Contents

Preface *xi*

PART I: THE STRUCTURE OF MATTER 1

Chapter 1: The Microscopic World: Atoms and Molecules 3

1.1 Development of the Atomic Theory: Relative Atomic Weights 3
1.2 Atomic Magnitudes 5
1.3 The Charge-to-Mass Ratio of the Electron: 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
3.6 The Particle in a One-Dimensional Box 65
3.7 The Indeterminacy or Uncertainty Principle 69
3.8 Expectation Values; Summary of Postulates 71
3.9 Particles in Two- and Three-Dimensional 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

4.1 Finite Potential Barriers 94
4.2 The Quantum Mechanical Harmonic Oscillator 97
4.3 The Hydrogen Atom 99
4.4 The Shapes of Orbitals 104
4.5 Transitions between Energy Levels 105

Chapter 5: The Structure of Atoms 115

5.1 Electron Spin; Magnetic Phenomena 115
5.2 The Pauli Exclusion Principle; the Aufbau 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
5.7 Fine Structure and Spin–Orbit Interaction 139
Appendix 5A: The Stern–Gerlach Experiment 142

Chapter 6: The Chemical Bond in the Simplest Molecules: H_2^+ and H_2 147

6.1 Bonding Forces between Atoms 147
6.2 The Simplest Molecule: The Hydrogen Molecule-Ion, H_2^+ 152
6.3 H_2^+: Molecular Orbitals and the LCAO Approximation 154
6.4 H_2^+: Obtaining the Energy Curve 157
6.5 H_2^+: Correlation of Orbitals; Excited States 159
6.6 The H_2 Molecule: Simple MO Description 165
6.7 Symmetry Properties of Identical Particles 167
6.8 H_2: The Valence Bond Representation 1
6.9 H_2: Beyond the Simple MO and VB Approximations 172
6.10 H_2: Excited Electronic States 174
Appendix 6A: Orthogonality 177
Appendix 6B: Hermitian Operators 178

Chapter 7: More about Diatomic Molecules 182

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

7.3 Spectra of Diatomic Molecules 193
7.4 The Ionic 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_2O: 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_2 252
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 Ions and Other Coordination Compounds: Simple Polyhedra 280
9.6 Chirality and Optical Rotation 282
9.7 Chiral and Other Complex Ions 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

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_3 561
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 659
A. 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

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
Appendix III: Glossary of Symbols 1025
Appendix IV: Searching the Scientific Literature 1037

Index 1047