

STUDIES IN MODERN THERMODYNAMICS 4

THERMO- DYNAMICS

Principles Characterizing
Physical and Chemical Processes

J.M. HONIG

ELSEVIER SCIENTIFIC PUBLISHING COMPANY

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1 **Biochemical Thermodynamics** edited by M.N. Jones

2 **Principles of Thermodynamics** by J.A. Beattie and I. Oppenheim

3 **Phase Theory** by H.A.J. Oonk

PREFACE

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 changes; 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 which 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. T. Landsberg, F. H. MacDougall, A. Münster, A. B. Pippard, I. Prigogine, P. A. Rock, M. W. Zemansky. Specific sources which 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 proof-reading 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 which I could not readily answer and was thereby indirectly responsible for the tenor of the present volume.

Lastly, 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

TABLE OF CONTENTS

	Page
PREFACE.	v
CHAPTER 1	
FUNDAMENTALS	1
1.0 Introductory Comments.	1
1.1 Introductory Definitions	1
1.2 Temperature and the Zeroth Law of Thermodynamics	6
1.3 Temperatures, Temperature Scales, and Temperature Measurements	8
1.4 Mathematical Apparatus	14
1.5 Thermodynamic Forces	25
1.6 The Concept of Work.	27
1.7 Appendix. Derivation for the Element of Work in the Presence of Electromagnetic Fields.	37
1.8 The First Law of Thermodynamics and the Concept of Heat.	39
1.9 The First Law of Thermodynamics as a Parable	47
1.10 The Carathéodory Approach to the Second Law of Thermodynamics. Preliminaries.	48
1.11 Appendix. Mathematical Preparations for the Second Law of Thermodynamics. Holonomicity.	50
1.12 Appendix. Mathematical Proof for the Necessary Condition of Carathéodory's Theorem	55
1.13 The Second Law of Thermodynamics	58
1.14 An Entropy Analogy	63
1.15 Cyclic Processes in Relation to Reversibility and Irreversibility. Carnot Efficiency.	64
1.16 Constraints and Equilibrium.	70
1.17 Correlation of Temperatures, Entropies, and Energies	76
1.18 Functions of State in Thermodynamics	80
1.19 Heat, Calorimetry, and Thermochemistry	95
1.20 Numerical Calculation of Entropies	100
1.21 The Third Law of Thermodynamics.	108
1.22 The Gibbs-Duhem Equation and Its Analogs	112
1.23 Thermodynamics of Open Systems	118
1.24 Inequalities in Thermodynamics	125

CHAPTER 2	Page
EQUILIBRIUM IN IDEAL SYSTEMS.	128
2.0 Thermodynamics of Ideal Systems with Several Components and Phases.	128
2.1 Coexistence of Phases: The Gibbs Phase Rule.	128
2.2 Achievement of Equilibrium.	132
2.3 Systems of One Component and Several Phases: The Clausius-Clapeyron Equation.	136
2.4 Properties of Ideal Gases	146
2.5 Properties of Ideal Solutions in Condensed Phases	151
2.6 The Duhem-Margules Equation and its Consequences.	155
2.7 Temperature Dependence of Composition of Solutions.	157
2.8 Lowering of the Freezing Point and Elevation of the Boiling Point of a Solution	158
2.9 Chemical Equilibrium: General Principles and Application to Ideal Gases.	163
2.10 Chemical Equilibrium in Homogeneous Ideal Solutions	171
2.11 Chemical Equilibrium in Ideal Heterogeneous Systems	174
2.12 Equilibrium Involving Ideal Mixtures in Two Phases.	178
2.13 Entropy Production During Irreversible Processes.	180
2.14 Entropy and Irreversibility in Chemical Reactions: The Chemical Affinity	181
 CHAPTER 3	
CHARACTERIZATION OF NONIDEAL SYSTEMS.	184
3.0 Introductory Remarks.	184
3.1 Thermodynamic Treatment of Nonideal Gases	184
3.2 Temperature and Pressure Dependence of Activity Coefficients for a Gas	188
3.3 Thermodynamic Treatment of Real Solutions	190
3.4 Characterization of Nonideal Solutions. Preliminaries.	192
3.5 Standardization of Thermodynamic Descriptions of Nonideal Solutions	197
3.6 Reformulation of the Thermodynamic Description of Nonideal Solutions	203
3.7 Characterization of Equilibrium in Nonideal Solutions	205
3.8 Thermochemistry	217
3.9 Reduction to Ideal Cases.	220
3.10 Variations of Activity, Activity Coefficients, and Equilibrium Constants with Temperature and Pressure	222

