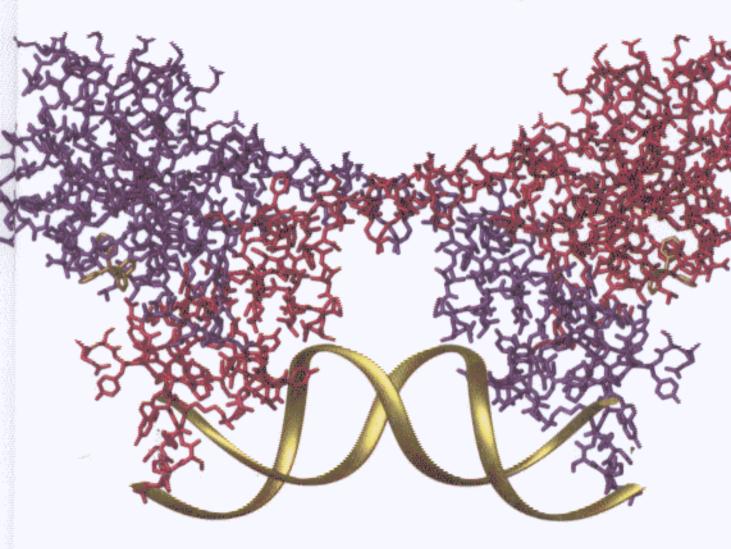
# PHYSICAL CHEMISTRY

Principles and Applications in Biological Sciences
FOURTH EDITION



TINOCO SAUER WANG PUGLISI

# CONTENTS

Preface xvii
About the Authors xix

# C H A T E R

#### Introduction

The Human Genome and Beyond 4
Transcription and Translation 6
lon Channels 10
References 11
Suggested Reading 12
Problem 12

# CHA 2 TER

#### The First Law: Energy Is Conserved

Concepts 15
Applications 16
Energy Conversion

Energy Conversion and Conservation 16

Systems and Surroundings 17

Energy Exchanges 18

First Law of Thermodynamics 28

Describing the State of a System 29

Variables of State 29

Equations of State 31

Paths Connecting Different States 33

Dependence of the Energy and Enthalpy of a Pure Substance on P, V, and T 36

Relations Between Heat Exchanges and DE and DH 44

Phase Changes 45

Chemical Reactions 47

Heat Effects of Chemical Reactions 47

Temperature Dependence of  $\Delta H = 50$ 

The Energy Change  $\Delta E$  for a Reaction 51

Standard Enthalpies (or Heats) of Formation 51

Bond Energies 53

Molecular Interpretations of Energy and Enthalpy 56

Summary 57

State Variables 57

Unit Conversions 57

General Equations 57





Pressure-Volume Work Only 58
Solids and Liquids 58
Gases 59
Phase Changes 59
Chemical Reactions 60
Mathematics Needed for Chapter 2 60
References 61
Suggested Reading 61
Problems 61

# C H A $\frac{3}{3}$ T E R

#### The Second Law: The Entropy of the Universe Increases

Concepts 69
Applications 69
Historical Develo

Historical Development of the Second Law: The Carnot Cycle 69

A New State Function, Entropy 73

The Second Law of Thermodynamics: Entropy Is Not Conserved 75

Molecular Interpretation of Entropy 77

Fluctuations 79

Measurement of Entropy 81

Chemical Reactions 81

Third Law of Thermodynamics 82

Temperature Dependence of Entropy 82

Temperature Dependence of the Entropy Change for a

Chemical Reaction 83

Entropy Change for a Phase Transition 84

Pressure Dependence of Entropy 85

Spontaneous Chemical Reactions 87

Gibbs Free Energy 87

ΔG and a System's Capacity to Do Nonexpansion Work 87

Spontaneous Reactions at Constant T and P 88

Calculation of Gibbs Free Energy 89

Temperature Dependence of Gibbs Free Energy 91

Pressure Dependence of Gibbs Free Energy 94

Phase Changes 97

Helmholtz Free Energy 97

Noncovalent Reactions 92

Hydrophobic Interactions, 100

Proteins and Nucleic Acids 101

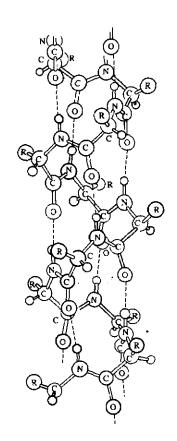
Use of Partial Derivatives in Thermodynamics 106

