Contents

Preface xi

1. The Zeroth and the First Law

1.1 Introduction 1
1.2 Temperature 2
1.3 The Reduction of Thermal to Mechanical Concepts 2
1.4 Zero Law and Thermal Equation of State 3
1.5 Quasi-static and Adiabatic Processes 6
1.6 First Law and Caloric Equation of State 6
1.7 Some Important Applications to Ideal Gas Systems 7
1.8 Completion of Hydrodynamical Equations by Thermodynamics 13
1.9 Application to Simple Fluid Motion (One-dimensional, Steady, and Locally Adiabatic) 14
1.10 Shock Waves 16
1.11 Characteristic Functions 18

2. The Second Law

2.1 The Second Law of Thermodynamics 21
2.2 Integrating Factor for Differential Form 23
2.3 System with Three Degrees of Freedom 24
2.4 The General Case 27
2.5 Entropy 28
2.6 The Absolute Temperature and the Ideal Gas Temperature 29
2.7 Completion of Second Law 30
2.8 Examples of Entropy Changes in Nonquasi-static Processes 31
2.9 Reversibility and Quasi-static Processes 34
2.10 Kelvin and Clausius Formulations 36
2.11 The Second Law and Temperature Order 36
2.12 Carathéodory Statement of Second Law 37

3. One-component Systems, Phase Transitions, and Low Temperatures

3.1 Qualitative Description of a One-component System 43
3.2 Thermodynamic Relations Holding for Simple Systems 44
3.3 Minimal Thermodynamic Description 47
3.4 Other Characteristic Functions 47
3.5 Phase Transition of First Order 49
3.6 Phase Transition of Second Order 51
3.7 Qualitative Remarks on Phase Transitions 53
3.8 Empirical Determination of the Absolute Temperature Scale 53
3.9 Experimental Realization of Very Low Temperatures and the Joule-Kelvin Effect 55
3.10 Adiabatic Demagnetization 56

4. The Third Law and the Behavior of Matter Near Absolute Zero

4.1 Qualitative Behavior of Matter Near Absolute Zero 63
4.2 Phase Diagram of Liquid Helium 64
4.3 Helium II and Superfluidity 65
4.4 Two Fluid Model 66
4.5 Landau Criterion for Superfluidity 69
4.6 Critical Velocity 70
4.7 Superconductivity 71
4.8 Thermodynamics of Transition 73
4.9 London Equations 75
4.10 Quantization of Magnetic Flux 75
4.11 Microscopic Theory 76
4.12 General Remarks on Superconductivity and Superfluidity 77
4.13 The Experimental Basis of the Third Law 77
4.14 Unattainability Formulation of Third Law 79

5. General Conditions of Thermodynamic Equilibrium and Other Applications

5.1 Second Law for Open Systems Subject to General Interactions 83
5.2 Chemical Reactions 85
5.3 Ideal Gases 86
5.4 Equilibrium of Heterogeneous System 89

5.5 Remarks on Extensive and Intensive (Specific) Thermodynamic Variables 90
5.6 Phase Rule 91
5.7 General Conditions of Equilibrium and the Internal Energy 92
5.8 Stability and Thermodynamic Inequalities 94
5.9 Displacement of Chemical Equilibrium 97
5.10 Other Applications 98

6. Statistical Foundations of Thermodynamics

6.1 Introduction 101
6.2 Phase Space 102
6.3 Liouville Theorem 103
6.4 Integrals of Motion 104
6.5 Steady State Ensembles and Thermodynamic Equilibrium 105
6.6 Coarse-grained Density 106
6.7 The Boltzmann H-function 107
6.8 Extensive Property of H 109
6.9 Dependence of $\bar{H}$ on Time 109
6.10 Dependence of $\bar{\bar{H}}$ on Time (The $\bar{\bar{H}}$ Theorem) 110
6.11 Examples of Change in $\bar{\bar{H}}$ with Time 111
6.12 Schematic Discussion of General Case 112
6.13 Ergodic Theory and the Approach to Equilibrium 113
6.14 Canonical Ensembles and Statistical Equilibrium 115
6.15 Displacement of Equilibrium and the Second Law 116
6.16 Other Thermodynamic Relations 118
6.17 Molecular Distributions 119
6.18 Grand Canonical Distribution 121
6.19 Adaptation of Argument to Quantum Theory 121
6.20 Third Law 123
6.21 Density Matrix and Quantum Partition Function 124

7. Applications to Some Simple Systems

7.1 Ideal Systems 131
7.2 System of Oscillators 132
7.3 Debye Crystal (Caloric Equation) 134
7.4 Debye Crystal (Thermal Equation) 137
7.5 Electromagnetic Field 139
7.6 Paramagnetism 141
7.7 Adiabatic Demagnetization and the Third Law 145
7.8 Negative Temperatures 147

8. Thermodynamics of Ideal Quantum Gases

8.1 Quantum Statistics of Ideal Gases 151
8.2 Partition Function of Ideal Gases 152
8.3 Equations of State 158

8.4 Weak Degeneracy 159
8.5 Strong Degeneracy 161
8.6 Examples of Degenerate Fermi-Dirac Systems 162
8.7 The Degenerate Nonrelativistic Einstein-Bose System (The Superfluid) 164
8.8 Specific Heat and Pressure of the Degenerate Nonrelativistic Einstein-Bose System 165
8.9 The Degenerate Relativistic Einstein-Bose System (The Photon Gas) 166

9. The Grand Partition Function and Second Quantization

9.1 The Grand Canonical Ensemble 169
9.2 Expectation Values and Fluctuations 172
9.3 Equations of State from Grand Partition Function 174
9.4 Thermodynamic Stability of Open Systems 175
9.5 Grand Partition Function of Ideal Gas 177
9.6 Operator Formalism for Grand Partition Function (Second Quantization) 179

10. Phase Transitions in Statistical Mechanics

10.1 General Remarks on the Problem of Phase Transitions 187
10.2 The Many-body Problem and the Nonideal Gas 190
10.3 Ferromagnetic Transitions and the Ising Model 192
10.4 Equations of State of Finite Systems 194
10.5 The Thermodynamic Limit and Phase Transitions 196
10.6 Lattice Gas and Phase Transitions 198
10.7 Connection with the Theory of the Nonideal Gas 201
10.8 Phase Transitions of a Quantum Fluid 202
10.9 The B. C. S. Solution 203
10.10 Coherence in the Condensed State 205

11. The Approach to Thermodynamic Equilibrium

11.1 Introduction 211
11.2 Population Numbers as Variables 211
11.3 Alternative Derivation of the Entropy 213
11.4 Kinetic Description 214
11.5 Change of $\bar{H}$ in Time 216
11.6 Equilibrium 217
11.7 Remarks on the H-theorem and Boltzmann's Equation 218
11.8 Remarks on the Quantum Mechanical Boltzmann Problem 220
11.9 Irreversible Thermodynamics 221
11.10 Ensemble Averages 222

11.11 Onsager's Theorem 222
11.12 Rate of Entropy Production 224
11.13 Thermo-osmosis (Thermomechanical Effect) 224
11.14 Thermoelectric Effect 226
11.15 Arbitrariness in Choice of Forces 228
11.16 Positive Definiteness of Entropy Production 229

Appendix A. Analysis of the Kelvin and Clausius Formulations 233

B. Collection of Thermodynamic Formulas 238

C. London Rigidity 239

D. Time Dependence of $\overline{H}$ in Quantum Theory 242

Index 245