Page

3.11	Determination of Activity Coefficients by Measurement of Vapor Pressures.	226
3.12	Activity of Solvent and Solute from Lowering of Freezing Point Data	237
3.13	Mixing in Nonideal Solutions	241
3.14	Phase Stability: General Consequences of Deviations from Ideality	250
3.15	Discussion of Several Types of Phase Diagrams.	257
3.16	Variation of Mutual Solubility with Temperature.	266

CHAPTER 4

THERMODYNAMIC PROPERTIES OF ELECTROLYTES		274
4.0	Introductory Comments.	274
4.1	Activities and Activity Coefficients for Strong Electrolytes	274
4.2	Theoretical Determination of Activities in Electrolyte Solutions: The Debye-Hückel Equation.	278
4.3	Experimental Determination of Activities and Activity Coefficients of Strong Electrolytes.	281
4.4	Equilibrium Properties of Weak Electrolytes.	287
4.5	The Electrochemical Potential.	291
4.6	Galvanic and Electrolysis Cells: General Discussion	293
4.7	Galvanic Cells: General Treatment	296
4.8	Types of Electrodes.	304
4.9	Liquid Junction Potentials	305
4.10	Concentration and Activity Dependence of the EMF	308
4.11	Types of Operating Cells	311
4.12	Thermodynamic Quantities from EMF Measurements	316
4.13	Applications of EMF Measurements	318

CHAPTER 5

THERMODYNAMIC PROPERTIES OF SYSTEMS IN EXTERNAL FIELDS

5.0	Introductory Commentary.	324
5.1	Thermodynamics of Gravitational Fields	324
5.2	Adsorption Thermodynamics.	330
5.3	Heats of Adsorption.	343
5.4	Thermodynamics of Radiation.	351
5.5	Appendix: Alternative Derivation for Radiation Pressure	355

	Page
5.6 Effects of Electric Fields on Thermodynamic Properties of Matter.	357
5.7 Appendix: Methods for Treatment of Integrals with Variable Limits.	367
5.8 Thermodynamic Properties of Electromagnetic Fields: Systematics and Low Temperature Effects	368
5.9 Transitions to the Superconducting State (Soft Superconductors).	379
CHAPTER 6	
IRREVERSIBLE THERMODYNAMICS	382
6.0 Introduction.	382
6.1 Shock Phenomena	382
6.2 Irreversible Thermodynamics: Introductory Comments - The First and Second Laws in Local Form	390
6.3 The Linear Phenomenological Equations, and the Onsager Reciprocity Conditions.	398
6.4 Steady-State Conditions and Prigogine's Theorem	401
6.5 Thermomolecular Mechanical Effects.	403
6.6 The Soret Effect.	406
6.7 Electrokinetic Phenomena.	408
6.8 Thermoelectric Effects.	414
6.9 Irreversible Phenomena in Two Dimensions.	418
6.10 Chemical Processes.	423
6.11 Coupled Reactions: Special Example	426
6.12 Coupled Reactions: General Case	428
CHAPTER 7	
FINAL SPECULATION ABOUT ULTIMATE TEMPERATURES - THE FOURTH LAW OF THERMODYNAMICS.	431
INDEX	433

(e) Homogeneous and Heterogeneous System: A homogeneous system is uniform throughout in all its physical properties. A heterogeneous system is comprised of several different homogeneous parts in close proximity.

(f) Subsystem: A portion of a system, singled out for special study.

(g) Continuous System: One whose physical properties vary continuously as a function of position within the system.

(h) Open (Closed) Systems: Systems in which an exchange of matter with its surroundings are (are not) allowed to occur.

(i) Permeable Boundaries: Boundaries that enclose an open system.

