### Contents

Preface xi

PART I: THE STRUCTURE OF MATTER

### Chapter 1: The Microscopic World: Atoms and Molecules 3

- Development of the Atomic Theory: Relative 1.1 Atomic Weights 3
- Atomic Magnitudes 5 1.2
- The Charge-to-Mass Ratio of the Electron: 1.3 Thomson's Method 6
- 1.4 The Charge of the Electron: Millikan's Method 10
- 1.5 Mass Spectrometry 12
- 1.6 The Atomic Mass Scale and the Mole 15
- 1.7 The Periodic Table 16

#### Chapter 2: Origins of the Quantum Theory of Matter 21

- 2.1 The Franck–Hertz Experiment 21
- 2.2 The Photoelectric Effect 24
- 2.3 X-rays and Matter 25
- 2.4 The Emission Spectra of Atoms 28
- 2.5 The Nuclear Atom 29
- 2.6 The Problem of Black-Body Radiation 33
- 2.7 The Concept of Action 35
- 2.8 The Harmonic Oscillator 36
- 2.9 Action Quantized: The Heat Capacity of Solids 39
- 2.10 Some Orders of Magnitude 41
- 2.11 Bohr's Model of the Atom 42

Appendix 2A: Rutherford Scattering 47

#### Chapter 3: Matter Waves in Simple Systems 53

- 3.1 The de Broglie Hypothesis 53
- 3.2 The Nature of Waves 55
- 3.3 Dispersion Relations and Wave Equations: The Free Particle 57
- 3.4 Operators 60
- 3.5 Eigenfunctions and Eigenvalues 62
- The Particle in a One-Dimensional Box 65 3.6
- The Indeterminacy or Uncertainty Principle 69 3.7
- Expectation Values; Summary of Postulates 3.8 71
- Particles in Two- and Three-Dimensional 3.9 Boxes 74
- 3.10 Particles in Circular Boxes 76
- 3.11 Particles in Spherical Boxes 82

3.12 The Rigid Rotator 86 Appendix 3A: More on Circular Coordinates and the Circular Box 89

### **Chapter 4: Particles in Varying Potential** Fields; Transitions 94

Finite Potential Barriers 94 4.1

1

- The Quantum Mechanical Harmonic 4.2 Oscillator 97
- 4.3 The Hydrogen Atom 99
- The Shapes of Orbitals 104 4.4
- Transitions between Energy Levels 105 4.5

#### **Chapter 5: The Structure of Atoms** 115

- Electron Spin; Magnetic Phenomena 115 5.1
- The Pauli Exclusion Principle; the Aufbau 5.2 Principle 118
- 5.3 Electronic Configurations of Atoms 120
- 5.4 Calculation of Atomic Structures 122
- 5.5 Atomic Structure and Periodic Behavior 128
- 5.6 Term Splitting and the Vector Model 133
- Fine Structure and Spin–Orbit Interaction 139 5.7

Appendix 5A: The Stern–Gerlach Experiment 142

#### Chapter 6: The Chemical Bond in the Simplest Molecules: H<sub>2</sub><sup>+</sup> and H<sub>2</sub> 147

- Bonding Forces between Atoms 147 6.1
- 6.2 The Simplest Molecule: The Hydrogen Molecule-Ion, H<sup>+</sup><sub>2</sub> 152
- H<sub>2</sub><sup>+</sup>: Molecular Orbitals and the LCAO 6.3 Approximation 154
- 6.4 H<sub>2</sub><sup>+</sup>: Obtaining the Energy Curve 157
- 6.5 H<sub>2</sub><sup>+</sup>: Correlation of Orbitals; Excited States 159
- The H<sub>2</sub> Molecule: Simple MO Description 165 6.6
- Symmetry Properties of Identical 6.7 Particles 167
- 6.8 H<sub>2</sub>: The Valence Bond Representation 170
- H<sub>2</sub>: Beyond the Simple MO and VB 6.9 Approximations 172

6.10 H<sub>2</sub>: Excited Electronic States 174 Appendix 6A: Orthogonality 177 Appendix 6B: Hermitian Operators 178

#### Chapter 7: More about Diatomic Molecules 182

- Vibrations of Diatomic Molecules 182 7.1 7.2
- Rotations of Diatomic Molecules 190

