

SIXTH EDITION

# Principles of Modern Chemistry

**DAVID W. OXTOBY**

*Pomona College*

**H.P. GILLIS**

*University of California–Los Angeles*

**ALAN CAMPION**

*The University of Texas at Austin*

Images of orbitals in Chapters 4, 5, 6 and 8 contributed by

**HATEM H. HELAL**

*California Institute of Technology*

**KELLY P. GAITHER**

*The University of Texas at Austin*

**THOMSON**

  
**BROOKS/COLE**™

Australia • Brazil • Canada • Mexico • Singapore • Spain  
United Kingdom • United States

# Contents

---

## UNIT I

### Introduction to the Study of Modern Chemistry 1

#### CHAPTER 1

#### The Atom in Modern Chemistry 2

- 1.1 The Nature of Modern Chemistry 2
- 1.2 Macroscopic Methods for Classifying Matter 5
- 1.3 Indirect Evidence for the Existence of Atoms: Laws of Chemical Combination 8
- 1.4 The Physical Structure of Atoms 14
- 1.5 Imaging Atoms, Molecules, and Chemical Reactions 22

#### CHAPTER 2

#### Chemical Formulas, Chemical Equations, and Reaction Yields 29

- 2.1 The Mole: Weighing and Counting Molecules 30
- 2.2 Empirical and Molecular Formulas 34
- 2.3 Chemical Formula and Percentage Composition 35
- 2.4 Writing Balanced Chemical Equations 37
- 2.5 Mass Relationships in Chemical Reactions 39
- 2.6 Limiting Reactant and Percentage Yield 41

## UNIT II

Chemical Bonding and Molecular  
Structure 52

## CHAPTER 3

## Chemical Bonding: The Classical Description 54

- 3.1 The Periodic Table 56
- 3.2 Forces and Potential Energy in Atoms 59
- 3.3 Ionization Energies and the Shell Model of the Atom 63
- 3.4 Electronegativity: The Tendency of Atoms to Attract Electrons 69
- 3.5 Forces and Potential Energy in Molecules: Formation of Chemical Bonds 72
- 3.6 Ionic Bonding 75
- 3.7 Covalent and Polar Covalent Bonding 78
- 3.8 Lewis Diagrams for Molecules 85
- 3.9 The Shapes of Molecules: Valence Shell Electron-Pair Repulsion Theory 92
- 3.10 Oxidation Numbers 97
- 3.11 Inorganic Nomenclature 100

## CHAPTER 4

## Introduction to Quantum Mechanics 114

- 4.1 Preliminaries: Wave Motion and Light 116
- 4.2 Evidence for Energy Quantization in Atoms 119
- 4.3 The Bohr Model: Predicting Discrete Energy Levels 127
- 4.4 Evidence for Wave-Particle Duality 131
- 4.5 The Schrödinger Equation 141
- 4.6 Quantum Mechanics of Particle-in-a-Box Models 145
- 4.7 Quantum Harmonic Oscillator 155

## CHAPTER 5

## Quantum Mechanics and Atomic Structure 169

- 5.1 The Hydrogen Atom 171
- 5.2 Shell Model for Many-Electron Atoms 184
- 5.3 Aufbau Principle and Electron Configurations 189
- 5.4 Shells and the Periodic Table: Photoelectron Spectroscopy 194
- 5.5 Periodic Properties and Electronic Structure 198

## CHAPTER 6

## Quantum Mechanics and Molecular Structure 211

- 6.1 Quantum Picture of the Chemical Bond 213
- 6.1.6 A Deeper Look** *Nature of the Chemical Bond in  $H_2^+$*  222
- 6.2 De-localized Bonds: Molecular Orbital Theory and the Linear Combination of Atomic 223
- 6.2.5 A Deeper Look** *Potential Energy and Bond Formation in the LCAO Approximation* 242
- 6.2.6 A Deeper Look** *Small Polyatomic Molecules* 245
- 6.3 Photoelectron Spectroscopy for Molecules 247
- 6.4 Localized Bonds: The Valence Bond Model 252
- 6.5 Comparison of Linear Combination of Atomic Orbitals and Valence Bond Methods 261

## CHAPTER 7

## Bonding in Organic Molecules 275

- 7.1 Petroleum Refining and the Hydrocarbons 276
- 7.2 The Alkanes 277
- 7.3 The Alkenes and Alkynes 282
- 7.4 Aromatic Hydrocarbons 288
- 7.5 Fullerenes 290
- 7.6 Functional Groups and Organic Reactions 292
- 7.7 Pesticides and Pharmaceuticals 300