(j) Semipermeable Boundaries: Boundaries which permit passage of certain chemical species, but which are impenetrable to others.

(k) Diathermic Boundaries: Boundaries which are impermeable to matter flow but which permit other changes to occur inside the enclosed system through heating or cooling of the surroundings.

(l) Adiabatic Boundaries and Systems: Boundaries which are impervious to matter flow and which render the enclosed system totally unresponsive to processes in which the surroundings are heated or cooled.

(m) Isolated System: One which is surrounded by boundaries which render the enclosed system totally unresponsive to any changes in the surroundings.

Commentary: For a distinction between adiabatically isolated and completely isolated systems, see Ex. 1.1.7. One should also note that systems may be perturbed through external manipulations of applied fields (e.g., electromagnetic, radiation, or gravitational fields). These perturbations can be achieved in all situations excepting the isolated system. Boundaries of a system may be physical, or, in some cases, imaginary ones.

(n) Thermodynamic Properties: Physical attributes that are selected for a description of systems on a macroscopic scale.

(o) Thermodynamic Equilibrium: A state of the system where, as a necessary condition, none of its properties changes measurably over a period of time exceedingly long compared to any possible observations on the system.

Commentary: In each instance the system needs to be checked out, as a sufficiency condition, by subjecting it through external manipulations to all sorts of changes in properties. If the response is out of proportion to such applied deformations and the system cannot be returned to its earlier state on lifting the deformations, it could not have been at equilibrium: If the system is restored to its initial state on completion of the checking process, the system is at equilibrium with respect to the tests that have been conducted.

In practice it may be difficult to decide whether the equilibrium state has been achieved or not, especially if the system is subject to very sluggish processes. In particular, sufficient time must be allowed for a system to complete its response to external perturbations. Generally, it is acceptable to

ignore processes which are so slow as to produce no significant changes over time periods that are long compared to the observation interval. For example, one may usually ignore the effect of cosmological changes on everyday laboratory experiments. A reasonable rule of thumb involves the relaxation time of any process: where the latter is very large compared to the interval of the measurements on the system one may regard a state of equilibrium or steady state to have prevailed during the experimentation.

As an example of problems arising in connection with the sufficiency condition, consider the case of a mixture of H_2 and O_2 in a balloon at room temperature. The fact that there is no important change in the content of the balloon over many hours does not establish that equilibrium prevails, as the introduction of platinum black as a catalyst shows: A small disturbance of the system in this manner leads to a large, irreversible change in its properties. On the other hand, once H_2 , O_2 , and H_2O are formed in appropriate amounts, changes introduced by heating and cooling are reversible and lead to only small excursions of the system from its newly formed state.

(p) Reservoir: A source or sink used for exchanging matter with the system or altering the properties by suitable manipulations to be discussed later. A reservoir is always assumed to be of such large size that its physical characteristics remain essentially unaffected during any exchange process.

(q) Coordinates, Variables (of State), Degrees of Freedom: All three refer to quantities needed to characterize the state of a system at any instant.

Commentary: Ordinarily one selects a linearly independent set of variables for the above characterization. For systems at equilibrium this characterization is achieved with a minimum number of coordinates whose values are independent of the history by which the equilibrium state was reached.

(r) Intensive (Extensive) Variables: Variables whose value is independent of (depends on) the size and the quantity of matter within the region which is being scrutinized.

(s) Thermodynamic Function of State: A mathematical interrelation between several variables of state, which describes a property of the system.

Commentary: Generally, such functions are useful only where a system is at or very close to equilibrium, because only in these circumstances can a simple functional interrelation be anticipated.

(t) State Space, Configuration Space, or Phase Space: An abstract space constructed as an aid in the visualization of processes. Each variable is assigned an axis on which any point represents a numerical value of the variable. A (hyper-) space is then formed by a mutually orthogonal disposition of these axes about a common origin.

(u) Representative Point: Any point in phase space which reflects the physical properties of the system for which the phase space was constructed.

(v) Macroscopic Process: Any change in the system which leads to an alteration of its large-scale properties.

(w) Path: The succession of states traversed by the system in its passage from an initial state to a final state.

