CONTENTS

CHAPTER

1 GAS THEORY, 1

(a) Introduction, 1. (b) A Simplified Model of the Perfect Gas, 3. (c) The Number of Molecules with a Given Velocity, 5. (d) The Classical Perfect Gas, Pressure, 8. (e) The Maxwell-Boltzmann Distribution Law, 10. (f) The Average Velocity, 14. (g) The Number of Molecules Hitting a Wall, 17. (h) The Mean Free Path, 18. (i) Viscosity, 22. (j) Heat Conduction, 26. (k) Diffusion, 27. (l) The Scope of Statistical Mechanics, 31.

2 MECHANICAL AND QUANTUM-MECHANICAL PRELIMINARIES, 33

(a) Introduction, 33. (b) Coordinates, 35. (c) Momenta, 36. (d) Classical Mechanics and Phase Space, 38. (e) The Uncertainty Principle, 41. (f) Quantum States, 42. (g) Quantum States of Some Simple Systems, 45. (h) The Combination of Independent Systems, 49. (i) Equal Probability of Single States, 53. (j) Liouville Theorem and Equal Probability in Phase Space, 58. (k) Identical Particles, Einstein-Bose and Fermi-Dirac Systems, 63.

3 TERMINOLOGY AND DEFINITIONS, 68

(a) The States of a Thermodynamic System. 68. (b) Forces of a Thermodynamic System, 70. (c) The Distribution of Independent Molecules in Space, 74. (d) The Concept of a Distribution, 78. (e) The Most Probable Distribution, 80. (f) Idealized Systems and Inhibitions, 81. (g) Summary, 85.

4 THE DERIVATION OF THE LAWS OF THERMODYNAMICS, 86

(a) Introduction, 86. (b) Characteristics of the Logarithm of Ω, 87. (c) The Quantity $S = k \ln \Omega$, 92. (d) Identification of Entropy, Temperature, and Pressure, 95. (e) The Limits of Validity of the Second Law of Thermodynamics, 98. (f) The Relation between Entropy and the Uncertainty in the Energy, 100. (g) The Third Law of Thermodynamics, 103. (h) The Conditions of Equilibrium and the Chemical Potential μ, 104.

5 THE PERFECT MONATOMIC GAS, 109

(a) The Mathematical Representation of the System, 109. (b) The Distribution of Energy among the Atoms, 110. (c) The Most Probable Distribution, 112. (d) Boltzmann Statistics, 114. (e) The Equation of State, 117. (f) Maxwell-Boltzmann Distribution, 119. (g) Evaluation of e^{α} and Limit of Applicability of Boltzmann Statistics, 120.

6 THE PERFECT GAS WITH INTERNAL DEGREES OF FREEDOM, 123

(a) Introduction, 123. (b) The Partition Function, 123. (c) The Separation of the Partition Function as a Product, 127. (d) The General Equations, 129. (e) The Distribution of Molecules among Internal States, 132. (f) The Influence of the Zero of Energy, 134. (g) The Influence of Nuclear Spin, 135. (h) The Entropy of Isotope Mixing, 138. (i) The Internal Partition Function of a Monatomic Gas, 140. (j) The Classical Internal Partition Function of Molecules, 144.

CHAPTER

7 DIATOMIC GASES, 149

(a) The Ideal Diatomic Molecule, 149. (b) The Partition Function of a Rotator, 151. (c) The Partition Function of an Oscillator, 157. (d) The General Diatomic Molecule, 160. (e) The Classical Equations for the General Diatomic Molecule, 167. (f) Molecules Composed of Two Identical Atoms, 172.

8 POLYATOMIC GASES, 179

(a) Introduction, 179. (b) The Number of Degrees of Freedom, 181. (c) Vibrational Contributions, 183. (d) Rotation, 191. (e) The Symmetry Number, 195.

9 MIXTURES OF GASES AND CHEMICAL EQUILIBRIUM, 200

(a) Introduction, 200. (b) Gaseous Mixtures, 201. (c) Chemical Equilibrium, 203. (d) The Entropy of Isotope Mixing, 209. (e) An Interpretation of the Equilibrium Equation, 213. (f) Estimation of Equilibrium Constants, 215.

10 GENERAL EQUATIONS FOR SYSTEMS COMPOSED OF DEPENDENT PARTICLES, 218

(a) Introduction, 218. (b) The Equation for the Work Function A, 220. (c) Application to the Perfect Gas, 223. (d) Systems of Fixed Energy, 225. (e) Energy Fluctuations in Systems of Fixed Temperature, 227. (f) The Semi-Classical Expression for Q, 228. (g) The Configuration Integral Q_τ, 229. (h) The Probability of a Configuration, 230. (i) An Alternative Derivation, 232. (j) Summary of Thermodynamic Equations, 235.

