Contents

PREFACE xvi

1 Fundamental Concepts of Thermodynamics 1

- 1.1 What Is Thermodynamics and Why Is It Useful? 1
- 1.2 Basic Definitions Needed to Describe Thermodynamic Systems 2
- 1.3 Thermometry 4
- 1.4 Equations of State and the Ideal Gas Law 6
- 1.5 A Brief Introduction to Real Gases 9
- 2 Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics 15
- 2.1 The Internal Energy and the First Law of Thermodynamics 15
- 2.2 Work 16
- 2.3 Heat 19
- 2.4 Heat Capacity 21
- 2.5 State Functions and Path Functions 23
- 2.6 Equilibrium, Change, and Reversibility 25
- 2.7 Comparing Work for Reversible and Irreversible Processes 26
- 2.8 Determining ΔU and Introducing Enthalpy, a New State Function 30
- 2.9 Calculating q, w, ΔU and ΔH for Processes Involving Ideal Gases 31
- 2.10 The Reversible Adiabatic Expansion and Compression of an Ideal Gas 35
- 3 The Importance of State Functions: Internal Energy and Enthalpy 41
- 3.1 The Mathematical Properties of State Functions 41
- 3.2 The Dependence of U on V and T 46
- 3.3 Does the Internal Energy Depend More Strongly on V or T? 48
- 3.4 The Variation of Enthalpy with Temperature at Constant Pressure 51
- 3.5 How are C_P and C_V Related? 53
- 3.6 The Variation of Enthalpy with Pressure at Constant Temperature 54
- 3.7 The Joule–Thomson Experiment 57
- 3.8 Liquefying Gases Using an Isenthalpic Expansion 59

4 Thermochemistry 63

- 4.1 Energy Stored in Chemical Bonds Is Released or Taken Up in Chemical Reactions 63
- 4.2 Internal Energy and Enthalpy Changes Associated with Chemical Reactions 64
- 4.3 Hess's Law Is Based on Enthalpy Being a State Function 67
- 4.4 The Temperature Dependence of Reaction Enthalpies 69
- 4.5 The Experimental Determination of ΔU and ΔH for Chemical Reactions 71
- 4.6 (Supplemental) Differential Scanning Calorimetry 73
- 5 Entropy and the Second and Third Laws of Thermodynamics 79
- 5.1 The Universe Has a Natural Direction of Change 79
- 5.2 Heat Engines and the Second Law of Thermodynamics 80
- 5.3 Introducing Entropy 85
- 5.4 Calculating Changes in Entropy 86
- 5.5 Using Entropy to Calculate the Natural Direction of a Process in an Isolated System 89
- 5.6 The Clausius Inequality 91
- 5.7 The Change of Entropy in the Surroundings and $\Delta S_{total} = \Delta S + \Delta S_{surroundings}$ 92
- 5.8 Absolute Entropies and the Third Law of Thermodynamics 94
- 5.9 Standard States in Entropy Calculations 98
- 5.10 Entropy Changes in Chemical Reactions 98
- 5.11 (Supplemental) Energy Efficiency: Heat Pumps, Refrigerators, and Real Engines 100
- 5.12 (Supplemental) Using the Fact That S Is a State Function to Determine the Dependence of S on V and T 107
- 5.13 (Supplemental) The Dependence of S on T and P 108
- 5.14 (Supplemental) The Thermodynamic Temperature Scale 109

6 Chemical Equilibrium 115

- 6.1 The Gibbs Energy and the Helmholtz Energy 116
- 6.2 The Differential Forms, of U, H, A, and G 120