## CHAPTER 8

## Bonding in Transition Metal Compounds and Coordination Complexes 313

- 8.1 Chemistry of the Transition Metals 314
- 8.2 Bonding in Simple Molecules That Contain Transition Metals 318
- 8.3 Introduction to Coordination Chemistry 328
- 8.4 Structures of Coordination Complexes 334
- 8.5 Crystal Field Theory: Optical and Magnetic Properties 339
- 8.6 Optical Properties and the Spectrochemical Series 345
- 8.7 Bonding in Coordination Complexes 348

## UNIT III

Kinetic Molecular Description of the States  
of Matter 362

## CHAPTER 9

## The Gaseous State 364

- 9.1 The Chemistry of Gases 365
- 9.2 Pressure and Temperature of Gases 367
- 9.3 The Ideal Gas Law 374
- 9.4 Mixtures of Gases 377
- 9.5 The Kinetic Theory of Gases 379
- 9.6 **A Deeper Look** *Distribution of Energy among Molecules* 386
- 9.7 Real Gases: Intermolecular Forces 388
- 9.8 **A Deeper Look** *Molecular Collisions and Rate Processes* 393

## CHAPTER 10

## Solids, Liquids, and Phase Transitions 409

- 10.1 Bulk Properties of Gases, Liquids, and Solids: Molecular Interpretation 410
- 10.2 Intermolecular Forces: Origins in Molecular Structure 415
- 10.3 Intermolecular Forces in Liquids 423
- 10.4 Phase Equilibrium 426
- 10.5 Phase Transitions 428
- 10.6 Phase Diagrams 430

## CHAPTER 11

## Solutions 441

- 11.1 Composition of Solutions 442
- 11.2 Nature of Dissolved Species 446
- 11.3 Reaction Stoichiometry in Solutions: Acid–Base Titrations 449
- 11.4 Reaction Stoichiometry in Solutions: Oxidation–Reduction Titrations 452
- 11.5 Phase Equilibrium in Solutions: Nonvolatile Solutes 458
- 11.6 Phase Equilibrium in Solutions: Volatile Solutes 467
- 11.7 Colloidal Suspensions 471

## UNIT IV

## Equilibrium in Chemical Reactions 484

## CHAPTER 12

Thermodynamic Processes  
and Thermochemistry 486

- 12.1 Systems, States, and Processes 488
- 12.2 The First Law of Thermodynamics: Internal Energy, Work, and Heat 491
- 12.3 Heat Capacity, Enthalpy, and Calorimetry 497
- 12.4 Illustrations of the First Law of Thermodynamics in Ideal Gas Processes 500
- 12.5 Thermochemistry 503
- 12.6 Reversible Processes in Ideal Gases 512

## CHAPTER 13

Spontaneous Processes and Thermodynamic  
Equilibrium 529

- 13.1 The Nature of Spontaneous Processes 530
- 13.2 Entropy and Spontaneity: A Molecular Statistical Interpretation 533
- 13.3 Entropy and Heat: Experimental Basis of the Second Law of Thermodynamics 537
- 13.4 A Deeper Look** *Carnot Cycles, Efficiency, and Entropy* 540
- 13.5 Entropy Changes and Spontaneity 543
- 13.6 The Third Law of Thermodynamics 550
- 13.7 The Gibbs Free Energy 552

## CHAPTER 14

## Chemical Equilibrium 569

- 14.1 The Nature of Chemical Equilibrium 570
- 14.2 The Empirical Law of Mass Action 574
- 14.3 Thermodynamic Description of the Equilibrium State 580
- 14.4 The Law of Mass Action for Related and Simultaneous Equilibria 587
- 14.5 Equilibrium Calculations for Gas-Phase and Heterogeneous Reactions 591
- 14.6 The Direction of Change in Chemical Reactions: Empirical Description 597

- 14.7 The Direction of Change in Chemical Reactions: Thermodynamic Explanation 603
- 14.8 Distribution of a Single Species between Immiscible Phases: Extraction and Separation Processes 606