Relations Among Partial Derivatives 107

Summary 111

State Variables 111

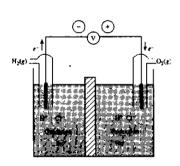
Unit Conversions 111



General Equations 111 ΔG and a System's Capacity to Do Nonexpans on Work 111 Spontaneous Reactions at Constant T and P Changes in Entropy and Gibbs Free Energy 112 References 113 Suggested Reading 113

# CHA4 TER

#### Free Energy and Chemical Equilibria



Concepts 121

Problems 113

Applications 122

Chemical Potential (Partial Molar Gibbs Free Energy) 122

Gibbs Free Energy and the Chemical Potential 122

The Sum Rule for Partial Molar Quantities 123

Chemical Potential and Directionality of Chemical Reaction 123

Reactions of Gases: The Ideal Gas Approximation : 125

Dependence of Chemical Potential on Partial Pressures 125

Equilibrium Constant 127

Nonideal Systems 130

Activity 130

Standard States 131

Activity Coefficients of Ions 139

The Equilibrium Constant and the Standard Gibbs Free Energies

of the Reactants and Products 141

Calculation of Equilibrium Concentrations: Ideal Solutions 144

Temperature Dependence of the Equilibrium Constant 150

Galvanic Cells 153

Standard Electrode Potentials 156

Concentration Dependence of \$\%\$ 158

Biochemical Applications of Thermodynamics 159

Thermodynamics of Metabolism 165

Biological Redox Reactions 170

NADH-Q Reductase 47f

Cytochrome Reductase 172

Cytochrome c Oxidase 172

Double Strand Formation in Nucleic Acids 172

Ionic Effect on Protein-Nucleic Acid Interactions 175

Summary 176

Chemical Potential (Partial Molar Gibbs Free Energy) 176

Standard States and Activities 177

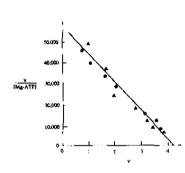
Gibbs Free-Energy Change and Equilibrium Constant for a Chemical Reaction 178

Galvanic Cells 178

Mathematics Needed for Chapter 4 179
References 179
Suggested Reading 179
Problems 179

