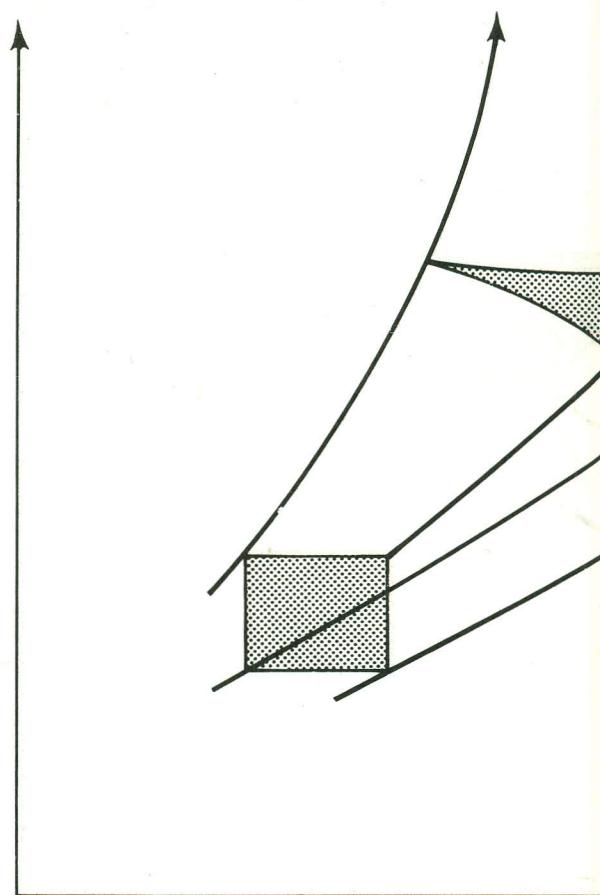


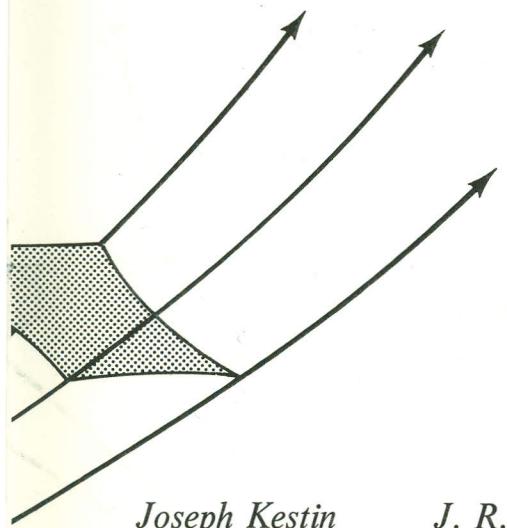
A COURSE IN STATISTICAL THERMODYNAMICS

Joseph Kestin/J. R. Dorfman

A COURSE IN



STATISTICAL THERMODYNAMICS



Joseph Kestin

DIVISION OF ENGINEERING
BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

J. R. Dorfman

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

ACADEMIC PRESS
New York San Francisco London
A Subsidiary of Harcourt Brace Jovanovich, Publishers

12/12448

INSTITUT
FÜR METEOROLOGIE U. KLIMATOLOGIE
UNIVERSITÄT HANNOVER
HERRENHAUSER STR. 2 • 3000 HANNOVER 21

CONTENTS

<i>Preface</i>	xi
<i>Acknowledgments</i>	xv

Introduction	1
---------------------	---

Chapter 1. Summary of Classical Thermodynamics

1.1. The Two Views of Matter	3
1.2. Definitions and Concepts	5
1.3. Equilibrium and Nonequilibrium Thermodynamics	9
1.4. The Laws of Thermodynamics	9
1.5. Continuum Thermodynamics	17
Problems for Chapter 1	20
List of Symbols for Chapter 1	25

Part 1.

FUNDAMENTAL THEORY

Chapter 2. Introduction to Statistical Thermodynamics and Mechanical Models

2.1. Prefatory Remarks	29
2.2. Microscopic Description of Thermodynamic Systems. Statistical Thermodynamics, Classical and Quantum Mechanics	30
2.3. Mechanical Models	36
Problems for Chapter 2	53
List of Symbols for Chapter 2	56

Chapter 3. Quantum Mechanics

3.1.	Description of the Motion	59
3.2.	The Physical Basis of Quantum Mechanics	61
3.3.	The Wave Function	62
3.4.	The Mathematical Basis of Quantum Mechanics. Schrödinger's Equation	65
3.5.	Stationary States. Schrödinger's Time- Independent Equation	69
3.6.	Complementarity and Heisenberg's Uncertainty Principle	72
3.7.	Translational Motion of a Single, Independent Molecule	74
3.8.	Particle in a Container	80
3.9.	Two Identical Particles in a Container	84
3.10.	Quantization of Rotation	87
3.11.	Quantization of Vibration	94
3.12.	Collection of Independent Particles	98
3.13.	Spin	100
3.14.	Density of Quantum Cells in Phase Space	101
3.15.	Spectroscopy	107
3.16.	Summary of Results from Quantum Mechanics Problems for Chapter 3	110
	List of Symbols for Chapter 3	112
		118

Chapter 4. Topics in Mathematics

4.1.	Combinatorial Formulas	121
4.2.	Most Probable Distribution Subject to a Constraint	131
4.3.	On Approximating a Series by an Integral	137
4.4.	The Statistical Method Problems for Chapter 4	140
	List of Symbols for Chapter 4	154