- 7.3 Spectra of Diatomic Molecules 193
- 7.4 The lonic Bond 200
- 7.5 Homonuclear Diatomic Molecules: Molecular Orbitals and Orbital Correlation 203
- 7.6 Homonuclear Diatomic Molecules: Aufbau Principle and Structure of First-Row Molecules 208
- 7.7 Introduction to Heteronuclear Diatomic Molecules: Electronegativity 213
- 7.8 Bonding in LiH: Crossing and Noncrossing Potential Curves 216
- 7.9 Other First-Row Diatomic Hydrides 218
- 7.10 Isoelectronic and Other Series 221
- Appendix 7A: Perturbation Theory 224

### Chapter 8: Triatomic Molecules 229

- 8.1 Electronic Structure and Geometry in the Simplest Cases:  $H_3$  and  $H_3^+$  229
- 8.2 Dihydrides: Introduction to the Water Molecule 234
- 8.3 Hybrid Orbitals 236
- 8.4 Delocalized Orbitals in H<sub>2</sub>O: The General MO Method 238
- 8.5 Bonding in More Complex Triatomic Molecules 245
- 8.6 Normal Coordinates and Modes of Vibration 247
- 8.7 A Solvable Example: The Vibrational Modes of CO<sub>2</sub> 252
- 8.8 Transitions and Spectra of Polyatomic Molecules: Rotations and Vibrations 254
- 8.9 Transitions and Spectra of Polyatomic Molecules: Magnetic Transitions 255
- 8.10 Transitions and Spectra of Polyatomic Molecules: Electronic Transitions 256

#### Chapter 9: Larger Polyatomic Molecules 261

- 9.1 Small Molecules 261
- 9.2 Catenated Carbon Compounds; Transferability 265
- 9.3 Other Extended Structures 271
- 9.4 Some Steric Effects 275
- 9.5 Complex lons and Other Coordination Compounds: Simple Polyhedra 280
- 9.6 Chirality and Optical Rotation 282
- 9.7 Chiral and Other Complex lons 283
- 9.8 Magnetic Properties of Complexes 285
- 9.9 Electronic Structure of Complexes 288 Appendix 9A: Schmidt Orthogonalization 294

### Chapter 10: Intermolecular Forces 298

- 10.1 Long-Range Forces: Interactions between Charge Distributions 298
- 10.2 Empirical Intermolecular Potentials 303
- 10.3 Weakly Associated Molecules 307

### Chapter 11: The Structure of Solids 313

- 11.1 Some General Properties of Solids 313
- 11.2 Space Lattices and Crystal Symmetry 315 11.3 X-ray Diffraction from Crystals: The Bragg
- Model 317
- 11.4 The Laue Model 320
- 11.5 Determination of Crystal Structures 322
- 11.6 Techniques of Diffraction 324
- 11.7 Molecular Crystals 325
- 11.8 Structures of Ionic Crystals 329
- 11.9 Binding Energy of Ionic Crystals 331
- 11.10 Covalent Solids 334
- 11.11 The Free-Electron Theory of Metals 335
- 11.12 The Band Theory of Solids 339
- 11.13 Conductors, Insulators, and Semiconductors 343
- 11.14 Other Forms of Condensed Matter 345

### PART II: MATTER IN EQUILIBRIUM: STATISTICAL MECHANICS AND THERMODYNAMICS 351

# Chapter 12: The Perfect Gas at Equilibrium and the Concept of Temperature 353

- 12.1 The Perfect Gas: Definition and Elementary Model 353
- 12.2 The Perfect Gas: A General Relation between Pressure and Energy 355
- 12.3 Some Comments about Thermodynamics 357
- 12.4 Temperature and the Zero-th Law of Thermodynamics 359
- 12.5 Empirical Temperature: The Perfect Gas Temperature Scale 361
- 12.6 Comparison of the Microscopic and Macroscopic Approaches 364

## Chapter 13: The First Law of Thermodynamics 369

- 13.1 Microscopic and Macroscopic Energy in a Perfect Gas 369
- 13.2 Description of Thermodynamic States 371
- 13.3 The Concept of Work in Thermodynamics 373
- 13.4 Intensive and Extensive Variables 375
- 13.5 Quasi-static and Reversible Processes 376
- 13.6 The First Law: Internal Energy and Heat 379
- 13.7 Some Historical Notes 381
- 13.8 Microscopic Interpretation of Internal Energy and Heat 382
- 13.9 Constraints, Work, and Equilibrium 383

