply a linear superposition of discussions found in many other textbooks. Again, great stress is placed on the benefits of a systematic development of every topic, starting with modest beginnings, and reaping a whole cornucopia of results through self-contained logical operations and mathematical manipulations.

I am greatly indebted to many persons for providing help, advice, and criticism. Where appropriate I have acknowledged in footnotes the sources that I have closely followed in my expositions. In revising the earlier versions I am indebted to Professor Dor Ben-Amotz for many insightful discussions, especially those relating to irreversible phenomena. I also value the editorial help by personnel at Elsevier, Inc.

The book is dedicated to my parents who helped instill a love of the arts and sciences, to my late wife Gertrude Claryce Dahlbom Honig, to my present, equally wonderful wife, Josephine Neely Vamos Honig, and to the many children, both grown and young, who constitute the immediate family. All of them have been

very understanding in my complete absorption in the preparation of the current volume.

I hope the present volume will be found useful to all who are interested in the fascinating field of classical thermodynamics.

July 2006

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Preface to the Second Edition

The present volume is an upgraded version of a reference text published by Elsevier under the same title in 1982. The goals of the presentation have remained unaltered: to provide a self-contained exposition of the main areas of thermodynamics and to demonstrate how from a few fundamental concepts one obtains a whole cornucopia of results through the consistent application of logic and mathematical operations.

The book retains the same format. However, Section 1.16 has been completely rewritten, and several new sections have been added to clarify concepts or to add further insights. Principal among these are the full use of thermodynamic information for characterizing the Joule–Thomson effect, a reformulation of the basic principles underlying the operation of electrochemical cells, and a brief derivation of the Onsager reciprocity conditions. Several short sections containing sample calculations have also been inserted at locations deemed to be particularly instructive in illustrating the application of basic principles to actual problems. A special effort has also been made to eliminate the typographical errors of the earlier edition. The author would appreciate comments from readers that pertain to remaining errors or to obscure presentations.

It remains to thank those whose diligence and hard work have made it possible to bring this work to fruition: Ms. Virginia Burbrink, who undertook much of the enormous task of converting the typography of the earlier edition to the present word processor format; Ms. Gail Shively, who completed this onerous task and patiently dealt with all of the unexpected formatting problems; and Ms. Sophia Onayo, who compiled the index and the table of contents. Purdue University has provided a very comfortable milieu in which both the writing and the later revision of the book were undertaken.

It is a pleasure to express my appreciation to various individuals at Academic Press who encouraged me to prepare the revised text and who were most cooperative in getting the book to press.

Last, this task could not have been completed without the support of my beloved wife, Josephine Vamos Honig, who gave me much moral support after the death of my first wife, as well as during the book revision process, and to whom I shall remain ever grateful.

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Preface to the First Edition

The publication of yet another text on the well-explored topic of thermodynamics requires some commentary: such a venture may be justified on the grounds that as scientists our perceptions of any subject matter continually change; even as traditional and established an area as chemical thermodynamics is not exempt from such a subtle transmutation. Thus, there appears to be merit in a continuing series of expositions of the discipline of thermodynamics that differ perceptibly from linear combinations of discussions found in prior texts and monographs.

In the present volume there occur several departures from conventional treatments, among them: (i) the presentation of the Second Law based on a simplified approach to Carathéodory's method; (ii) a reasonably comprehensive treatment of thermodynamics of systems subjected to externally applied fields—special emphasis has been placed on the systematics of electromagnetic fields and on gas adsorption processes, concerning which there has been much confusion; (iii) detailed investigations on the uniqueness of predictions of properties of solutions, in the face of a bewildering array of standard states, of methods for specifying composition, and of equilibrium constants; (iv) a rationalization scheme for the interpretation of phase diagrams; (v) a discussion of the thermodynamics of irreversible processes, centered on the macroscopic equations. Most of the above topics are not covered in detail in existing texts.

Throughout, emphasis has been placed on the logical structure of the theory and on the need to correlate every analysis with experimental operating conditions and constraints. This is coupled with an attempt to remove the mystery that seems so often to surround the basic concepts in thermodynamics. Repeatedly, the attention of the reader is directed to the tremendous power inherent in the systematic development of the subject matter. Only the classical aspects of the problem are taken up; no attempt has been made to introduce the statistical approach, since the subject matter of classical thermodynamics is self-consistent and complete, and rests on an independent basis.

The course of study is aimed at graduate students who have had prior exposure to the subject matter at a more elementary level. The author has had reasonable success in the presentation of these topics in a two-semester graduate class at Purdue University; in fact, the present book is an outgrowth of lecture notes for this course. No worked numerical examples have been provided, for there exist many excellent books in which different sets of problems have been worked out in detail. However, many problems are included as exercises at various levels of difficulty, which the student can use to become facile in numerical work.

