THERMODYNAMICS
AND AN INTRODUCTION TO
THERMOSTATISTICS

SECOND EDITION

HERBERT B. CALLEN

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PREFACE

Twenty-five years after writing the first edition of *Thermodynamics* I am gratified that the book is now the thermodynamic reference most frequently cited in physics research literature, and that the postulational formulation which it introduced is now widely accepted. Nevertheless several considerations prompt this new edition and extension.

First, thermodynamics advanced dramatically in the 60s and 70s, primarily in the area of critical phenomena. Although those advances are largely beyond the scope of this book, I have attempted to at least describe the nature of the problem and to introduce the critical exponents and scaling functions that characterize the non-analytic behavior of thermodynamic functions at a second-order phase transition. This account is descriptive and simple. It replaces the relatively complicated theory of second-order transitions that, in the view of many students, was the most difficult section of the first edition.

Second, I have attempted to improve the pedagogical attributes of the book for use in courses from the junior undergraduate to the first year graduate level, for physicists, engineering scientists and chemists. This purpose has been aided by a large number of helpful suggestions from students and instructors. Many explanations are simplified, and numerous examples are solved explicitly. The number of problems has been expanded, and partial or complete answers are given for many.

Third, an introduction to the principles of statistical mechanics has been added. Here the spirit of the first edition has been maintained; the emphasis is on the underlying simplicity of principles and on the central train of logic rather than on a multiplicity of applications. For this purpose, and to make the text accessible to advanced undergraduates, I have avoided explicit non-commutivity problems in quantum mechanics. All that is required is familiarity with the fact that quantum mechanics predicts discrete energy levels in finite systems. However, the formulation is designed so that the more advanced student will properly interpret the theory in the non-commutative case.

Fourth, I have long been puzzled by certain conceptual problems lying at the foundations of thermodynamics, and this has led me to an interpretation of the "meaning" of thermodynamics. In the final chapter—an "interpretive postlude" to the main body of the text—I develop the thesis that thermostatistics has its roots in the *symmetries* of the fundamental laws of physics rather than in the quantitative content of those laws. The discussion is qualitative and descriptive, seeking to establish an intuitive framework and to encourage the student to see science as a coherent structure in which thermodynamics has a natural and fundamental role.

Although both statistical mechanics and thermodynamics are included in this new edition, I have attempted neither to separate them completely nor to meld them into the undifferentiated form now popular under the rubric of "thermal physics." I believe that each of these extreme options is misdirected. To divorce thermodynamics completely from its statistical mechanical base is to rob thermodynamics of its fundamental physical origins. Without an insight into statistical mechanics a scientist remains rooted in the macroscopic empiricism of the nineteenth century, cut off from contemporary developments and from an integrated view of science. Conversely, the amalgamation of thermodynamics and statistical mechanics into an undifferentiated "thermal physics" tends to eclipse thermodynamics. The fundamentality and profundity of statistical mechanics are treacherously seductive; "thermal physics" courses almost perforce give short shrift to macroscopic operational principles.* Furthermore the amalgamation of thermodynamics and statistical mechanics runs counter to the "principle of theoretical economy"; the principle that predictions should be drawn from the most general and least detailed assumptions possible. Models, endemic to statistical mechanics, should be eschewed whenever the general methods of macroscopic thermodynamics are sufficient. Such a habit of mind is hardly encouraged by an organization of the subjects in which thermodynamics is little more than a subordinate clause.

The balancing of the two distinct components of the thermal sciences is carried out in this book by introducing the subject at the macroscopic level, by formulating thermodynamics so that its macroscopic postulates are precisely and clearly the theorems of statistical mechanics, and by frequent explanatory allusions to the interrelationships of the two components. Nevertheless, at the option of the instructor, the chapters on statistical mechanics can be interleaved with those on thermodynamics in a sequence to be described. But even in that integrated option the basic macroscopic structure of thermodynamics is established *before* statistical reasoning is introduced. Such a separation and sequencing of the subjects

*The American Physical Society Committee on Applications of Physics reported [*Bulletin of the APS*, Vol. 22 #10, 1233 (1971)] that a survey of industrial research leaders designated thermodynamics above all other subjects as requiring increased emphasis in the undergraduate curriculum. That emphasis subsequently has *decreased*.

preserves and emphasizes the hierarchical structure of science, organizing physics into coherent units with clear and easily remembered interrelationships. Similarly, classical mechanics is best understood as a self-contained postulatory structure, only *later* to be validated as a limiting case of quantum mechanics.

Two primary curricular options are listed in the "menu" following. In one option the chapters are followed in sequence (Column A alone, or followed by all or part of column B). In the "integrated" option the menu is followed from top to bottom. Chapter 15 is a short and elementary statistical interpretation of entropy; it can be inserted immediately after Chapter 1, Chapter 4, or Chapter 7.