# CHA 5 TER

# Free Energy and Physical Equilibria



Concepts 187

Applications 187

Membranes and Transport 187

Ligand Binding 188

Colligative Properties 188

Phase Equilibria 188

One-Component Systems 189

Boiling Point and Freezing Point 189

Solutions of Two or More Components 193

Equilibrium Dialysis 197

The Scatchard Equation 198

Cooperative Binding and Anticooperative Binding 202

Free Energy of Transfer Between Phases 206

Donnan Effect and Donnan Potential 210

Membranes 213

Lipid Molecules 213

Lipid Bilayers 214

Phase Transitions in Lipids, Bilayers, and Membranes 216

Surface Tension 218

Surface Free Energy 222

Vapor Pressure and Surface Tension 224

Biological Membranes 225

Active and Passive Transport 227

Colligative Properties 231

Molecular-Weight Determination 239

Vapor-Pressure Lowering 240

Summary 241

Phase Equilibrium 241

Solutions 242

References 244

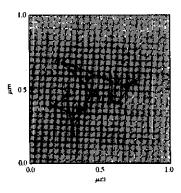
Suggested Reading 245

Internet 245

Problems 245

# C H A 6 T E R

#### Molecular Motion and Transport Properties



Concepts 253

Applications 254

Kinetic Theory 255

Brownian Motion and Random Molecular Motion 255

Velocities of Molecules, Translational Kinetic Energy, and Temperature 256

Maxwell-Boltzmann Distribution of Velocities 261

Molecular Collisions 265

Mean Free Path 266

Diffusion 267

The Random Walk and Diffusion in a Gas 267

Diffusion Coefficient and Fick's First Law 269

Fick's Second Law 271

Determination of the Diffusion Coefficient 272

Relationship Between the Diffusion Coefficient and the Mean-Square

Displacement 273

Determination of the Diffusion Coefficient by Laser Light Scattering 274

Diffusion Coefficient and Molecular Parameters 275

Solvation 276

Shape Factor 277

Diffusion Coefficients of Random Coils 279

Sedimentation 279

Determination of the Sedimentations Coefficient 281

Standard Sedimentation Coefficient 283

Determination of Molecular Weights from Sedimentation

and Diffusion 285

Determination of Molecular Weights from Sedimentation Equilibrium 285

Density-Gradient Centrifugation 288

Viscosity 289

Measurement of Viscosity 290

Viscosities of Solutions 291

Electrophoresis 291

Gel Electrophoresis 292

DNA Sequencing 293

Divisorquencing 250

Double-Stranded DNA 294

DNA Fingerprinting 294

Conformations of Nucleic Acids 296

Pulsed-Field Gel Electrophoresis 297

Protein Molecular Weights 299

Protein Charge 300

Macromolecular Interactions 301

Size and Shape of Macromolecules 30:

Summary 302

Kinetic Theory 302

Diffusion 304

Sedimentation 304
Frictional Coefficient and Molecular Parameters 305
Combination of Diffusion and Sedimentation 305
Viscosity 305
Electrophoresis 306
Gel Electrophoresis 306
References 307
Suggested Reading 307
Problems 307

# CHA7TER

#### Kinetics: Rates of Chemical Reactions

Concepts 315 Applications 316 Kinetics 316 Rate Law 318 Order of a Reaction 318 Experimental Rate Data 320 Zero-Order Reactions 321 First-Order Reactions 322 Second-Order Reactions 329 Renaturation of DNA as an Example of a Second-Order Reaction 334 Reactions of Other Orders 338 Determining the Order and Rate Constant of a Reaction 338 Reaction Mechanisms and Rate Laws 341 Parallel Reactions 343 Series Reactions (First Order) 345 Equilibrium and Kinetics 349 Complex Reactions 351 Deducing a Mechanism from Kinetic Data 352 Temperature Dependence 354 Transition-State Theory 357 Electron Transfer Reactions: Marcus Theory 360 Ionic Reactions and Salt Effects 362 Isotopes and Stereochemical Properties

Very Fast Reactions 365 Relaxation Methods 365 Relaxation Kinetics 366

Vision 377

Photosynthesis 378 Summary 381

Zero-Order Reactions 381 First-Order Reactions 381

Diffusion-Controlled Reactions 372 Photochemistry and Photobiology 374 Second-Order Reactions 382
Temperature Dependence 383
Electron Transfer Reactions: Marcus Theory 385
Relaxation Kinetics 385
Diffusion-Controlled Reactions 386
Absorption of Light 386
Photochemistry 386
Mathematics Needed for Chapter 7 387
References 387
Suggested Reading 388
Problems 388

# CHA 8 TER

#### **Enzyme Kinetics**

Uncatalyzed

71 kJ

Catalase

H<sub>2</sub>O<sub>2</sub>

Reaction coordinate

Concepts 401

Applications 401
Catalytic Antibodies and RNA Enzymes-Ribozymes 401
Enzyme Kinetics 403

Michaelis-Menten Kinetics 406 Kinetic Data Analysis 409 Two Intermediate Complexes 413