- 6.3 The Dependence of the Gibbs and Helmholtz Energies on P, V, and T 121
- 6.4 The Gibbs Energy of a Reaction Mixture 124
- 6.5 The Gibbs Energy of a Gas in a Mixture 125
- 6.6 Calculating the Gibbs Energy of Mixing for Ideal Gases 126
- 6.7 Calculating ΔG_R° for a Chemical Reaction 127
- 6.8 Introducing the Equilibrium Constant for a Mixture of Ideal Gases 129
- 6.9 Calculating the Equilibrium Partial Pressures in a Mixture of Ideal Gases 131
- 6.10 The Variation of K_P with Temperature 132
- 6.11 Equilibria Involving Ideal Gases and Solid or Liquid Phases 134
- 6.12 Expressing the Equilibrium Constant in Terms of Mole Fraction or Molarity 135
- 6.13 The Dependence of ξ_{eq} on T and P 136
- 6.14 (Supplemental) A Case Study: The Synthesis of Ammonia 137
- 6.15 (Supplemental) Expressing U and H and Heat Capacities Solely in Terms of Measurable Quantities 142
- 6.16 (Supplemental) Measuring ΔG for the Unfolding of Single RNA Molecules 146
- 6.17 (Supplemental) The Role of Mixing in Determining Equilibrium in a Chemical Reaction 147

7 The Properties of Real Gases 155

- 7.1 Real Gases and Ideal Gases 155
- 7.2 Equations of State for Real Gases and Their Range of Applicability 156
- 7.3 The Compression Factor 160
- 7.4 The Law of Corresponding States 163
- 7.5 Fugacity and the Equilibrium Constant for Real Gases 166
- 8 Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases 173
- 8.1 What Determines the Relative Stability of the Solid, Liquid, and Gas Phases? 173
- 8.2 The Pressure–Temperature Phase Diagram 176
- 8.3 The Phase Rule 181
- 8.4 The Pressure-Volume and Pressure-Volume-Temperature Phase Diagrams 182

- 8.5 Providing a Theoretical Basis for the *P*–*T* Phase Diagram 184
- 8.6 Using the Clausius–Clapeyron Equation to Calculate Vapor Pressure as a Function of T 185
- 8.7 The Vapor Pressure of a Pure Substance Depends on the Applied Pressure 188
- 8.8 Surface Tension 189
- 8.9 (Supplemental) Chemistry in Supercritical Fluids 192
- 8.10 (Supplemental) Liquid Crystal Displays 193

9 Ideal and Real Solutions 199

- 9.1 Defining the Ideal Solution 200
- 9.2 The Chemical Potential of a Component in the Gas and Solution Phases 201
- 9.3 Applying the Ideal Solution Model to Binary Solutions 202
- 9.4 The Temperature–Composition Diagram and Fractional Distillation 206
- 9.5 The Gibbs–Duhem Equation 208
- 9.6 Colligative Properties 210
- 9.7 The Freezing Point Depression and Boiling Point Elevation 210
- 9.8 The Osmotic Pressure 213
- 9.9 Real Solutions Exhibit Deviations from Raoult's Law 214
- 9.10 The Ideal Dilute Solution 217
- 9.11 Activities Are Defined with Respect to Standard States 219
- 9.12 Henry's Law and the Solubility of Gases in a Solvent 222
- 9.13 Chemical Equilibrium in Solutions 223
- 9.14 Solutions Formed from Partially Miscible Liquids 227
- 9.15 The Solid–Solution Equilibrium 228

10 Electrolyte Solutions 233

- 10.1 The Enthalpy, Entropy, and Gibbs Energy of Ion Formation in Solutions 234
- 10.2 Understanding the Thermodynamics of Ion Formation and Solvation 236
- 10.3 Activities and Activity Coefficients for Electrolyte Solutions 238
- 10.4 Calculating γ_{\pm} Using the Debye-Hückel Theory 241
- 10.5 Chemical Equilibrium in Electrolyte Solutions 245

- 1 1 Electrochemical Cells, Batteries, and Fuel Cells 249
- 11.1 The Effect of an Electrical Potential on the Chemical Potential of Charged Species 250
- 11.2 Conventions and Standard States in Electrochemistry 251
- 11.3 Measurement of the Reversible Cell Potential 254
- 11.4 Chemical Reactions in Electrochemical Cells and the Nernst Equation 254
- 11.5 Combining Standard Electrode Potentials to Determine the Cell Potential 256
- 11.6 Obtaining Reaction Gibbs Energies and Reaction Entropies from Cell Potentials 257
- 11.7 The Relationship between the Cell EMF and the Equilibrium Constant 258
- 11.8 Determination of E° and Activity Coefficients Using an Electrochemical Cell 260
- 11.9 Cell Nomenclature and Types of Electrochemical Cells 260
- 11.10 The Electrochemical Series 262
- 11.11 Thermodynamics of Batteries and Fuel Cells 263
- 11.12 The Electrochemistry of Commonly Used Batteries 263
- 11.13 Fuel Cells 265
- 11.14 (Supplemental) Electrochemistry at the Atomic Scale 267
- 11.15 (Supplemental) Using Electrochemistry for Nanoscale Machining 273
- 11.16 (Supplemental) Absolute Half-Cell Potentials 274