The chapters listed below the first dotted line are freely flexible with respect to sequence, or to inclusion or omission. To balance the concrete and particular against more esoteric sections, instructors may choose to insert parts of Chapter 13 (Properties of Materials) at various stages, or to insert the Postlude (Chapter 21, Symmetry and Conceptual Foundations) at any point in the course.

The minimal course, for junior year undergraduates, would involve the first seven chapters, with Chapter 15 and 16 optionally included as time permits.

Philadelphia, Pennsylvania **Herbert B. Callen**

1. Postulates	
	15.
2. Conditions of Equilibrium	
3. Formal Relations and Sample Systems	
4. Reversible Processes; Engines	
	15. Statistical Mechanics in Entropy Representation
5. Legendre Transformations	
6. Extremum Principles in Legendre Representation	
7. Maxwell Relations	
	15.
	16. Canonical Formalism
	17. Generalized Canonical Formulation
8. Stability	
9. First-Order Phase Transitions	

- - -

10. Critical Phenomena	18. Quantum Fluids
11. Nernst	19. Fluctuations
12. Summary of Principles	20. Variational Properties and Mean Field Theory
13. Properties of Materials	
14. Irreversible Thermodynamics	

- - -

21. Postlude: Symmetry and the Conceptual Foundations of Thermodynamics

Errata for Callen / Thermodynamics & Intro. to Thermostatistics, 2nd ed.
Please send additional corrections to the author, at

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P 21 Label on ordinate of Figure should be $10^5/32$ instead of 10^4.

P 25 In answer to Prob. 1.8-6:

$U-U_0 = A(P r^{\gamma} - P_0) + ...$ instead of $U-U_0 = A P_0 (r^{\gamma} - 1) + ...$

P 53 In last line of first paragraph of Prob. 2.7-2: temperature should be singular (instead of temperatures)

P 70 Interchange β and γ in each of the three diagrams of Fig 3.2.

P 72 In last line of Prob. 3.4-2: idea should be ideal

P 81 Replace entire Problem 3.7-3 by:

3.7-3 If the energy of the unstretched rubber band were found to increase quadratically with T, so that eq'n. 3.58 were to be replaced by $U = cL_0T^2$, would equation 3.59 require alteration?

Again find the fundamental equation of the rubber band.

P86 In line above Example: 3.8-6 should be 3.9-6

P 88 In Prob. 3.9-4, first line: Prob. 1.9-1(a) should be Prob. 1.10-1(a).

P 92 Third line should read: Two such systems, with equal heat capacities, have initial temperatures T_{10}

P 94 In Prob. 4.1-1: In second line: delete "each".

In third line: ...fixed volumes v_1 and v_2. The temperature.....

P109 In 4th & 9th lines of prob. 4.5-2: Change "compressed" to "expanded".

P110 In last line of Prob. 4.5-5: Example 1 should be Problem 4.5-1

P117 In Problem 4.6-8, last sentence should be:

Apply equation 4.9 to a differential process and integrate to calculate the work delivered to a reversible work source. Corroborate by over-all energy and entropy conservation.

In last sentence of Prob. 4.6-9: Replace T_i by B, P_i & replace B by V_i.

In Prob. 4.6-10, on last two lines of page: Replace A by B.

P119 On last line of page: $(T_h-T_c)/T_c$ should be $(T_h-T_c)/T_h$

P 122 On next-to-last line of page: 4.7-5 should be 4.7-4.

P127 In equation 4.28: The "square brackets" should be squared.

P 150 In next-to-last line of Problem 5.3-8: k should be k_B

In Problem 5.8-10: Strike out labels " a) " and " b) ". The last two lines should be: An analogous additivity does not hold for any other potential expressed in terms of its natural variables.

P 167 Last line of Prob. 6.3-3 should be: J/mole-K. Carry calculations only to first order in b/v and a/RTv.

P 172 In third line of Problem 6.4-1: 10^{-1} Pa should be 10^4 Pa.

In answer of Problem 6.4-1: c) H_2 and H_2O depleted

d) $\epsilon = 3/5$, $x_{H_2O} = 5/16$ e) $N = 2/3$, $x_{H_2O} = .59$

P 200 On lower left hand corner of middle square: Replace T by I

P 203 In 5th line of 3rd paragraph : change "energy" to "entropy"

P 206 In equation 8.6: $\leq$ should be $\geq$

In 5th line of 2nd paragraph: change "also be negative" to "must be positive".

At end of second paragraph: change (8.7) to (8.6).

P 207 In second display equation of Prob. 8.1-1: change $\leq$ to $\geq$

In Problem 8.1-2, second line should read: that S is a concave function of U, V, and also of N.