The author's indebtedness to other sources should be readily apparent. He profited greatly from fundamental insights offered in two slim volumes: *Classical Thermodynamics* by H.A. Buchdahl and *Methods of Thermodynamics* by H. Reiss. Also, he found instructive the perusal of sources, texts, and monographs on classical thermodynamics authored by C.J. Adkins, I.V. Bazarov, H.B. Callen, S. Glasstone, E.A. Guggenheim, G.N. Hatsopoulos and J.H. Keenan, W. Kauzmann, J. Kestin, R. Kubo, P.J. Landsberg, F.H. MacDougall, A. Münster, A.B. Pippard, I. Prigogine, P.A. Rock, and M.W. Zemansky. Specific sources that have been consulted are acknowledged in appropriate sections in the text. He is greatly indebted to Professor L.L. Van Zandt for assistance in formulating the thermodynamic characterization of electromagnetic fields. Most of all, he has enormously profited from the penetrating insight, unrelenting criticism, and incisive comments of his personal friend and colleague Professor J.W. Richardson. Obviously, the remaining errors are the author's responsibility, concerning which any correspondence from readers would be appreciated.

It is a pleasant duty to acknowledge the efforts of several secretaries, Jane Biddle, Cheryl Zachman, Nancy Holder, Susan Baker, and especially Konie Young and Barbara Rosenberg—all of whom cheerfully cooperated in transforming illegible sets of paper scraps into a rough draft. Special thanks go to Hali Myers, who undertook the Herculean task of typing the final version; without her persistence the manuscript could not have been readied for publication. Dr. Madhuri Pai contributed greatly by assisting with the proofreading of the final manuscript.

In a matter of personal experience, it is appropriate to acknowledge several meaningful discussions with my father, the late Richard M. Honig, who was an expert in jurisprudence and who readily saw the parallels between scientific methodology and the codification of law. He persisted with questions concerning the nature of thermodynamics that I could not readily answer and was thereby indirectly responsible for the tenor of the present volume.

Last, it is important to thank my immediate family, particularly my beloved wife, Trudy, for much patient understanding and for many sacrifices, without which the work could have been neither undertaken nor completed.

J.M. Honig
July 1981

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Chapter 1

Fundamentals

1.0 Introductory Remarks

Thermodynamics is an overarching discipline in the sense that all physical phenomena can be described and analyzed in terms of a general macroscopic framework that contains parameters which may be determined by experiment. It is truly remarkable that with the minimal input of only four postulates, and by the systematic application of mathematical logic, a whole cornucopia of results can be produced for use in the interpretation of experiments and for predictive purposes in a wide variety of physical disciplines. In this book an attempt will be made to stress both the systematics that provides the cornucopia as well as the need to establish a close link between theory and experiment. The exposition will encompass mostly the areas of physical chemistry and parts of physics, but the principles expounded below should enable the reader to apply the thermodynamic discipline and methodology to other areas of research.

The fundamental concepts are introduced in the form of four basic laws. The procedure is reasonably axiomatic, so that one can deal with (i) the concept of temperature without initially having to refer to heat flow; (ii) the definition of energy as a function of state, and the definition of heat flow as a deficit function; (iii) the introduction of the entropy function that does not depend on a generalization of the performance characteristics of heat engines. A comparison of the entropy changes for a given process carried out reversibly and irreversibly is then used to obtain a variety of fundamental results. This in a natural manner leads to the introduction of several functions of state; considerable emphasis is placed on systematically exploiting their mathematical properties. The important concept of homogeneous functions of degree one is then introduced and is used to analyze the properties of open systems. This chapter ends with a study of stability problems.

The reader should investigate not only the details of the derivations but also the internal structure of every presentation, and should note the benefits of a systematic approach to the study of thermodynamic principles.

1.1 Introductory Definitions

Before launching into the concepts of thermodynamics it is important to agree on the meaning of several basic terms. These are discussed below:

System. A region in space that is identified as a useful object of study and set apart from the remainder of the cosmos for that purpose.

Surroundings. Regions immediately outside and contiguous to the system.

Boundaries. Partitions separating a system from its surroundings.

Comments. It is very important to set boundaries properly and to distinguish appropriately between system and surroundings. Failure to do so can lead to erroneous conclusions. Boundaries may be real, such as walls or partitions, or may be conceptual, such as geometric surfaces.

Body. The content of a specific system.

Comments. To be amenable to thermodynamic treatment an actual body must be of adequate size, such that normal fluctuations in its properties are minute compared to their average values, and such that physical measurements do not significantly perturb the properties of the body. The volume of such a body must generally be at least of the order of 10^{-15} cm^{-3} .

Homogeneous vs. heterogeneous systems. Homogeneous systems are uniform in properties over their entire volume. Otherwise such systems are heterogeneous.

Subsystem. A portion of the region of a system singled out for special study.

Isolated systems. Systems totally unresponsive to any changes that occur in the surroundings, or that have no surroundings.¹

Closed (open) systems. Systems in which transfer of matter to or from the surroundings cannot (can) occur. A closed system may nevertheless be subject to manipulation through external agents such as electric or magnetic fields.

Permeable (semipermeable) boundaries. Boundaries that enclose an open system (that permit passage of certain chemical species while excluding other species).