Chapter 5. Foundations of Statistical Thermodynamics

5.1.	Introductory Remarks	163
5.2.	The Statistical Method	165
5.3.	Gibbsian Ensembles	167
5.4.	Liouville's Equation	169
5.5.	Geometrical Structure of the Statistical Sample Space	176
5.6.	Relation between Theories Based on Different Ensembles	177

5.7. Microcanonical Ensemble	178
5.8. Canonical Ensemble	179
5.9. Grand Canonical Ensemble	181
5.10. Statistical Interpretation of Entropy	181
5.11. Method of the Most Probable Distribution	185
5.12. Partition Function	196
5.13. Change in the Partition Function during a Reversible Process	198
5.14. Comparison with Classical Thermodynamics	200
5.15. Explicit Formulas; Chemical Potential	203
5.16. Boltzmann's Principle	205
5.17. The Laws of Thermodynamics	207
5.18. The Method of the Most Probable Distribution and the Grand Canonical Ensemble	213
5.19. Summary	218
Problems for Chapter 5	219
List of Symbols for Chapter 5	222

Chapter 6. Properties of Perfect Gases

6.1. Method	225
6.2. The Partition Function of a Perfect Gas	226
6.3. Pressure and Thermal Equation of State of a Perfect Gas	231
6.4. The Classical Partition Function	234
6.5. Equipartition of Energy in Classical Statistical Mechanics	238
6.6. The Maxwellian Velocity Distribution	241
6.7. Monatomic Gases	245
6.8. Entropy and the Sackur-Tetrode Equation	246
6.9. Internal Degrees of Freedom	252
6.10. Summarizing Remarks	262
6.11. Mixtures of Chemically Inert Perfect Gases	263
6.12. Reacting Perfect Gases. Law of Mass Action	268
6.13. Spectroscopic and Calorimetric Entropy of a Gas	277
6.14. Absolute Vapor-Pressure Curve	279
Problems for Chapter 6	281
List of Symbols for Chapter 6	291

*Part 2.***APPLICATIONS***Chapter 7. Properties of Real Gases*

7.1. Introductory Remarks	297
7.2. Quantum or Classical Partition Function	298

7.3.	The Configurational Partition Function	299
7.4.	First Approximation to Configurational Partition Function	301
7.5.	The Second Virial Coefficient	304
7.6.	Third Virial Coefficient	310
7.7.	Higher Approximations and Other Thermodynamic Properties	313
7.8.	The van der Waals Equation of State	314
7.9.	The Law of Corresponding States	317
7.10.	Properties of a Pure Substance near the Critical Point	325
	Problems for Chapter 7	331
	List of Symbols for Chapter 7	336

Chapter 8. Degenerate Perfect Gases

8.1.	Prefatory Remarks	339
8.2.	The Quantum-Mechanical Partition Function	340
8.3.	The Kronecker Delta Function	342
8.4.	The Average Occupation Numbers	343
8.5.	The Perfect Quantum Gas	351
8.6.	The Weakly Degenerate Gas	353
8.7.	The Strongly Degenerate Fermi Gas	358
8.8.	The Degenerate Boson Gas. The Bose-Einstein Condensation	365
	Problems for Chapter 8	372
	List of Symbols for Chapter 8	378

Chapter 9. Properties of Solids

9.1.	Prefatory Remarks	381
9.2.	The Properties of Crystalline Solids	382
9.3.	Debye's Theory	387
9.4.	Phonons	394
9.5.	The Band Theory of Solids	398
9.6.	Thermionic Emission	407
	Problems for Chapter 9	410
	List of Symbols for Chapter 9	413

Chapter 10. Radiation

10.1.	A Descriptive Introduction	417
10.2.	Properties of Electromagnetic Radiation	423
10.3.	The Photon Gas in Equilibrium	426
10.4.	Emission and Absorption of Black-Body Radiation	437

10.5. Relation between Black-Body Emissive Power and Spectral Density of Specific Energy	446
10.6. The Stefan-Boltzmann Law	447
10.7. The International Practical Temperature Scale of 1968	448
10.8. Kirchhoff's Law	448
10.9. Radiative Atomic Transitions. The Einstein Coefficients	451
10.10. The Laser	452
Problems for Chapter 10	454
List of Symbols for Chapter 10	459

Chapter 11. Magnetic Properties

11.1. Introduction	461
11.2. Fundamental Equation of Paramagnetic System	463
11.3. The Mechanical Model	469
11.4. The Partition Function	472
11.5. Magnetization	475
11.6. Classical Limit	478
11.7. Ferromagnetism	479
Problems for Chapter 11	484
List of Symbols for Chapter 11	486

Chapter 12. Kinetic Theory of Gases

12.1. Prefatory Remarks	489
12.2. Some Elementary Ideas	490
12.3. A Dynamical Derivation of the Perfect-Gas Law	493
12.4. The Mean Free Path	497
12.5. The Mean Free Path and Transport Properties	501
Problems for Chapter 12	518
List of Symbols for Chapter 12	523

Chapter 13. The Boltzmann Equation

13.1. Introduction	525
13.2. The Rate Equation	525
13.3. The Dynamics of a Binary Collision	530
13.4. The Boltzmann Equation	536
13.5. Concluding Remarks	538
13.6. Approach to Equilibrium. The <i>H</i> -Theorem	539
Problems for Chapter 13	543
List of Symbols for Chapter 13	544

Chapter 14. Fluctuations

14.1.	Introduction	547
14.2.	The Probability of a Thermodynamic Fluctuation	548
14.3.	Fluctuations in a Subsystem	550
14.4.	Brownian Motion	557
	Problems for Chapter 14	558
	List of Symbols for Chapter 14	561
<i>Tables</i>		563
<i>Index</i>		567