Competition and Inhibition 415

Competitive Inhibition 416
Noncompetitive Inhibition 418

Allosteric Effects 419 Single-Molecule Kinetics 422

Summary 423

Typical Enzyme Kinetics 423 Michaelis-Menten Mechanism 424

Monod-Wyman-Changeux Mechanism 425 Mathematics Needed for Chapter 8 425

References 426

Suggested Reading 426 Problems 427

# C H A **9** T E R

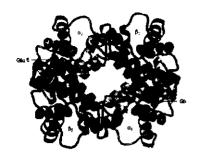
Molecular Structures and Interactions: Theory Concepts 437

Applications 437

The Process of Vision 438

Origins of Quantum Theory 441
Blackbody Radiation 442

Photoelectric Effect 444



Electrons as Waves 444 Heisenberg Uncertainty Principle 445 Quantum Mechanical Calculations 446 Wave Mechanics and Wavefunctions Schrödinger's Equation 449 Solving Wave Mechanical Problems 451 Outline of wave Mechanical Procedures 452 Particle in a Box 455 Tunneling 463 Simple Harmonic Oscillator 465 Rigid Rotator 468 Hydrogen Atom Electron Distribution 470 Electron Distribution in a Hydrogen Atom 471 Many-Electron Atoms 476 Molecular Orbitals 479 Hybridization 484 Delocalized Orbitals 486 Molecular Structure and Molecular Orbitals 489 Geometry and Stereochemistry 489 Transition Metal Ligation 491 Charge Distributions and Dipole Moments 493 Intermolecular and Intramolecular Forces 493 Bond Stretching and Bond Angle Bending 494 Rotation Around Bonds 495 Noncovalent Interactions 497 Electrostatic Energy and Coulomb's Law 497 Net Atomic Charges and Dipole Moments 500 Dipole-Dipole Interactions 503 London Attraction 505 van der Waals Repulsion 506 London-van der Waals Interaction 507 The Lowest-Energy Conformation 508 Hydrogen Bonds 510 Hydrophobic and Hydrophilic Environments 512 Molecular Dynamics Simulation 514 Monte Carlo Method 1514 Molecular Dynamićs Method 515 Outlook 516 Summary 517 Photoelectric Effect 517 Wave-Particle Duality 517 Heisenberg Uncertainty Principle 517 Schrödinger's Equation 518 Some Useful Operators

