## CONTENTS

PAK		
	ERAL PRINCIPLES OF SSICAL THERMODYNAMICS	1
	duction The Nature of Thermodynamics and the Basis of mostatistics	2
1 TF	HE PROBLEM AND THE POSTULATES	5
1.1	The Temporal Nature of Macroscopic Measurements	5
1.2	The Spatial Nature of Macroscopic Measurements	6
1.3	The Composition of Thermodynamic Systems	9
1.4	The Internal Energy	11
1.5	Thermodynamic Equilibrium	13
1.6	Walls and Constraints	15
1.7	Measurability of the Energy	16
1.8	Quantitative Definition of Heat—Units	18
1.9	The Basic Problem of Thermodynamics	25
1.10	The Entropy Maximum Postulates	27
2 TI	HE CONDITIONS OF EQUILIBRIUM	35
2.1	Intensive Parameters	35
2.2	Equations of State	37
2.3	Entropic Intensive Parameters	40
2.4	Thermal Equilibrium—Temperature	43
2.5	Agreement with Intuitive Concept of Temperature	45
2.6	Temperature Units	46
2.7	Mechanical Equilibrium	49
2.8	Equilibrium with Respect to Matter Flow	54
2.9	Chemical Equilibrium	56

	DME FORMAL RELATIONSHIPS,	
	ND SAMPLE SYSTEMS	59
3.1	The Euler Equation	59
3.2	The Gibbs-Duhem Relation	60
3.3	Summary of Formal Structure	63
3.4	The Simple Ideal Gas and Multicomponent	
	Simple Ideal Gases	66
3.5	The "Ideal van der Waals Fluid"	74
3.6	Electromagnetic Radiation	78
3.7	The "Rubber Band"	80
3.8	Unconstrainable Variables; Magnetic Systems	81
3.9	Molar Heat Capacity and Other Derivatives	84
	EVERSIBLE PROCESSES AND THE	
	AXIMUM WORK THEOREM	91
4.1	Possible and Impossible Processes	91
4.2	Quasi-Static and Reversible Processes	95
4.3	Relaxation Times and Irreversibility	99
4.4	Heat Flow: Coupled Systems and Reversal of Processes	101
4.5	The Maximum Work Theorem	103
4.6	Coefficients of Engine, Refrigerator, and	
	Heat Pump Performance	113
4.7	The Carnot Cycle	118
4.8	Measurability of the Temperature and of the Entropy	123
4.9	Other Criteria of Engine Performance; Power Output and	
	"Endoreversible Engines"	125
4.10	Other Cyclic Processes	128
5 A	LTERNATIVE FORMULATIONS	
A]	ND LEGENDRE TRANSFORMATIONS	131
5.1	The Energy Minimum Principle	131
5.2	Legendre Transformations	137
5.3	Thermodynamic Potentials	146
5.4	Generalized Massieu Functions	151
	HE EXTREMUM PRINCIPLE IN THE	
L	EGENDRE TRANSFORMED REPRESENTATIONS	153
6.1	The Minimum Principles for the Potentials	153
6.2	The Helmholtz Potential	157
6.3	The Enthalpy; The Joule-Thomson or "Throttling" Process	160
6.4	The Gibbs Potential; Chemical Reactions	167
6.5	Other Potentials	172
6.6	Compilations of Empirical Data; The Enthalpy of Formation	173
6.7	The Maximum Principles for the Massieu Functions	179

	Conten	ts XIII
7 M	IAXWELL RELATIONS	181
7.1	The Maxwell Relations	181
7.2	A Thermodynamic Mnemonic Diagram	183
7.3	A Procedure for the Reduction of Derivatives in	10.
	Single-Component Systems	186
7.4	Some Simple Applications	190
7.5	Generalizations: Magnetic Systems	199
8 S	TABILITY OF THERMODYNAMIC SYSTEMS	203
8.1	Intrinsic Stability of Thermodynamic Systems	203
8.2	Stability Conditions for Thermodynamics Potentials	207
8.3	Physical Consequences of Stability	209
8.4	Le Chatelier's Principle; The Qualitative Effect	
	of Fluctuations	210
8.5	The Le Chatelier-Braun Principle	212
9 F	IRST-ORDER PHASE TRANSITIONS	215
9.1	First-Order Phase Transitions in Single-Component Systems	215
9.2	The Discontinuity in the Entropy-Latent Heat	222
9.3	The Slope of Coexistence Curves; the Clapeyron Equation	228
9.4	Unstable Isotherms and First-Order Phase Transitions	233
9.5	General Attributes of First-Order Phase Transitions	243
9.6	First-Order Phase Transitions in Multicomponent	
	Systems—Gibbs Phase Rule	245
9.7	Phase Diagrams for Binary Systems	248
10 C	RITICAL PHENOMENA	255
10.1	Thermodynamics in the Neighborhood of the Critical Point	255
10.2	Divergence and Stability	261
10.3	Order Parameters and Critical Exponents	263
10.4	Classical Theory in the Critical Region; Landau Theory	265
10.5	Roots of the Critical Point Problem	270
10.6	Scaling and Universality	272
11 T	HE NERNST POSTULATE	277
11.1	Nernst's Postulate, and the Principle of Thomsen	
200 16 00 00	and Bertholot	277
11.2	Heat Capacities and Other Derivatives at Low Temperatures	280
11.3	The "Unattainability" of Zero Temperature	281
	UMMARY OF PRINCIPLES	***
	OR GENERAL SYSTEMS	283
12.1	General Systems The Postulates	283
17.7.	LUC FORHBRIES	/X ·