12 From Classical to Quantum Mechanics 281

- 12.1 Why Study Quantum Mechanics? 281
- 12.2 Quantum Mechanics Arose Out of the Interplay of Experiments and Theory 282
- 12.3 Blackbody Radiation 283
- 12.4 The Photoelectric Effect 285
- 12.5 Particles Exhibit Wave-Like Behavior 287
- 12.6 Diffraction by a Double Slit 287
- 12.7 Atomic Spectra and the Bohr Model of the Hydrogen Atom 291

13 The Schrödinger Equation 297

- 13.1 What Determines if a System Needs to Be Described Using Quantum Mechanics? 297
- 13.2 Classical Waves and the Nondispersive Wave Equation 302

- 13.3 Waves Are Conveniently Represented as Complex Functions 305
- 13.4 Quantum Mechanical Waves and the Schrödinger Equation 307
- 13.5 Solving the Schrödinger Equation: Operators, Observables, Eigenfunctions, and Eigenvalues 308
- 13.6 The Eigenfunctions of a Quantum Mechanical Operator Are Orthogonal 310
- 13.7 The Eigenfunctions of a Quantum Mechanical Operator Form a Complete Set 313
- 13.8 Summing Up the New Concepts 314
- 14 The Quantum Mechanical Postulates 319
- 14.1 The Physical Meaning Associated with the Wave Function 320
- 14.2 Every Observable Has a Corresponding Operator 321
- 14.3 The Result of an Individual Measurement 321
- 14.4 The Expectation Value 322
- 14.5 The Evolution in Time of a Quantum Mechanical System 325
- 15 Using Quantum Mechanics on Simple Systems 327
- 15.1 The Free Particle 327
- 15.2 The Particle in a One-Dimensional Box 329
- 15.3 Two- and Three-Dimensional Boxes 333
- 15.4 Using the Postulates to Understand the Particle in the Box and Vice Versa 334
- 16 The Particle in the Box and the Real World 345
- 16.1 The Particle in the Finite Depth Box 345
- 16.2 Differences in Overlap between Core and Valence Electrons 346
- 16.3 Pi Electrons in Conjugated Molecules Can Be Treated as Moving Freely in a Box 347
- 16.4 Why Does Sodium Conduct Electricity and Why Is Diamond an Insulator? 348
- 16.5 Tunneling through a Barrier 350
- 16.6 The Scanning Tunneling Microscope 351
- 16.7 Tunneling in Chemical Reactions 354
- 16.8 (Supplemental) Quantum Wells and Quantum Dots 355

17 Commuting and Noncommuting Operators and the Surprising Consequences of Entanglement 365

- 17.1 Commutation Relations 365
- 17.2 The Stern-Gerlach Experiment 367
- 17.3 The Heisenberg Uncertainty Principle 370
- 17.4 (Supplemental) The Heisenberg Uncertainty Principle Expressed in Terms of Standard Deviations 373
- 17.5 (Supplemental) A Thought Experiment Using a Particle in a Three-Dimensional Box 376
- 17.6 (Supplemental) Entangled States, Teleportation, and Quantum Computers 378

18 A Quantum Mechanical Model for the Vibration and Rotation of Molecules 387

- 18.1 Solving the Schrödinger Equation for the Quantum Mechanical Harmonic Oscillator 387
- 18.2 Solving the Schrödinger Equation for Rotation in Two Dimensions 392
- 18.3 Solving the Schrödinger Equation for Rotation in Three Dimensions 395
- 18.4 The Quantization of Angular Momentum 397
- 18.5 The Spherical Harmonic Functions 399
- 18.6 (Optional Review) The Classical Harmonic Oscillator 402
- 18.7 (Optional Review) Angular Motion and the Classical Rigid Rotor 406
- 18.8 (Supplemental) Spatial Quantization 407