11 THE CRYSTALLINE SOLID, 237

(a) The Crystal, 237. (b) Harmonic Vibrations, 237. (c) Classical Calculation, 240. (d) Another Derivation of the Classical Formulas, 242. (e) Quantum-Mechanical Treatment, 243. (f) A One-Dimensional Crystal Model, 246. (g) The Frequencies of Simple Isotropic Lattices, 248. (h) The Debye Formula, 251. (i) Deviations from the Debye Formula, 255. (j) Strain and Stress Variables, 258.

12 THE VAN DER WAALS EQUATION, 262

(a) Introduction, 262. (b) The Approximate Statistical Treatment, 263. (c) The Interpretation of a and b, 266. (d) The Law of Corresponding States, 269. (e) Condensation and the van der Waals Equation, 272. (f) Phase Changes and a General Equation of State, 274.

13 THE IMPERFECT GAS, 277

(a) Introduction, 277. (b) The Cluster Integrals b_l, 278. (c) Simplification of the Configuration Integral Equation, 282. (d) The Maximum Term in $Q_\tau/N!$, 283. (e) The Limiting Case of the Perfect Gas, 284. (f) The Equation for the Cluster Integrals in Terms of Irreducible Integrals β_k, 285. (g) Development in Inverse Powers of v, 288. (h) The Thermodynamic Properties of the Imperfect Gas, 291. (i) Summary of the Method, 294.

14 CONDENSATION AND THE CRITICAL REGION, 295

(a) Introduction, 295. (b) The Value of the Cluster Integrals b_l for Large Values of l, 297. (c) Large Clusters Present at Equilibrium, 299. (d) The

CHAPTER

Pressure and Free Energy in the Condensation Range, 301. (e) The Determination of the Volume per Molecule, v_s, of the Saturated Vapor, 303. (f) The Dependence of the Irreducible Integrals on the Temperature, 305. (g) The Critical Point, 308. (h) The Temperature T_m, 310. (i) The Physical Interpretation of T_m, 311. (j) The Thermodynamic Functions of the Saturated Vapor, 314. (k) Phase Changes in the Condensed Phase, 317. (l) The Cell Method of Calculating Liquid Partition Functions, 319.

15 ELECTRIC AND MAGNETIC FIELDS, 327

(a) Introduction, 327. (b) Rigid Dipoles in an Electric Field, 327. (c) The Dielectric Constant, 331. (d) Electronic Polarization, 331. (e) Comparison with Refractive Index and Experimental Data, 333. (f) Non-Rigid Molecules, 335. (g) The Lorentz-Lorenz Force, 338. (h) Para- and Diamagnetism, 340. (i) Paramagnetism in Quantum Mechanics, 342. (j) Ferromagnetism, 348. (k) Magnetic Cooling, 352. (l) Thermodynamic Equations in Electric Fields, 356. (m) The Calculation of F in a Field, 359.

16 DEGENERATE GASES, 363

(a) Introduction, 363. (b) Definition of Black-Body Radiation, 365. (c) The Quantum States of Radiation, 368. (d) The Planck Black-Body Distribution Law, 369. (e) The Thermodynamic Functions of the Radiation Field, 372. (f) The Degenerate Fermi-Dirac Gas at Zero Temperature, 374. (g) The Integrals Occurring in the Equations for the Fermi-Dirac Gas, 378. (h) The Thermodynamic Functions of a Degenerate Fermi-Dirac Gas, 385. (i) Electrons in Metals, 387. (j) The Richardson Effect, 390. (k) Approximate Calculation of the Heat and Electrical Conductivity of Metals, 397. (l) The Maxwell-Boltzmann Collision Equation and Its Application to Electrons in Metals, 401. (m) Electrical and Heat Conductivity and the Thermoelectric Effect, 407. (n) Liquid Helium II, 414. (o) The Degenerate Bose-Einstein Gas, 416.

APPENDIX, 427

(I) The Notation of Calculus, 427. (II) Some Definite Integrals, 430. (III) The Euler-Maclaurin Summation Formula, 431. (IV) The Factorial and the Stirling Approximation, 432. (V) The Volume of an N-dimensional Sphere, 433. (VI) The Method of Undetermined Multipliers, 433. (VII) Combinatory Problems, 435. (VIII) General Thermodynamic Relationships, 438. (IX) Summary of Thermodynamic Functions of a Perfect Gas, 440. (X) The Coefficient of the Term $\Pi\beta_k^{n_k}$ in b_l, 455. (XI) Application of the Theory of Functions to the Functions Appearing in the Theory of the Imperfect Gas, 459. (XII) Constants of Diatomic Molecules, 468. (XIII) Physical Constants, 470. (XIV) Conversion of Energy Units, 471. (XV) Greek Alphabet, 472.

GLOSSARY OF SYMBOLS, 473

PROBLEMS, 483

AUTHOR INDEX, 487

SUBJECT INDEX, 489