An Introduction to Thermodynamics and Statistical Mechanics, Second Edition

This introductory textbook for standard undergraduate courses in thermodynamics has been completely rewritten to explore a greater number of topics more clearly and concisely. Starting with an overview of important quantum behaviors, the book teaches students how to calculate probabilities in order to provide a firm foundation for later chapters. It then introduces the ideas of "classical thermodynamics" – internal energy, interactions, entropy, and the fundamental second law. These ideas are explored both in general and as they are applied to more specific processes and interactions. The remainder of the book deals with "statistical mechanics" – the study of small systems interacting with huge reservoirs.

The changes in this Second Edition have been made as a result of more than 10 years of classroom testing and feedback from students. To help students review the important concepts and test their newly gained knowledge, each topic ends with a boxed summary of ideas and results. Every chapter has numerous homework problems, covering a broad range of difficulties. Answers are given to odd-numbered problems, and solutions to even-numbered problems are available to instructors at www.cambridge.org/9780521865579.

KEITH STOWE is a professor of physics at California Polytechnic State University and has worked there for 32 years. He has spent time at the University of Washington, Harvard, the University of North Carolina, and the University of Michigan. As well as having written the First Edition of *Introduction to Thermodynamics and Statistical Mechanics*, he has also written books on ocean science.

An Introduction to Thermodynamics and Statistical Mechanics

Second Edition

Keith Stowe California Polytechnic State University



CAMBRIDGE UNIVERSITY PRESS Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo, Delhi, Tokyo, Mexico City

Cambridge University Press The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org Information on this title: www.cambridge.org/9780521865579

© K. Stowe 2007

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published, second edition 2007 3rd printing 2011

A catalogue record for this publication is available from the British Library

ISBN 978-0-521-86557-9 Hardback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication, and does not guarantee that any content on such websites is, or will remain, accurate or appropriate. Information regarding prices, travel timetables, and other factual information given in this work is correct at the time of first printing but Cambridge University Press does not guarantee the accuracy of such information thereafter.

Contents

Preface		page vii
List of constants, conversions, and prefixes		xii
Par	rt I Setting the scene	1
1	Introduction	3
Par	t II Small systems	23
2	Statistics for small systems	25
3	Systems with many elements	40
Par	t III Energy and the first law	63
4	Internal energy	65
5	Interactions between systems	79
	·	
Part IV States and the second law		99
6	Internal energy and the number of accessible states	101
7	Entropy and the second law	117
8	Entropy and thermal interactions	135
Par	t V Constraints	153
9	Natural constraints	155
10	Models	186
11	Choice of variables	210
12	Special processes	226
13	Engines	252
14	Diffusive interactions	287
Par	t VI Classical statistics	327
15	Probabilities and microscopic behaviors	329
16	Kinetic theory and transport processes in gases	352
17	Magnetic properties of materials	369
18	The partition function	382

v

vi

Contents

Part VII Quantum statistics		399
19	Introduction to quantum statistics	401
20	Quantum gases	422
21	Blackbody radiation	438
22	The thermal properties of solids	457
23	The electrical properties of materials	477
24	Low temperatures and degenerate systems	504
Appendices		531
Further reading		537
Problem solutions		538
Index		551

Preface

Goals

The subject of thermodynamics was being developed on a postulatory basis long before we understood the nature or behavior of the elementary constituents of matter. As we became more familiar with these constituents, we were still slow to place our trust in the "new" field of quantum mechanics, which was telling us that their behaviors could be described correctly and accurately using probabilities and statistics.

The influence of this historical sequence has lingered in our traditional thermodynamics curriculum. Until recently, we continued to teach an introductory course using the more formal and abstract postulatory approach. Now, however, there is a growing feeling that the statistical approach is more effective. It demonstrates the firm physical and statistical basis of thermodynamics by showing how the properties of macroscopic systems are direct consequences of the behaviors of their elementary constituents. An added advantage of this approach is that it is easily extended to include some statistical mechanics in an introductory course. It gives the student a broader spectrum of skills as well as a better understanding of the physical bases.

This book is intended for use in the standard junior or senior undergraduate course in thermodynamics, and it assumes no previous knowledge of the subject. I try to introduce the subject as simply and succinctly as possible, with enough applications to indicate the relevance of the results but not so many as might risk losing the student in details. There are many advanced books of high quality that can help the interested student probe more deeply into the subject and its more specialized applications.

I try to tie everything straight to fundamental concepts, and I avoid "slick tricks" and the "pyramiding" of results. I remain focused on the basic ideas and physical causes, because I believe this will help students better understand, retain, and apply the tools and results that we develop.

Active learning

I think that real learning must be an *active* process. It is important for the student to apply new knowledge to specific problems as soon as possible. This should be a

viii

Preface

daily activity, and problems should be attempted while the knowledge is still fresh. A routine of frequent, timely, and short problem-solving sessions is far superior to a few infrequent problem-solving marathons. For this reason, at the end of each chapter the text includes a very large number of suggested homework problems, which are organized by section. Solutions to the odd-numbered problems are at the end of the book for instant feedback.