(x) Quasistatic Process: One which consists of a succession of equilibrium states, each of which differs only infinitesimally from its predecessor. The surroundings may be irretrievably altered in such a transition, and in a return path, the universe may end up in a final state which differs from the initial state.

(y) Reversible Process: One whose path may be exactly reversed by an infinitesimal change in operating conditions; the original state of a system undergoing such a process may be restored without incurring any other changes in the universe.

(z) Irreversible Process: One which occurs spontaneously, generally while the system exhibits severe departures from equilibrium. The original state of the system which has undergone an irreversible change can be restored only at the expense of other permanent changes in the universe.

Commentary: Not all conceivable processes to which a system could in principle be subjected can actually be realized; we shall encounter such cases later. Operationally, the distinction between reversible and irreversible processes introduces an element of patience. Only if one waits a long time between successive steps which involve just infinitesimal alterations in the system can one hope to produce reversible changes. Clearly, all dissipative effects such as friction must be avoided also.

The distinction between quasistatic and reversible processes may be illustrated by an example. In a paramagnetic material a slow increase and subsequent decrease of the applied magnetic field leads to a gradual magnetization and subsequent gradual restoration of the initial unmagnetized state. In a ferromagnetic medium, the gradual application of a magnetic field will lead to a progressive magnetization of the system, but on gradual removal of the applied field, hysteresis effects cause the system to go, in a succession of quasistatic states, to a different final state, in which a degree of magnetization is preserved even in the absence of the field. Thus, a reversible process is necessarily quasistatic, but the converse may not hold.

(aa) Steady State Process: Processes which induce no net alterations in the state of a system but which do alter the state of the surroundings.

Commentary: Steady state conditions are distinguished from equilibrium by the occurrence of processes in which inputs and outputs for the systems remain in balance, so that no net alterations occur within the system. However, those processes do cause alterations in the surroundings. For example, in the passage of a constant electric current through a wire, which is the system, the number

of electrons in any section of the wire remains constant because of the requirement of conservation of charge. The rise in temperature due to joule heating will ultimately be balanced off by increased heat flow to the surroundings. The wire is then involved in a steady state process. However, the battery which produces the current and the surroundings to the wire undergo irreversible changes.

(bb) Fictitious Processes: These are changes which can be forced on a system in a thought-experiment but cannot be performed in actuality.

Commentary: Such processes are useful aids for visualization and didactic purposes; an early example is provided in Sec. 1.5.

The above discussion points up a matter of tacit understanding. It is presumed that the reader possesses an intuitive grasp of the concept of mass and of mechanical variables, such as volume V or pressure p . By contrast, items relating to the transfer of energy must be very carefully explained through the various laws of thermodynamics before they are utilized. We shall also be able at a later point to supply better definitions for adiabatic and diathermic processes, and for steady-state conditions.

EXERCISES

1.1.1 Is it appropriate to classify a definition as being correct or incorrect? Conventional or unconventional? Complete or incomplete? Consistent or inconsistent?

1.1.2 If a definition is labelled as differing from the accepted norm, does that make the definition incorrect?

1.1.3 Are there any conceivable circumstances under which a proffered definition should be rejected? Explain.

1.1.4 A solid is connected to a battery by wires and a current is allowed to flow. Must the battery be considered as a part of the system? Explain.

1.1.5 An electrical heater is imbedded in a solid, and connecting wires are attached to a 110 volt line. Is the heater necessarily part of the system which includes the solid? Explain.

1.1.6 Provide several examples which illustrate the distinction between quasistatic and reversible processes.

1.1.7 Distinguish clearly between boundaries which enclose an adiabatic and those which enclose an isolated system. For this purpose, enumerate several changes in surroundings which can alter the properties of an adiabatically enclosed system.

1.2 TEMPERATURE AND THE ZEROth LAW OF THERMODYNAMICS

The zeroth law of thermodynamics is based on a statement which emphasizes the transitive property that two bodies in equilibrium with a third are in equilibrium with each other. Here we restrict ourselves to the case where the mechanical variables of pressure p and volume V suffice to describe a system at equilibrium; however, this approach can easily be generalized.