## Chapter 14: Thermochemistry and Its Applications 388

- 14.1 Heat Capacity and Enthalpy 388
- 14.2 Energy and Enthalpy Changes in Chemical Reactions 392

#### viii • Contents

- 14.3 Thermochemistry of Physical Processes 394
- 14.4 Introduction to Phase Changes 397
- 14.5 Standard States 398
- 14.6 Thermochemistry of Solutions 400
- 14.7 Molecular Interpretation of Physical Processes 404
- 14.8 Bond Energies 405
- 14.9 Some Energy Effects in Molecular Structures 409
- 14.10 Lattice Energies of Ionic Crystals 411

#### Chapter 15: The Concept of Entropy: Relationship to the Energy-Level Spectrum of a System 420

- 15.1 The Relationship between Average Properties and Molecular Motion in an *N*-Molecule System: Time Averages and Ensemble Averages 421
- 15.2 Ensembles and Probability Distributions 425
- 15.3 Some Properties of a System with Many Degrees of Freedom: Elements of the Statistical Theory of Matter at Equilibrium 428
- 15.4 The Influence of Constraints on the Density of States 431
- 15.5 The Entropy: A Potential Function for the Equilibrium State 435

Appendix 15A: Comments on Ensemble Theory 443 Appendix 15B:  $\Omega(E)$  as a System Descriptor 448 Appendix 15C: The Master Equation 450

#### Chapter 16: The Second Law of Thermodynamics: The Macroscopic Concept of Entropy 454

- 16.1 The Second Law of Thermodynamics 454
- 16.2 The Existence of an Entropy Function for Reversible Processes 456
- 16.3 Irreversible Processes: The Second-Law Interpretation 459
- 16.4 The Clausius and Kelvin Statements Revisited 463
- 16.5 The Second Law as an Inequality 465
- 16.6 Some Relationships between the Microscopic and Macroscopic Theories 466
- Appendix 16A: Poincaré Recurrence Times and Irreversibility 468

# Chapter 17: Some Applications of the Second Law of Thermodynamics 476

- 17.1 Choice of Independent Variables 476
- 17.2 The Available Work Concept 478
- 17.3 Entropy Changes in Reversible Processes 479
- 17.4 Entropy Changes in Irreversible Processes 482
- 17.5 Entropy Changes in Phase Transitions 484

# Chapter 18: The Third Law of Thermodynamics 488

- 18.1 The Magnitude of the Entropy at T = 0 489
- 18.2 The Unattainability of Absolute Zero 494

18.3 Experimental Verification of the Third Law 495

### **Chapter 19: The Nature of the Equilibrium State 499**

- 19.1 Properties of the Equilibrium State of a Pure Substance 499
- 19.2 Alternative Descriptions of the Equilibrium State for Different External Constraints 503
- 19.3 The Stability of the Equilibrium State of a One-Component System 506
- 19.4 The Equilibrium State in a Multicomponent System 508
- 19.5 Chemical Equilibrium 512
- 19.6 Thermodynamic Weight: Further Connections between Thermodynamics and Microscopic Structure 513
- 19.7 An Application of the Canonical Ensemble: The Distribution of Molecular Speeds in a Perfect Gas 518

#### Chapter 20: An Extension of Thermodynamics to the Description of Nonequilibrium Processes 524

- 20.1 General Form of the Equations of Continuity 525
- 20.2 Conservation of Mass and the Diffusion Equation 526
- 20.3 Conservation of Momentum and the Navier-Stokes Equation 527
- 20.4 Conservation of Energy and the Second Law of Thermodynamics 530
- 20.5 Linear Transport Processes 533
- 20.6 Negative Temperature 535
- 20.7 Thermodynamics of Systems at Negative Absolute Temperature 537

Appendix 20A: Symmetry of the Momentum Flux Tensor 543

## Chapter 21: The Properties of Pure Gases and Gas Mixtures 546

- 21.1 Thermodynamic Description of a Pure Gas 546
- 21.2 Thermodynamic Description of a Gas Mixture 554
- 21.3 Thermodynamic Description of Gaseous Reactions 559
- 21.4 An Example: The Haber Synthesis of NH<sub>3</sub> 561
- 21.5 Statistical Molecular Theory of Gases and Gas Reactions 565
  - A. The Partition Function 565
  - B. The Heat Capacity of a Perfect Gas of Diatomic Molecules 570
- 21.6 The Statistical Molecular Theory of the Equilibrium Constant 575
- 21.7 The Statistical Molecular Theory of the Real Gas 577