19 The Vibrational and Rotational Spectroscopy of Diatomic Molecules 413

- 19.1 An Introduction to Spectroscopy 413
- 19.2 Absorption, Spontaneous Emission, and Stimulated Emission 415
- 19.3 An Introduction to Vibrational Spectroscopy 417
- 19.4 The Origin of Selection Rules 420
- 19.5 Infrared Absorption Spectroscopy 422
- 19.6 Rotational Spectroscopy 425
- 19.7 (Supplemental) Fourier Transform Infrared Spectroscopy 430
- 19.8 (Supplemental) Raman Spectroscopy 432

19.9 (Supplemental) How Does the Transition Rate between States Depend on Frequency? 434

20 The Hydrogen Atom 445

- 20.1 Formulating the Schrödinger Equation 445
- 20.2 Solving the Schrödinger Equation for the Hydrogen Atom 446
- 20.3 Eigenvalues and Eigenfunctions for the Total Energy 447
- 20.4 The Hydrogen Atom Orbitals 453
- 20.5 The Radial Probability Distribution Function 455
- 20.6 The Validity of the Shell Model of an Atom 459

21 Many-Electron Atoms 463

- 21.1 Helium: The Smallest Many-Electron Atom 463
- 21.2 Introducing Electron Spin 465
- 21.3 Wave Functions Must Reflect the Indistinguishability of Electrons 466
- 21.4 Using the Variational Method to Solve the Schrödinger Equation 470
- 21.5 The Hartree–Fock Self-Consistent Field Method 472
- 21.6 Understanding Trends in the Periodic Table from Hartree-Fock Calculations 479

22 Quantum States for Many-Electron Atoms and Atomic Spectroscopy 487

- 22.1 Good Quantum Numbers, Terms, Levels, and States 488
- 22.2 The Energy of a Configuration Depends on Both Orbital and Spin Angular Momentum 489
- 22.3 Spin-Orbit Coupling Breaks Up a Term into Levels 496
- 22.4 The Essentials of Atomic Spectroscopy 497
- 22.5 Analytical Techniques Based on Atomic Spectroscopy 500
- 22.6 The Doppler Effect 502
- 22.7 The Helium-Neon Laser 503
- 22.8 Laser Isotope Separation 507
- 22.9 Auger Electron and X-Ray Photoelectron Spectroscopies 508
- 22.10 Selective Chemistry of Excited States: O(³P) and O(¹D) 511
- 22.11 (Supplemental) Configurations with Paired and Unpaired Electron Spins Differ in Energy 511

- 23 The Chemical Bond in Diatomic Molecules 517
- 23.1 The Simplest One-Electron Molecule: H₂⁺ 517
- 23.2 The Molecular Wave Function for Ground-State H⁺₂ 519
- 23.3 The Energy Corresponding to the H⁺₂ Molecular Wave Functions ψ_g and ψ_u 520
- 23.4 A Closer Look at the H⁺₂ Molecular Wave Functions ψ_g and ψ_u 523
- 23.5 Combining Atomic Orbitals to Form Molecular Orbitals 526
- 23.6 Molecular Orbitals for Homonuclear Diatomic Molecules 530
- 23.7 The Electronic Structure of Many-Electron Molecules 534
- 23.8 Bond Order, Bond Energy, and Bond Length 537
- 23.9 Heteronuclear Diatomic Molecules 539
- 23.10 The Molecular Electrostatic Potential 540
- 24 Molecular Structure and Energy Levels for Polyatomic Molecules 547
- 24.1 Lewis Structures and the VSEPR Model 547
- 24.2 Describing Localized Bonds Using Hybridization for Methane, Ethene, and Ethyne 550
- 24.3 Constructing Hybrid Orbitals for Nonequivalent Ligands 553
- 24.4 Using Hybridization to Describe Chemical Bonding 556
- 24.5 Predicting Molecular Structure Using Qualitative Molecular Orbital Theory 558
- 24.6 How Different Are Localized and Delocalized Bonding Models? 561
- 24.7 Qualitative Molecular Orbital Theory for Conjugated and Aromatic Molecules: The Hückel Model 563
- 24.8 From Molecules to Solids 568
- 24.9 Making Semiconductors Conductive at Room Temperature 570