xiv	Contents

12.3	The Intensive Parameters	284
12.4	Legendre Transforms	285
12.5	Maxwell Relations	285
12.6	Stability and Phase Transitions	286
12.7	Critical Phenomena	287
12.8	Properties at Zero Temperature	287
13 P	ROPERTIES OF MATERIALS	289
13.1	The General Ideal Gas	289
13.2	Chemical Reactions in Ideal Gases	292
13.3	Small Deviations from "Ideality"—The Virial Expansion	297
13.4	The "Law of Corresponding States" for Gases	299
13.5	Dilute Solutions: Osmotic Pressure and Vapor Pressure	302
13.6	Solid Systems	305
14 IF	RREVERSIBLE THERMODYNAMICS	307
14.1	General Remarks	307
14.2	Affinities and Fluxes	308
14.3	Purely-Resistive and Linear Systems	312
14.4	The Theoretical Basis of the Onsager Reciprocity	314
14.5	Thermoelectric Effects	316
14.6	The Conductivities	319
14.7	The Seebeck Effect and the Thermoelectric Power	320
14.8	The Peltier Effect	323
14.9	The Thomsen Effect	324
PAI	RT II	
	TISTICAL MECHANICS	
15 S	TATISTICAL MECHANICS IN THE	
E	NTROPY REPRESENTATION:	
T	HE MICROCANONICAL FORMALISM	329
15.1	, ,	329
15.2	The Einstein Model of a Crystalline Solid	333
15.3	The Two-State System	337
15.4	A Polymer Model—The Rubber Band Revisited	339
15.5	Counting Techniques and their Circumvention;	2.40
	High Dimensionality	343
	HE CANONICAL FORMALISM; STATISTICAL	2.40
-	The Probability Distribution	349
16.1 16.2	The Probability Distribution Additive Energies and Factorizability of the Partition Sum	349 353
10.2	Additive Elicigies and Pactorizatinity of the Partition Sum	333

		Contents	xv
16.3	Internal Modes in a Gas		355
16.4	Probabilities in Factorizable Systems		358
16.5	Statistical Mechanics of Small Systems: Ensembles		360
16.6	Density of States and Density-of-Orbital States		362
16.7	The Debye Model of Non-metallic Crystals		364
16.8	Electromagnetic Radiation		368
16.9	The Classical Density of States		370
16.10	The Classical Ideal Gas		372
16.11	High Temperature Properties—The Equipartition Theorem		375
	NTROPY AND DISORDER; GENERALIZED		
	ANONICAL FORMULATIONS		379
17.1	Entropy as a Measure of Disorder		379
17.2			382
17.3	The Grand Canonical Formalism		385
_	UANTUM FLUIDS		393
18.1	Quantum Particles; A "Fermion Pre-Gas Model"		393
18.2	The Ideal Fermi Fluid		399
18.3	The Classical Limit and the Quantum Criteria		402
18.4	The Strong Quantum Regime; Electrons in a Metal		405
18.5	The Ideal Bose Fluid		410
18.6	Non-Conserved Ideal Bose Fluids; Electromagnetic		
10.5	Radiation Revisited		412
18.7	Bose Condensation		413
	LUCTUATIONS		423
19.1	The Probability Distribution of Fluctuations		423
19.2	Moments and The Energy Fluctuations		424
19.3	General Moments and Correlation Moments		426
	ARIATIONAL PROPERTIES, PERTURBATION		
	XPANSIONS, AND MEAN FIELD THEORY		433
20.1	The Bogoliubov Variational Theorem		433
20.2	Mean Field Theory		440
20.3			440
	the Binary Alloy		449
РАБ	RT III		
	UNDATIONS		
	OSTLUDE: SYMMETRY AND THE CONCEPTUAL		
	OUNDATIONS OF THERMOSTATISTICS		455
21.1	Statistics		455

xvi	Contents	
21.2	Symmetry	458
21.3	Noether's Theorem	460
21.4	Energy, Momentum and Angular Momentum; the Generalized	
	"First Law" of Thermodynamics	461
21.5	Broken Symmetry and Goldstone's Theorem	462
21.6	Other Broken Symmetry Coordinates—Electric and	
	Magnetic Moments	465
21.7	Mole Numbers and Gauge Symmetry	466
21.8	Time Reversal, the Equal Probability of Microstates,	
	and the Entropy Principle	467
21.9	Symmetry and Completeness	469
APP	ENDIX A	
	IE RELATIONS INVOLVING	
PAR	TIAL DERIVATIVES	473
<b>A.1</b>	Partial Derivatives	473
A.2	Taylor's Expansion	474
A.3	Differentials	475
A.4	Composite Functions	475
A.5	Implicit Functions	476
A DD	ENDIX B	
	ENDIA B ENETIC SYSTEMS	479
GEN	ERAL REFERENCES	485
INDEX		487