Appendix 21A: Influence of Symmetry of the Wave Function on the Distribution over States: Fermi–Dirac and Bose–Einstein Statistics 585

Appendix 21B: Symmetry Properties of the Molecular Wave Function: Influence of Nuclear Spin on the Rotational Partition Function 589

Appendix 21C: The Semiclassical Partition Function; The Equation of State of an Imperfect Gas 591

## Chapter 22: Thermodynamic Properties of Solids 597

- 22.1 Differences between Gases and Condensed Phases 597
- 22.2 The Influence of Crystal Symmetry on Macroscopic Properties 597
- 22.3 Microscopic Theory of the Thermal Properties of Crystalline Solids 601
- 22.4 The Contribution of Anharmonicity to the Properties of a Crystal 608
- 22.5 Some Properties of Complex Solids and of Imperfect Solids 610

22.6 Electronic Heat Capacity of Metals 612

Appendix 22A: Evaluation of Fermi-Dirac Integrals 615

### Chapter 23: Thermodynamic Properties of Liquids 619

- 23.1 Bulk Properties of Liquids 619
- 23.2 The Structure of Liquids 623
- 23.3 Relationships between the Structure and the Thermodynamic Properties of a Simple Liquid 629
- 23.4 The Molecular Theory of Monoatomic Liquids: General Remarks 631
- 23.5 The Molecular Theory of Monoatomic Liquids: Approximate Analyses 636
- 23.6 The Molecular Theory of Polyatomic Liquids 642

Appendix 23A: X-ray Scattering from Liquids: Determination of the Structure of a Liquid 647 Appendix 23B: Functional Differentiation 649

### Chapter 24: Phase Equilibria in One-Component Systems 655

- 24.1 General Survey of Phase Equilibria 655
- 24.2 Thermodynamics of Phase Equilibria in One-Component Systems 659A. The Clausius-Clapeyron Equation 659
  - B. The Critical Point 663
- 24.3 Phase Transitions Viewed as Responses
- to Thermodynamic Instabilities 666 24.4 The Statistical Molecular Description of Phase Transitions 674
- Appendix 24A: The Scaling Hypothesis
- for Thermodynamic Functions 687
- Appendix 24B: Aspects of Density Functional Theory 689

# Chapter 25: Solutions of Nonelectrolytes 694

- 25.1 The Chemical Potential of a Component in an Ideal Solution 694
- 25.2 The Chemical Potential of a Component in a Real Solution 696
- 25.3 Partial Molar Quantities 699
- 25.4 Liquid–Vapor Equilibrium 700
- 25.5 Liquid–Solid Equilibrium 706
- 25.6 The Colligative Properties of Solutions: Boiling-Point Elevation, Freezing-Point Depression, and Osmotic Pressure 708
- 25.7 Chemical Reactions in Nonelectrolyte Solutions 711
- 25.8 More about Phase Equilibrium in Mixtures 712
- 25.9 Critical Phenomena in Mixtures 721
- 25.10 The Molecular Theory of Solutions of Nonelectrolytes 723
  - A. The Statistical Mechanics of Mixtures 723
  - B. Molecular Theory of Crystalline Mixtures 725
  - C. Molecular Theory of Liquid Mixtures 733

### Chapter 26: Equilibrium Properties of Solutions of Electrolytes 745

- 26.1 The Chemical Potential 745
- 26.2 Cells, Chemical Reactions, and Activity Coefficients 747
  - A. Determination of Solute Activities 750
  - B. Determination of an Equilibrium Constant 750
- 26.3 Comments on the Structure of Water 752
- 26.4 The Influence of Solutes on the Structure of Water 756
- 26.5 The Statistical Mechanics of Electrolyte Solutions 772
  - A. Debye–Hückel Theory 772
  - B. An Alternative View of the Debye–Hückel Approximation 776
  - C. Beyond the Debye-Hückel Approximation 777
  - D. Semiempirical Representation of the Properties of Electrolyte Solutions 782
- 26.6 Molten Salts and Molten Salt Mixtures 783
- 26.7 The Structure of an Electrolyte Solution Near an Electrode 790
  - A. The Structure of Water Near a Surface 790
  - B. The Electrolyte Solution–Electrode Interface 795