25 Electronic Spectroscopy 575

- 25.1 The Energy of Electronic Transitions 575
- 25.2 Molecular Term Symbols 576
- 25.3 Transitions between Electronic States of Diatomic Molecules 579
- 25.4 The Vibrational Fine Structure of Electronic Transitions in Diatomic Molecules 580
- 25.5 UV-Visible Light Absorption in Polyatomic Molecules 582

- 25.6 Transitions among the Ground and Excited States 584
- 25.7 Singlet-Singlet Transitions: Absorption and Fluorescence 585
- 25.8 Intersystem Crossing and Phosphorescence 587
- 25.9 Fluorescence Spectroscopy and Analytical Chemistry 588
- 25.10 Ultraviolet Photoelectron Spectroscopy 589
- 25.11 Single Molecule Spectroscopy 591
- 25.12 Fluorescent Resonance Energy Transfer (FRET) 593
- 25.13 Linear and Circular Dichroism 597
- 25.14 (Supplemental) Assigning + and to Σ Terms of Diatomic Molecules 599

26 Computational Chemistry 603

- 26.1 The Promise of Computational Chemistry 603
- 26.2 Potential Energy Surfaces 604
- 26.3 Hartree–Fock Molecular Orbital Theory: A Direct Descendant of the Schrödinger Equation 608
- 26.4 Properties of Limiting Hartree–Fock Models 610
- 26.5 Theoretical Models and Theoretical Model Chemistry 615
- 26.6 Moving Beyond Hartree–Fock Theory 616
- 26.7 Gaussian Basis Sets 621
- 26.8 Selection of a Theoretical Model 624
- 26.9 Graphical Models 637
- 26.10 Conclusion 645

27 Molecular Symmetry 659

- 27.1 Symmetry Elements, Symmetry Operations, and Point Groups 659
- 27.2 Assigning Molecules to Point Groups 661
- 27.3 The H₂O Molecule and the C_{2v} Point Group 663
- 27.4 Representations of Symmetry Operators, Bases for Representations, and the Character Table 668
- 27.5 The Dimension of a Representation 670
- 27.6 Using the C_{2v} Representations to Construct Molecular Orbitals for H₂O 674
- 27.7 The Symmetries of the Normal Modes of Vibration of Molecules 676
- 27.8 Selection Rules and Infrared versus Raman Activity 680
- 27.9 (Supplemental) Using the Projection Operator Method to Generate MOs That Are Bases for Irreducible Representations 681

- 28 Nuclear Magnetic Resonance Spectroscopy 687
- 28.1 Intrinsic Nuclear Angular Momentum and Magnetic Moment 687
- 28.2 The Energy of Nuclei of Nonzero Nuclear Spin in a Magnetic Field 689
- 28.3 The Chemical Shift for an Isolated Atom 691
- 28.4 The Chemical Shift for an Atom Embedded in a Molecule 692
- 28.5 Electronegativity of Neighboring Groups and Chemical Shifts 693
- 28.6 Magnetic Fields of Neighboring Groups and Chemical Shifts 694
- 28.7 Multiplet Splitting of NMR Peaks Arises through Spin–Spin Coupling 695
- 28.8 Multiplet Splitting When More Than Two Spins Interact 700
- 28.9 Peak Widths in NMR Spectroscopy 702
- 28.10 Solid-State NMR 704
- 28.11 NMR Imaging 704
- 28.12 (Supplemental) The NMR Experiment in the Laboratory and Rotating Frames 706
- 28.13 (Supplemental) Fourier Transform NMR Spectroscopy 708
- 28.14 (Supplemental) Two-Dimensional NMR 712