Eq'n 8.7 should be $\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} = -\frac{1}{T}\left(\frac{\partial T}{\partial U}\right)_{V,N} = -\frac{1}{NTc_v} \leq 0$

P 208 In Prob. 8.2-1 (e):change $U = D(S^4V/N^2)^{1/3}$ to $U = D(S^3V^4/N^5)^{1/2}$.

P 209 On 2nd line , add: Recall the "fluting condition" (equation 8.10).

In first eqn: mixed 2nd derivative in numerator should be squared.

In Problem 8.2-3, $>$ should be $\geq$.

P 210 In first line: 7.4-8 should be 3.9-5

Third line above Problems should be: so at constant volume than at constant pressure. And ...

P 214 Problem 8.4-1 should be 8.5-1.

P 225 Starting with the second line of Table 9.1, the second column is in units of MPa rather than kPa.

P 226 In heading of second column of Table: change kPa to MPa.

P 243 In Problem 9.4-11, second line: change 2.8 m^3 to 200 cm^3

In third line of same problem, add additional sentence:

Use the van der Waals constants of oxygen.

P 296 In Problem 13.2-3, first line: change "fraction" to "fractions"

Second line of same problem should read:

Pa, if the vessel initially had contained ...

In Problem 13.2-7, second line: change 3278 to 3200

In last line of same problem: change 8.25 Pa to .0429 MPa

P 332 In 3rd line from bottom: .....of two non-interacting subsystems of..

P 340 In Fig. 15.4: replace (=T) by (= $\mathcal{T}$)

P 354 In eq'ns 16.23 and 16.24: replace plus sign by minus sign

P370 In first two eqns on page: π should be π^2

P 390 On next-to-last line of page: Sign in first parenthesis in numerator, and in denominator, should be minus.

P 391 In third line: Fig. 15.3 should be Fig. 15.4

Pp 429-430 In Prob. 19.3-8: In sequence, change "mean square" to "rms", 10^{-3} to 10^{-6}, "mean square" to "rms", $2 \cdot 10^{-16}$ to 10^{-18}, 2/3 cm^3 to 1 mm^3, and "equal to" to "smaller than".

P 449 Section 20-4 should be 20-3.

P 456 In display equation at bottom of page:

Insert a 2 in denominator of last parenthesis : $(-X^2/2\sigma^2)$

P 458 In 9^{th} line from bottom : "qualitative" should be "quantitative"

P 492 Under "Steam tables:" , change page references as follows:

saturated, 224

superheated, 175, 176

CONTENTS

PART I
GENERAL PRINCIPLES OF CLASSICAL THERMODYNAMICS

PART I

GENERAL PRINCIPLES OF CLASSICAL THERMODYNAMICS

INTRODUCTION

The Nature of Thermodynamics and the Basis of ThermoStatistics

Whether we are physicists, chemists, biologists, or engineers, our primary interface with nature is through the properties of macroscopic matter. Those properties are subject to universal regularities and to stringent limitations. Subtle relationships exist among apparently unconnected properties.

The existence of such an underlying order has far reaching implications. Physicists and chemists familiar with that order need not confront each new material as a virgin puzzle. Engineers are able to anticipate limitations to device designs predicated on creatively imagined (but yet undiscovered) materials with the requisite properties. And the specific form of the underlying order provides incisive clues to the structure of fundamental physical theory.

Certain primal concepts of thermodynamics are intuitively familiar. A metallic block released from rest near the rim of a smoothly polished metallic bowl oscillates within the bowl, approximately conserving the sum of potential and kinetic energies. But the block eventually comes to rest at the bottom of the bowl. Although the mechanical energy appears to have vanished, an observable effect is wrought upon the material of the bowl and block; they are very slightly, but perceptibly, "warmer." Even before studying thermodynamics, we are qualitatively aware that the mechanical energy has merely been converted to another form, that the fundamental principle of energy conservation is preserved, and that the physiological sensation of "warmth" is associated with the thermodynamic concept of "temperature."

Vague and undefined as these observations may be, they nevertheless reveal a notable dissimilarity between thermodynamics and the other branches of classical science. Two prototypes of the classical scientific paradigm are mechanics and electromagnetic theory. The former addresses itself to the dynamics of particles acted upon by forces, the latter to the dynamics of the fields that mediate those forces. In each of these cases a new "law" is formulated—for mechanics it is Newton's Law (or Lagrange or Hamilton's more sophisticated variants); for electromagnetism it is the Maxwell equations. In either case it remains only to explicate the consequences of the law.

Thermodynamics is quite different. It neither claims a unique domain of systems over which it asserts primacy, nor does it introduce a new fundamental law analogous to Newton's or Maxwell's equations. In contrast to the specificity of mechanics and electromagnetism, the hallmark of thermodynamics is generality. Generality first in the sense that thermodynamics applies to all types of systems in macroscopic aggrega-