Consider a system enclosed by diathermic walls. As explained in Sec. 1.1, these enclosures prevent exchange of matter but do permit changes in state of the system by manipulations of the surroundings. An example of this situation is provided by a Bunsen burner that is placed below a flask containing ice, water and vapor; the diathermic glass walls of the beaker permit the ice to melt in response to the application of a flame exterior to the system (ice, water, steam) and boundary (flask).

Let two different systems be brought in contact with each other through diathermic walls. In a field-free region let system 1 be characterized by pressure p_1 and volume V_1 and system 2, by pressure p_2 and volume V_2 . Surround the composite system 1 + 2 by an isolating boundary and establish equilibrium. It is then the experience of mankind that the four quantities p_1, V_1, p_2, V_2 can no longer be varied arbitrarily and independently. Rather, having set three of the variables at specific values, the fourth is no longer adjustable but is determined by the chosen values for the others. This constraint may be manifested mathematically as a functional relation among the variables:

$$\beta_3(p_1, V_1, p_2, V_2) = 0 \quad (1.2.1)$$

where β_3 expresses the interrelation among the four variables appearing in the argument. In principle Eq. (1.2.1) may be solved for any one of the quantities in terms of the remaining three.

We now repeat the discussion for the distinct systems 1 and 3 which are to be combined into a composite and allowed to equilibrate; at equilibrium another functional interrelation holds, namely

$$\beta_2(p_1, V_1, p_3, V_3) = 0 \quad (1.2.2)$$

Likewise, combining systems 2 and 3 into a composite at equilibrium, we obtain

$$\beta_1(p_2, V_2, p_3, V_3) = 0 \quad (1.2.3)$$

The Zeroth Law of Thermodynamics asserts that if two bodies are in equilibrium with a third they are in equilibrium with each other.

As a result of the zeroth law Eqs. (1.2.1) and (1.2.2) imply Eq. (1.2.3). More generally, the applicability of any two of these relations implies the validity of the third.

As with any other law in science, the above statement cannot be accepted or rejected by a priori arguments. It is, instead, necessary to examine the physical consequences of the statement and to ascertain whether all physical observations are compatible with the law. This we proceed to do below.

Inasmuch as equilibrium has prevailed, system 3 has remained unaltered in the union with systems 1 or 2. Therefore, we rewrite (1.2.2) and (1.2.3) as

$$p_3 = \phi_1(p_2, V_2, V_3) = \phi_2(p_1, V_1, V_3) \quad (1.2.4)$$

in which we have 'solved' for p_3 , which thereby becomes the dependent variable. From (1.2.4) we obtain by difference a function termed λ , namely

$$\phi_1(p_2, V_2, V_3) - \phi_2(p_1, V_1, V_3) \equiv \lambda(p_1, V_1, p_2, V_2, V_3) = 0. \quad (1.2.5)$$

Comparing (1.2.5) with (1.2.1) and invoking the zeroth law one notes a glaring inconsistency, in that there appears to be a functional dependence of λ on V_3 which is absent from the function β_3 . Clearly, it makes no sense to have to refer to system 3 when considering the property of systems 1 + 2 in isolation. To preserve consistency we must demand that V_3 occur in ϕ_1 and ϕ_2 in such a manner that it cancels when Eq. (1.2.5) is constructed. This goal may be achieved in the most general form by writing

$$\phi_1 = \phi_1(p_2, V_2, V_3) = f_2(p_2, V_2) h(V_3) + q(V_3) \quad (1.2.6)$$

$$\phi_2 = \phi_2(p_1, V_1, V_3) = f_1(p_1, V_1) h(V_3) + q(V_3) \quad (1.2.7)$$

where f , h , and q are general functions of the indicated variables. Substitution in (1.2.4) thus yields

$$f_1(p_1, V_1) = f_2(p_2, V_2) \quad (1.2.8)$$

Similarly, consistent with the zeroth law,

$$f_1(p_1, V_1) = f_3(p_3, V_3) \quad (1.2.9)$$

Observe how in each case reference is now made only to the variables for the system under observation. Eqs. (1.2.8) or (1.2.9) may thus be used to characterize equilibrium. Moreover, Eq. (1.2.8) and (1.2.9) permit us to