29 Probability 719

- 29.1 Why Probability? 719
- 29.2 Basic Probability Theory 720
- 29.3 Stirling's Approximation 728
- 29.4 Probability Distribution Functions 729
- 29.5 Probability Distributions Involving Discrete and Continuous Variables 731
- 29.6 Characterizing Distribution Functions 734

$30\,$ The Boltzmann Distribution 743

- 30.1 Microstates and Configurations 743
- 30.2 Derivation of the Boltzmann Distribution 749
- 30.3 Dominance of the Boltzmann Distribution 754
- 30.4 Physical Meaning of the Boltzmann Distribution Law 756
- 30.5 The Definition of β 757

31 Ensemble and Molecular Partition Functions 765

31.1 The Canonical Ensemble 765

31.2 Relating Q to q for an Ideal Gas 767

- 31.3 Molecular Energy Levels 769
- 31.4 Translational Partition Function 769
- 31.5 Rotational Partition Function: Diatomics 772
- 31.6 Rotational Partition Function: Polyatomics 780
- 31.7 Vibrational Partition Function 781
- 31.8 The Equipartition Theorem 787
- 31.9 Electronic Partition Function 788
- 31.10 Review 791

32 Statistical Thermodynamics 797

- 32.1 Energy 797
- 32.2 Energy and Molecular Energetic Degrees of Freedom 801
- 32.3 Heat Capacity 806
- 32.4 Entropy 810
- 32.5 Residual Entropy 815
- 32.6 Other Thermodynamic Functions 816
- 32.7 Chemical Equilibrium 820

33 Kinetic Theory of Gases 829

- 33.1 Kinetic Theory of Gas Motion and Pressure 829
- 33.2 Velocity Distribution in One Dimension 832
- 33.3 The Maxwell Distribution of Molecular Speeds 836
- 33.4 Comparative Values for Speed Distributions: v_{ave} , v_{mp} , and v_{rms} 838
- 33.5 Gas Effusion 840
- 33.6 Molecular Collisions 842
- 33.7 The Mean Free Path 846

34 Transport Phenomena 851

- 34.1 What Is Transport? 851
- 34.2 Mass Transport: Diffusion 853
- 34.3 The Time Evolution of a Concentration Gradient 856
- 34.4 (Supplemental) Statistical View of Diffusion 858
- 34.5 Thermal Conduction 860
- 34.6 Viscosity of Gases 864
- 34.7 Measuring Viscosity 866
- 34.8 Diffusion in Liquids and Viscosity of Liquids 868
- 34.9 (Supplemental) Sedimentation and Centrifugation 870
- 34.10 Ionic Conduction 873

35 Elementary Chemical Kinetics 883

- 35.1 Introduction to Kinetics 884
- 35.2 Reaction Rates 885
- 35.3 Rate Laws 886

XIV CONTENTS

- 35.4 Reaction Mechanisms 892
- 35.5 Integrated Rate Law Expressions 893
- 35.6 (Supplemental) Numerical Approaches 897
- 35.7 Sequential First-Order Reactions 899
- 35.8 Parallel Reactions 904
- 35.9 Temperature Dependence of Rate Constants 906
- 35.10 Reversible Reactions and Equilibrium 908
- 35.11 (Supplemental) Perturbation-Relaxation Methods 911
- 35.12 (Supplemental) The Autoionization of Water: A *T*-Jump Example 913
- 35.13 Potential Energy Surfaces 914
- 35.14 Diffusion Controlled Reactions 916
- 35.15 Activated Complex Theory 918

36 Complex Reaction Mechanisms 929

- 36.1 Reaction Mechanisms and Rate Laws 929
- 36.2 The Preequilibrium Approximation 931
- 36.3 The Lindemann Mechanism 933
- 36.4 Catalysis 935
- 36.5 Radical-Chain Reactions 946
- 36.6 Radical-Chain Polymerization 949
- 36.7 Explosions 950
- 36.8 Photochemistry 952
- 36.9 Electron Transfer 963

Appendix A Math Supplement 977

Appendix B Data Tables 999

- Appendix C Point Group Character Tables 1017
- Appendix D Answers to Selected End-of-Chapter Problems 1027

Index 1043