

Contents

Preface vii

Introduction **I**

PART I PRINCIPLES OF THERMODYNAMICS

CHAPTER 1 The first law of thermodynamics **7**

1.1	Thermodynamic equilibrium	7
1.2	The language of thermodynamics: definitions	9
1.3	The first law of thermodynamics	12
1.4	Differential form of the first law: quasi-static work	14
1.5	The specific heats	16
1.6	The first law of thermodynamics for a moving continuum	19
	References	24
	Problems	24

CHAPTER 2 The second law of thermodynamics **28**

2.1	Introduction	28
2.2	Carnot's theorem and the second law of thermodynamics	29
2.3	Linear differential forms and exact differentials	30
2.4	Temperature and entropy	33
2.5	Entropy as a state function	36

2.6	The increasing property of entropy	39
2.7	The Clausius inequality: available energy	40
2.8	Summary	43
	References	44
	Problems	45
CHAPTER 3	The thermodynamic potentials: equilibrium	48
3.1	Introduction	48
3.2	Open assemblies: the chemical potential	49
3.3	Legendre transformations	50
3.4	Application of the Legendre transformation to thermodynamic variables: the thermodynamic potentials	52
3.5	Fundamental thermodynamic equations	55
3.6	Euler's theorem and the Gibbs-Duhem relation	58
3.7	Criteria of equilibria	60
3.8	Heterogeneous equilibrium: the phase rule	63
3.9	Chemical-reaction equilibrium	67
	References	70
	Problems	70
PART II	PRINCIPLES OF STATISTICAL MECHANICS	
CHAPTER 4	Quantum-mechanical foundations	75
4.1	Introduction	75
4.2	The postulates of elementary quantum mechanics	77
4.3	Assemblies of two or more identical systems: symmetric and antisymmetric wave functions	88
4.4	The density matrix	92
	References	95
	Problems	95
CHAPTER 5	Statistical ensembles	98
5.1	Introduction	98
5.2	Liouville's theorem and classical ensemble theory	100

5.3	Statistical ensembles in quantum mechanics	106
5.4	Summary	115
	References	115
	Problems	115

CHAPTER 6 The microcanonical, canonical, and grand canonical ensembles 117

6.1	Introduction	117
6.2	The microcanonical ensemble	118
6.3	The canonical ensemble	126
6.4	The grand canonical distribution	136
6.5	Generalized distributions	143
6.6	Assemblies of independent systems: Fermi-Dirac, Bose-Einstein, and Maxwell-Boltzmann distributions	144
6.7	Summary	151
	References	151
	Problems	151

PART III EQUILIBRIUM PROPERTIES OF SIMPLE ASSEMBLIES

A. Weakly Interacting Systems

CHAPTER 7 The perfect gas and mixtures of perfect gases 157

7.1	Introduction	157
7.2	The partition function for the translational degrees of freedom of a perfect-gas assembly	158
7.3	Internal degrees of freedom and internal partition functions	164
7.4	Mixtures of perfect gases	177
7.5	Chemical reaction equilibrium in perfect gas mixtures	182
7.6	Ionization equilibrium: the Saha equation	186
	References	188
	Problems	189

CHAPTER 8 Applications of Fermi-Dirac and Bose-Einstein statistics	192
8.1 Introduction	192
8.2 The ideal Fermi-Dirac gas: free electrons	194
8.3 The ideal Bose-Einstein gas	204
8.4 Black-body radiation: the photon gas	208
References	215
Problems	215
B. Strongly Interacting Systems	
CHAPTER 9 Imperfect gases and condensation: liquids	219
9.1 Introduction	219
9.2 Nonideal-gas properties: equations of state and thermodynamic functions	220
9.3 The classical canonical and grand canonical partition functions: the configuration integral	225
9.4 Cluster expansions of the configurational integral	227
9.5 The theory of condensation	235
9.6 Distribution functions and the theory of liquids	237
References	246
Problems	247
CHAPTER 10 Crystalline solids	251
10.1 Introduction	251
10.2 General relations for the perfect crystalline solid	252
10.3 The Einstein, Debye, and Born-von Kármán theories of the vibrations of an ideal crystal	255
10.4 Cooperative phenomena in crystals: the Ising model	271
References	282
Problems	283

APPENDIX A	Review of classical analytical mechanics	287
APPENDIX B	The equations of motion for a continuous medium	291
APPENDIX C	Energy considerations in the electrodynamics of continuous media	293
APPENDIX D	The transition from quantum to classical statistics: the classical limit of the canonical partition function	298
APPENDIX E	The quasi-classical canonical partition function for the rotational degrees of freedom of a rigid molecule	305
	Table of nomenclature	309
	Index	315