**CHAPTER 15****Acid–Base Equilibria 625**

- 15.1 Classifications of Acids and Bases 626
- 15.2 Properties of Acids and Bases in Aqueous Solutions: The Brønsted–Lowry Scheme 629
- 15.3 Acid and Base Strength 633
- 15.4 Equilibria Involving Weak Acids and Bases 639
- 15.5 Buffer Solutions 645
- 15.6 Acid–Base Titration Curves 649
- 15.7 Polyprotic Acids 654
- 15.8 A Deeper Look** *Exact Treatment of Acid–Base Equilibria* 658
- 15.9 Organic Acids and Bases: Structure and Reactivity 660

**CHAPTER 16****Solubility and Precipitation Equilibria 677**

- 16.1 The Nature of Solubility Equilibria 678
- 16.2 Ionic Equilibria between Solids and Solutions 681
- 16.3 Precipitation and the Solubility Product 684
- 16.4 The Effects of pH on Solubility 688
- 16.5 A Deeper Look** *Selective Precipitation of Ions* 690
- 16.6 Complex Ions and Solubility 692

**CHAPTER 17****Electrochemistry 705**

- 17.1 Electrochemical Cells 706
- 17.2 The Gibbs Free Energy and Cell Voltage 710
- 17.3 Concentration Effects and the Nernst Equation 718
- 17.4 Batteries and Fuel Cells 723
- 17.5 Corrosion and Its Prevention 728
- 17.6 Electrometallurgy 730
- 17.7 A Deeper Look** *Electrolysis of Water and Aqueous Solutions* 735

## UNIT V

Rates of Chemical and Physical  
Processes 748

## CHAPTER 18

## Chemical Kinetics 750

- 18.1 Rates of Chemical Reactions 751
- 18.2 Rate Laws 754
- 18.3 Reaction Mechanisms 761
- 18.4 Reaction Mechanisms and Rate 765
- 18.5 Effect of Temperature on Reaction Rates 770
- 18.6 A Deeper Look** *Reaction Dynamics* 773
- 18.7 Kinetics of Catalysis 775

## CHAPTER 19

## Nuclear Chemistry 793

- 19.1 Mass–Energy Relationships in Nuclei 794
- 19.2 Nuclear Decay Processes 798
- 19.3 Kinetics of Radioactive Decay 803
- 19.4 Radiation in Biology and Medicine 807
- 19.5 Nuclear Fission 809
- 19.6 Nuclear Fusion and Nucleosynthesis 813

## CHAPTER 20

## Interaction of Molecules with Light 825

- 20.1 General Aspects of Molecular Spectroscopy 826
- 20.2 Vibrations and Rotations of Molecules: Infrared and Microwave Spectroscopy 829
- 20.3 Excited Electronic States: Electronic Spectroscopy of Molecules 835
- 20.4 Nuclear Magnetic Resonance Spectroscopy 842
- 20.5 Introduction to Atmospheric Photochemistry 845
- 20.6 Photosynthesis 851



## UNIT VI

## Materials 862

## CHAPTER 21

## Structure and Bonding in Solids 864

- 21.1 Crystal Symmetry and the Unit Cell 865
- 21.2 Crystal Structure 871
- 21.3 Cohesion in Solids 875
- 21.4 A Deeper Look** *Lattice Energies of Crystals* 882
- 21.5 Defects and Amorphous Solids 884

## CHAPTER 22

## Inorganic Materials 895

- 22.1 Minerals: Naturally Occurring Inorganic Minerals 896
- 22.2 Properties of Ceramics 901
- 22.3 Silicate Ceramics 903
- 22.4 Nonsilicate Ceramics 908
- 22.5 Electrical Conduction in Materials 913
- 22.6 Band Theory of Conduction 917
- 22.7 Semiconductors 919
- 22.8 Pigments and Phosphors: Optical Displays 922

## CHAPTER 23

## Polymeric Materials and Soft Condensed Matter 929

- 23.1 Polymerization Reactions for Synthetic Polymers 930
- 23.2 Applications for Synthetic Polymers 934
- 23.3 Liquid Crystals 940
- 23.4 Natural Polymers 943

## Appendices A.1

- A Scientific Notation and Experimental Error A.2
- B SI Units, Unit Conversions, Physics for General Chemistry A.9
- C Mathematics for General Chemistry A.21
- D Standard Chemical Thermodynamic Properties A.37
- E Standard Reaction Potentials at 25°C A.45
- F Physical Properties of the Elements A.47
- G Solutions to the Odd-Numbered Problems A.57