PART III: PHYSICAL AND CHEMICAL KINETICS 803

## Chapter 27: Molecular Motion and Collisions 805

- 27.1 Kinematics 805
- 27.2 Forces and Potentials 808

- X 

  Contents
- 27.3 Collision Dynamics 809
- 27.4 Types of Collisions 812
- 27.5 Scattering Cross Sections 814
- 27.6 Elastic Scattering of Hard Spheres 817
- 27.7 Elastic Scattering of Atoms 817
- 27.8 Quantum Mechanical Scattering 818

# Chapter 28: The Kinetic Theory of Gases 820

- 28.1 Distribution Functions 820
- 28.2 Collision Frequency in a Dilute Gas 822
- 28.3 The Evolution of Velocity Distributions in Time 823
- 28.4 The Maxwell-Boltzmann Distribution 826
- 28.5 Collision Frequency for Hard-Sphere Molecules 829
- 28.6 Molecular Fluxes of Density, Momentum Density, and Energy Density 830
- 28.7 Effusion 833
- 28.8 Transport Properties of Gases 835
- 28.9 Energy Exchange Processes 840
- 28.10 Sound Propagation and Absorption 845

### Chapter 29: The Kinetic Theory of Dense Phases 854

- 29.1 Transport Properties in Dense Fluids 854
- 29.2 Some Basic Aspects of Brownian Motion 856
- 29.3 Stochastic Approach to Transport 860
- 29.4 Autocorrelation Functions and Transport Coefficients 863
- 29.5 Transport in Solids 866
- 29.6 Electrical Conductivity in Electrolyte Solutions 871

### Chapter 30: Chemical Kinetics 876

- 30.1 General Concepts of Kinetics 876 A. First-Order Reactions 878
  - B. Second-Order Reactions 878
- 30.2 Interactions between Reactive Molecules 882 Vignette: Quantum Mechanical Computations of Potential Energy Hypersurfaces, by H. F. Schaefer III 886
- 30.3 Collisions between Reactive Molecules 888
- Vignette: Femtochemistry—Reaction Dynamics with Atomic Resolution, by A. H. Zewail 896
- 30.4 Hard-Sphere Collision Theory: Reactive Cross Sections 905
- 30.5 Hard-Sphere Collision Theory: The Rate Coefficient 906
- 30.6 Activated-Complex Theory 911
- Vignette: Present-Day View of Transition State Theory, by D. G. Truhlar 913

- 30.7 Activated-Complex Theory: Thermodynamic Interpretation 916
- 30.8 Theory of Reaction Kinetics in Solution 919
- Vignette: Kramers' Theory of Reactions in Solutions, by M. O. Vlad and J. Ross 924
- Vignette: Chemical Reactions in Condensed Phases, by P. G. Wolynes 926
- 30.9 Linear Free-Energy Relationships 928
- 30.10 Experimental Methods in Kinetics 929
- 30.11 Analysis of Data for Complex Reactions 935
  - A. Third-Order Reactions 935
  - B. Reversible Reactions 935
  - C. Simultaneous Reactions 936
  - D. Consecutive Reactions 937
- 30.12 Mechanisms of Chemical Reactions 938
- 30.13 Biomolecular Reactions 942
- Vignette: Electron Transfer Reactions,
- by R. A. Marcus 945
- 30.14 Unimolecular Reactions 948
- 30.15 Termolecular Reactions 951

#### Chapter 31: Some Advanced Topics in Chemical Kinetics 958

- 31.1 More about Unimolecular Reactions 958
- 31.2 Kinetics of Photochemically Induced Reactions 961
- 31.3 Chain Reactions 966
- 31.4 Nonlinear Phenomena 970
- 31.5 Fluctuations in Chemical Kinetics 977
- 31.6 Symmetry Rules for Chemical Reactions 979
- 31.7 Introduction to Catalysis 983
- 31.8 Enzyme Catalysis 983
- 31.9 Acid-Base Catalysis 986
- 31.10 Metal-Ion Complex and Other Types of Homogeneous Catalysis 988
- 31.11 Heterogeneous Reactions: Adsorption of Gas on a Surface 990
- 31.12 Heterogeneous Catalysis 993
- 31.13 Kinetics of Electrode Reactions (a Vignette by C. E. D. Chidsey) 999
- Vignette: Applications of Physical Chemistry: A Biological Example, by B. Eisenberg 1011

Appendix I: Systems of Units 1019 Appendix II. Partial Derivatives 1022

1. 10 17

Appendix III: Glossary of Symbols 1025

Appendix IV: Searching the Scientific Literature 1037

×

Index 1047