Active learning can also be encouraged by streamlining the more passive components. The sooner the student understands the text material, the sooner he or she can apply it. For this reason, I have put the topics in what I believe to be the most learning-efficient order, and I explain the concepts as simply and clearly as possible. Summaries are frequent and are included within the chapters wherever I think would be helpful to a first-time student wrestling with the concepts. They are also shaded for easy identification. Hopefully, this streamlining of the passive aspects might allow more time for active problem solving.

Changes in the second edition

The entire book has been rewritten. My primary objective for the second edition has been to explore more topics, more thoroughly, more clearly, and with fewer words. To accomplish this I have written more concisely, combined related topics, and reduced repetition. The result is a modest reduction in text, in spite of the broadened coverage of topics.

In addition I wanted to correct what I considered to be the two biggest problems with the first edition: the large number of uncorrected typos and an incomplete description of the chemical potential. A further objective was to increase the number and quality of homework problems that are available for the instructor or student to select from. These range in difficulty from warm-ups to challenges. In this edition the number of homework problems has nearly doubled, averaging around 40 per chapter. In addition, solutions (and occasional hints) to the odd-numbered problems are given at the back of the book. My experience with students at this level has been that solutions give quick and efficient feedback, encouraging those who are doing things correctly and helping to guide those who stumble.

The following list expands upon the more important new initiatives and features in this edition in order of their appearance, with the chapters and sections indicated in parentheses.

- Fluctuations in observables, such as energy, temperature, volume, number of particles, etc. (Sections 3A, 3C, 7C, 9B, 19A)
- Improved discussion and illustrations of the chemical potential (Sections 5C, 8A, 9E, 14A)
- The explicit dependence of the number of accessible states on the system's internal energy, volume, and number of particles (Chapter 6)
- Behaviors near absolute zero (Sections 9H, 24A, 24B)

Preface

ix

- Entropy and the third law (Section 8D)
- A new chapter on interdependence among thermodynamic variables (Chapter 11)
- Thermal conduction, and the heat equation (Section 12E)
- A more extensive treatment of engines, including performance analysis (Section 13F), model cycles, a description of several of the more common internal combustion engines (Section 13H), and vapor cycles (Section 13I)
- A new chapter on diffusive interactions, including such topics as diffusive equilibrium, osmosis, chemical equilibrium, and phase transitions (Chapter 14)
- Properties of solutions (colligative properties, vapor pressure, osmosis, etc.) (Section 14B)
- Chemical equilibrium and reaction rates (Section 14C)
- A more thorough treatment of phase transitions (Section 14D)
- Binary mixtures, solubility gap, phase transitions in minerals and alloys, etc. (Section 14E)
- Conserved properties (Section 16E)
- Calculating the chemical potential for quantum systems (Section 19E)
- Chemical potential and internal energy for quantum gases (Section 20D)
- Entropy and adiabatic processes in photon gases (Section 21E)
- Thermal noise (Section 21F)
- Electrical properties of materials, including band structure, conductors, intrinsic and doped semiconductors, and p-n junctions (Chapter 23)
- Update of recent advances in cooling methods (Section 24A)
- Update of recent advances in Bose–Einstein condensation (Section 24B)
- Stellar collapse (Section 24C)

Organization

The book has been organized to give the instructor as much flexibility as possible. Some early chapters are essential for the understanding of later topics. Many chapters, however, could be skipped at a first reading or their order rearranged as the instructor sees fit. To help the instructor or student with these choices, I give the following summary followed by more detailed information.

Summary of organization

Part I Introduction

Chapter 1 essential if the students have not yet had a course in quantum mechanics. Summarizes important quantum effects

Part II Small systems

Chapter 2 and Chapter 3 insightful, but not needed for succeeding chapters

х

Preface

Part III Energy and the first law

Chapter 4, Chapter 5 and Chapter 6 essential

Part IVStates and the second lawChapter 6, Chapter 7 and Chapter 8essential

Part V Constraints

Chapter 9 essential Chapter 10, Chapter 11, Chapter 12, Chapter 13 and Chapter 14 any order, and any can be skipped

Part VI Classical statistics

Chapter 15 essential Chapter 16, Chapter 17 and Chapter 18 any order, and any can be skipped

Part VII Quantum statistics

Chapter 19, Chapter 20 A, B essential Chapter 21, Chapter 22, Chapter 23 and Chapter 24 any order, and any can be skipped

More details

Part I – Introduction Chapter 1 is included for the benefit of those students who have not yet had a course in quantum mechanics. It summarizes important quantum effects that are used in examples throughout the book.

Part II – Small systems Chapters 2 and 3 study systems with only a few elements. By studying small systems first the student develops both a better appreciation and also a better understanding of the powerful tools that we will need for large systems in subsequent chapters. However, these two chapters are not *essential* for understanding the rest of the book and may be skipped if the instructor wishes.

Part III – Energy and the first law Chapters 4 and 5 are intended to give the student an intuitive physical picture of what goes on within interacting systems on a microscopic scale. Although the mathematical rigor comes later, this physical understanding is essential to the rest of the book so these two chapters should not be skipped.