Systems Whose Schrödinger Equation Can Be Solved Exactly 519

Coulomb's Law 521

Dipoles and Their Interaction Energy 521

Intramolecular (Within) and Intermolecular (Between) Interactions 521

Mathematics Needed for Chapter 9

References 523

Suggested Reading 523

Problems 524

# C H 1 P 0 E R

Molecular Structures and Interactions: Spectroscopy

Concepts 531

Applications 532

Electromagnetic Spectrum 532

Color and Refractive Index 533

Absorption and Emission of Radiation 535

Radiation-Induced Transitions 536

Classical Oscillators 538

Quantum Mechanical Description 538

Lifetimes and Line Width 540

Role of Environment in Electronic Absorption Spectra 541

Beer-Lambert Law 543

Proteins and Nucleic Acids: Ultraviolet Absorption Spectra 548

Amino Acid Spectra 549

Polypeptide Spectra 549

Secondary Structure 551

Origin of Spectroscopic Changes 551

Nucleic Acids 552

Rhodopsin: A Chromorphic Protein 553

Fluorescence 554

Simple Theory 555

Excited-State Properties 556

Fluorescence Quenching 560

Excitation Transfer 561

Molecular Rulers 563

Fluorescence Polarization 564

Phosphorescence 565

Single-Moleculé Fluorescence Spectroscopy 565

Optical Rotatory Dispersion and Circular Dichroism 567

Polarized Light 568

Optical Rotation 571

Circular Dichroism 573

Circular Dichroism of Nucleic Acids and Proteins 573

Vibrational Spectra, Infrared Absorption, and Raman Scattering 576

Infrared Absorption 576

Raman Scattering 577

Nuclear Magnetic Resonance 579

The Spectrum 581

Interactions in Nuclear Magnetic Resonance 583

Chemical Shifts 583

Spin-Spin Coupling, Scalar Coupling, or J-Coupling 585

Relaxation Mechanisms 588

Nuclear Overhauser Effect 590

Multidimensional NMR Spectroscopy 590

Determination of Macromolecular Structure by Nuclear Magnetic Resonance 594

Electron Paramagnetic Resonance 596

Magnetic Resonance Imaging 597

Summary 598

Absorption and Emission 598

Excitation Transfer 600

Optical Rotatory Dispersion and Circular Dichroism 600

Nuclear Magnetic Resonance 600

References 601

Suggested Reading 601

Problems 603

# CHAPTER

# Molecular Distributions and Statistical Thermodynamics

Concepts 615

Applications 615

Binding of Small Molecules by a Polymer 616

Identical-and-Independent-Sites Model 617

Langmuir Adsorption Isotherm 619

Nearest-Neighbor Interactions and Statistical Weights 620

Cooperative Binding, Anticooperative Binding, and Excluded-Site Binding 622

N Identical Sites in a Linear Array with Nearest-Neighbor Interactions 625

Identical Sites in Nonlinear Arrays with Nearest-Neighbor Interactions 626

The Random Walk 628

Calculation of Some Mean Values for the Random-Walk Problem 630

Diffusion 634

Average Dimension of a Linear Polymer 634

Helix-Coil Transitions 636

Helix-Coil Transition in a Polypeptide 636

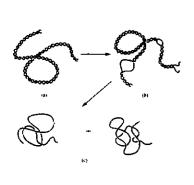
Helix-Coil Transition in a Double-Stranded Nucleic Acid 641

Statistical Thermodynamics 645

Statistical Mechanic Internal Energy 646

Work 647

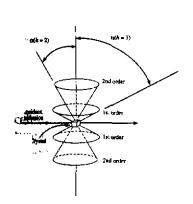
Heat 648



Most Probable (Boltzmann) Distribution 649
Quantum Mechanical Distributions 653
Statistical Mechanical Entropy 653
Examples of Entropy and Probability 654
Partition Function: Applications 658
Summary 659
Binding of Small Molecules by a Polymer 659
Random-Walk and Related Topics 660
Helix-Coil Transitions 660
Statistical Thermodynamics 661
Mathematics Needed for Chapter 11 662
References 662
Suggested Reading 663
Problems 663

# C H 1 P 2 E R

#### Macromolecular Structure and X-Ray Diffraction



Concepts 667
Applications 667
Visible Images 668
X Rays 668
Emission of X Rays 669

Image Formation 669
Scattering of X Rays 670
Diffraction of X Rays by a Crystal 675
Measuring the Diffraction Pattern 678
Bragg Reflection of X Rays 679
Intensity of Diffraction 681
Unit Cell 683

Determination of Molecular Structure 684
Calculation of Diffracted Intensities from Atomic
Coordinates: The Structure Factor 684
Calculation of Atomic Coordinates from Diffracted
Intensities 686
The Phase Problem 688
Direct Methods 688

Isomorphous Replacement 688

Multiwavelength Anomalous Diffraction 690

Determination of a Crystal Structure 691

Scattering of X Rays by Noncrystalline Materials 694

Absorption of X Rays 695

Extended Fine Structure of Edge Absorption 696

X Rays from Synchrotron Radiation 697

699

Electron Diffraction 698

Neutron Diffraction

#### xvi Contents

Electron Microscopy 700 Resolution, Contrast, and Radiation Damage 700 Transmission and Scanning Electron Microscopes 7 Image Enhancement and Reconstruction 701 Scanning Tunneling and Atomic Force Microscopy Summary 704 X-ray Diffraction 704 Neutron Diffraction 707 Electron Microscopy 707 Mathematics Needed for Chapter 12 707 References 708 Suggested Reading 708 Problems 709

Appendix 712
Answers 725
Index 728