Adiabatic systems. Systems whose properties are unaffected when their surroundings are heated or cooled.

Comment. A more appropriate definition for an adiabatic system will be provided in Section 1.7.

Phase. A physically and chemically homogeneous macroscopic region in a system.

Comment. In a system there may exist several sub-regions in distinct states of aggregation or composition.

Diathermic boundaries. Boundaries that do not permit matter to be exchanged between systems and their surroundings but that permit changes to take place in properties of the system by heating or cooling of the surroundings.

Thermodynamic properties. Physical or chemical attributes that specify the characteristic properties of a system.

Thermodynamic equilibrium. A state of a system where, as a necessary condition, none of the properties under study changes with time.

Comments. It is not a simple matter to determine whether a system is at equilibrium. One method described later involves subjecting the system to some process that takes the system away from its quiescent state under a set of prescribed conditions. If, on release of the constraint, the response is out of proportion to such a process and if the system does not then return to its original state it could not have been at equilibrium. If the system does return to its initial state without incurring any other changes in the universe then it is said to be in equilibrium with respect to the tests that have been conducted. It may be very difficult to decide whether equilibrium prevails in systems prone to very sluggish processes. In such situations one attempts to establish a relaxation time over which significant changes in properties are detectable when the system is externally perturbed. It is generally agreed that equilibrium prevails when no changes can be detected over intervals very large compared to the relaxation time.²

Reservoir. A source or sink used to exchange matter with, or through appropriate interactions, to alter the properties of an attached system. A reservoir is assumed to be of such immense size that its properties remain essentially unaltered during any interactions with the system.

Thermodynamic coordinates, variables, degrees of freedom. All three are used to designate linearly independent experimental macroscopic variables that are required to characterize the state of a system.

Comments. A minimum number of such variables is required to describe systems at equilibrium; their values do not depend on the manner in which the equilibrium state is reached.

Intensive (extensive) variables. Variables whose values are independent of (depend on) the size and/or quantity of matter contained in a system under study.

State space, configuration space, phase space. An abstract space spanned by coordinate axes, one for each thermodynamic coordinate, on which a given point represents the numerical value of that coordinate. A hyperspace is then formed by a mutually orthogonal disposition of these axes about a common origin.

Representative point. A point in phase space that corresponds to the state or characteristics of the system for which the state space was constructed.

Path. A succession of states traversed by a system in passing from a given initial to a given final state.

Quasistatic process. One that involves passage through a large succession of very closely spaced equilibrium states. In this process the surroundings may be altered such that on the return path to the original system configuration the universe ends up in a different state.

Reversible process. One whose path may be exactly reversed though a succession of very closely spaced equilibrium states, such that on reversal of the path both the system and its surroundings are restored to their original state.

Comments. The distinction between quasistatic and reversible processes may be illustrated by considering the magnetization of a paramagnetic and of a ferromagnetic material. In a paramagnet the gradual application of a magnetic field slowly magnetizes the sample, which can then be completely demagnetized by slowly eliminating the magnetic field—this process is reversible. A ferromagnet can be slowly magnetized by gradual application of a magnetic field, but on gradual elimination of the field the material remains partially magnetized. Here, a succession of equilibrium states, followed by the reverse, leaves the system in an altered configuration. This is an example of a quasistatic process. Reversible processes are necessarily quasistatic, but the reverse may not hold.

Steady state processes. Processes which do not alter the state of a system but do change the surroundings.

Comments. At equilibrium no changes in properties occur with time either in the system or in its surroundings. However, under steady state conditions inputs and outputs of the system remain in balance so that the properties of the system are not altered, but changes do occur in the surroundings as a result of such processes.³ A more scientific characterization is provided in Chapter 6.

Number of Independent Components. The least number of chemically distinct species whose mole numbers must be specified to prepare a particular phase.

Comments. Due account must be taken of any prevailing chemical equilibria since in such cases the concentrations of the various participating species cannot all be independently altered. The number of independent components may then be determined from the number of distinct chemical compounds present in the system minus the number of chemical equations that specify their interactions. This matter is taken up in Section 2.1.

Number of Degrees of Freedom. The number of state variables that can be altered independently and arbitrarily, within limits, without changing the number of phases within the system.

Before proceeding it is taken for granted that the reader has an intuitive understanding of the concept of mass and volume. Much of the subsequent discussion will initially be based on these concepts.

REMARKS AND QUERIES

- 1.1.1. The universe is an excellent paradigm of an isolated and closed system. Ordinarily, events occurring at astronomical time scales may be ignored in the consideration of physical and chemical processes occurring in the laboratory.
- 1.1.2. As an example of problems involving long time scales consider the reaction of hydrogen and oxygen in a balloon at room temperature. The fact that there seems to be no detectable change in the concentration of either constituent over many months does not mean that the system is equilibrated: insertion of platinum black as a catalyst leads to a measurable rate of formation of water, and heating the balloon with a torch leads to a violent reaction.