Part IV – States and the second law Chapters 6, 7, and 8 are the most important in the book. They develop the statistical basis for much of thermodynamics.

Part V – Constraints Chapter 9 derives the universal consequences of the fundamental ideas of the preceding three chapters. So this chapter shows why things must behave as they do, and why our "common sense" is what it is. Chapters 10–14

xi

all describe the application of constraints to more specific systems. None of these topics is essential, although some models in Chapter 10 would be helpful in understanding examples used later in the book; if Chapters 11 and 12 are covered, they should be done in numerical order. Topics in these five chapters include equations of state and models, the choice and manipulation of variables, isobaric, isothermal, and adiabatic processes, reversibility, important nonequilibrium processes, engines, diffusion, solutions, chemical equilibrium, phase transitions, and binary mixtures.

Part VI – Classical statistics Chapter 15 develops the basis for both classical "Boltzmann" and quantum statistics. So even if you go straight to quantum statistics, this chapter should be covered first. Chapters 16, 17, and 18 are applications of classical statistics, each of which has no impact on any other material in the book. So they may be skipped or presented in any order with no effect on subsequent material.

Part VII – Quantum statistics Chapter 19 introduces quantum statistics, and the first two sections of Chapter 20 introduce quantum gases. These provide the underpinnings for the subsequent chapters and therefore must be covered first. The remaining four (Chapters 21–24) are each independent and may be skipped or presented in any order, as the instructor chooses.

Acknowledgments

I wish to thank my students for their ideas, encouragement, and corrections, and my colleagues Joe Boone and Rich Saenz for their careful scrutiny and thoughtful suggestions. I also appreciate the suggestions received from Professors Robert Dickerson and David Hafemeister (California Polytechnic State University), Albert Petschek (New Mexico Institute of Mining and Technology), Ralph Baierlein (Wesleyan University), Dan Wilkins (University of Nebraska, Omaha), Henry White (University of Missouri), and I apologize to the many whose names I forgot to record.

List of constants, conversions, and prefixes

Constants

acceleration of gravity	$g = 9.807 \text{ m/s}^2$
Avogadro's number	$N_{\text{A}} = 6.022 \times 10^{23}$ particles/mole
Boltzmann's constant	$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$
Coulomb constant	$1/4\piarepsilon_0 = 8.988 imes10^9~{ m kg}~{ m m}^3/({ m s}^2~{ m C}^2)$
elementary unit of charge	$e = 1.602 \times 10^{-19} \text{ C}$
gas constant	$R = N_A k = 8.315 \text{ J/(K mole)}$
	= 0.08206 liter atm/(K mole)
gravitational constant	$G = 6.673 \times 10^{-11} \text{ m}^3/(\text{kg s}^2)$
magnetons	
Bohr magneton	$\mu_{B} =$ 9.274 $ imes$ 10 ⁻²⁴ J/T = 5.788 $ imes$ 10 ⁻⁵ eV/T
nuclear magneton	$\mu_{ m N} = 5.051 imes 10^{-27} \; { m J/T} = 3.152 imes 10^{-8} \; { m eV/T}$
masses	
atomic mass unit	$u = 1.661 \times 10^{-27} \text{ kg}$
electron mass	$m_{ m e} = 9.109 imes 10^{-31} ~ m kg$
neutron mass	$m_{ m n} = 1.675 imes 10^{-27} ~ m kg$
proton mass	$m_{ m p} = 1.673 imes 10^{-27} ~ m kg$
Planck's constant	$h = 6.626 \times 10^{-34} \text{ J s} = 4.136 \times 10^{-15} \text{ eV s}$
	$\hbar = h/2\pi = 1.055 \times 10^{-34} \text{ J s} = 6.582 \times 10^{-16} \text{ eV s}$
speed of light in vacuum	c= 2.998 $ imes$ 10 ⁸ m/s
Stefan–Boltzmann constant	$\sigma =$ 5.671 $ imes$ 10 ⁻⁸ W/(m ² K ⁴)

Conversions

 $\begin{array}{l} 1 \ {\mathring{A}} = 10^{-10} \ m \\ 1 \ liter = 10^{-3} \ m^3 \\ 1 \ atm = 1.013 \ \times \ 10^5 \ Pa \\ log_{10}x = 0.4343 \ ln \ x \\ e^x = 10^{0.4343x} \\ 1 \ eV = 1.602 \ \times \ 10^{-19} \ J \\ 1 \ cal = 4.184 \ J = 0.04129 \ liter \ atm \\ 1 \ T = 1 \ Wb/m^2 = 10^4 \ G \\ temperature \ (K) = temperature \ (^{\circ}C) + 273.15 \ K \end{array}$

xii

List of constants, conversions, and prefixes

xiii

Prefixes

tera	Т	10 ¹²
giga	G	10 ⁹
mega	Μ	10 ⁶
kilo	k	10 ³
centi	с	10 ⁻²
milli	m	10 ⁻³
micro	μ	10 ⁻⁶
nano	n	10 ⁻⁹
pico	р	10^{-12}
femto	f	10 ⁻¹⁵