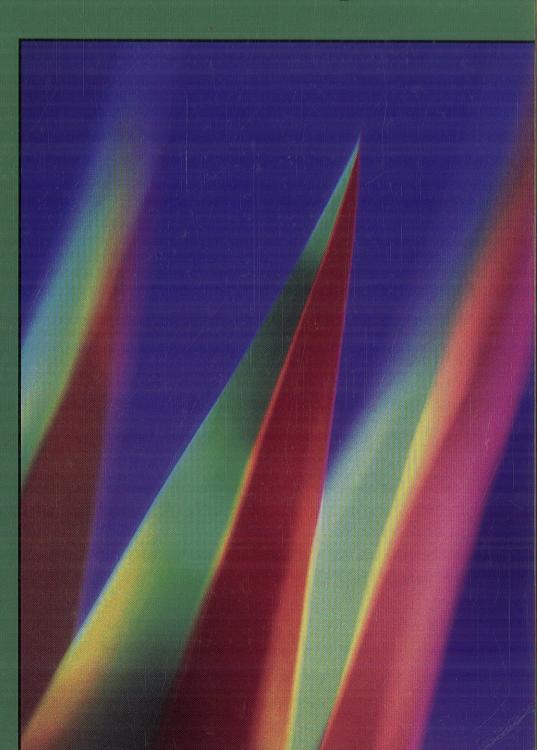


Physical Chemistry

Second Edition

Thomas Engel Philip Reid





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

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

11 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 Noncommutin	g
	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 H₂⁺ 519
- 23.3 The Energy Corresponding to the H₂⁺ 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
- 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 ∑ 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 H_2O 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 H_2O 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