

Physical Chemistry for the Biosciences

RAYMOND CHANG

WILLIAMS COLLEGE

"Raymond Chang has flawlessly condensed the fundamental concepts of physical chemistry clearly and concisely into a one-semester text, giving insightful illustrations that make intuitive sense to the reader. This text applies concepts in a way that will positively impact how physical chemistry is taught to students in the biological sciences."

—*Raymond Esquerra*, San Francisco State University

"Having read the text closely, I am most impressed by the enormous effort Raymond Chang has made in producing a very user-friendly text and the pains to which he has gone to explain all concepts as clearly as possible."

—*Keith Orrell*, University of Exeter

"In his new text, Chang clearly explains the fundamental principles of physical chemistry with an emphasis on biological systems. The mathematical derivations and examples are straightforward and easy to follow for undergraduate students."

—*Gary A. Lorigan*, Miami University

Famous for his clear writing and careful pedagogy, Chang's newest text is intended for use in a one-semester introductory course in physical chemistry for students of the biosciences. The author emphasizes the understanding of physical concepts rather than focussing on precise mathematical development or on actual experimental details. Only basic skills of differential and integral calculus are required to understand the equations. The extensive array of end-of chapter problems have both physiochemical and biological applications, and a detailed *Solutions Manual* is available.



NICHOLAS WHITMAN

About the Author:

Raymond Chang was born in Hong Kong and grew up in Shanghai and Hong Kong, China. He received his B.Sc. degree in chemistry from London University, England and his Ph.D. in physical chemistry from Yale University. After doing postdoctoral research at Washington University and teaching for a year at Hunter College of the City University of New York, he joined the chemistry department at Williams College. Chang is an editor of *The Chemical Educator* and is the author of books on general chemistry and spectroscopy, as well as an internationally best-selling text for a one year physical chemistry course.



University Science Books
www.uscibooks.com

About the cover:

The image on the cover shows water molecules as they move through the bovine aquaporin single file. A histidine residue protruding into the pore ensures that molecules larger than water cannot enter. Peter Agre shared the Nobel prize in Chemistry in 2003 for this work. (Image courtesy of Bing Jap.)

ISBN 1-891389-33-5



9 781891 389337

CHAPTER 1 Introduction 1

- 1.1 Nature of Physical Chemistry 1
- 1.2 Units 2
- 1.3 Atomic Mass, Molecular Mass, and the Chemical Mole 5

CHAPTER 2 Properties of Gases 7

- 2.1 Some Definitions 7
- 2.2 An Operational Definition of Temperature 8
- 2.3 Ideal Gases 8
 - Boyle's law 8 • Charles' and Gay-Lussac's Law 9 • Avogadro's Law 10 • The Ideal-Gas Equation 11 • Dalton's Law of Partial Pressures 12
- 2.4 Real Gases 14
 - The van der Waals Equation 15 • The Virial Equation of State 16
- 2.5 Condensation of Gases and the Critical State 18
- 2.6 Kinetic Theory of Gases 21
 - The Model 21 • Pressure of a Gas 21 • Kinetic Energy and Temperature 24
- 2.7 The Maxwell Distribution Laws 25
- 2.8 Molecular Collisions and the Mean Free Path 28
- 2.9 Graham's Laws of Diffusion and Effusion 30
- Problems 32

CHAPTER 3 The First Law of Thermodynamics 39

- 3.1 Work and Heat 39
 - Work 39 • Heat 43
- 3.2 The First Law of Thermodynamics 44
 - Enthalpy 46 • A Comparison of ΔU with ΔH 47
- 3.3 Heat Capacities 49
 - Constant-Volume and Constant-Pressure Heat Capacities 50
 - Molecular Interpretation of Heat Capacity 51 • A Comparison of C_V with C_P 53
- 3.4 Gas Expansion 55
 - Isothermal Expansions 55 • Adiabatic Expansions 56
- 3.5 Calorimetry 59
 - Constant-Volume Calorimetry 59 • Constant-Pressure Calorimetry 61
 - Differential Scanning Calorimetry 62
- 3.6 Thermochemistry 64
 - Standard Enthalpy of Formation 64 • Dependence of Enthalpy of Reaction on Temperature 68
- 3.7 Bond Energies and Bond Enthalpies 70
 - Bond Enthalpy and Bond Dissociation Enthalpy 71
- Problems 75

CHAPTER 4 The Second Law of Thermodynamics 81

- 4.1 Spontaneous Processes 81
- 4.2 Entropy 83
 - Statistical Definition of Entropy 83 • Thermodynamic Definition of Entropy 83 • The Carnot Heat Engine and Thermodynamic Efficiency 87
- 4.3 The Second Law of Thermodynamics 88
- 4.4 Entropy Changes 90
 - Entropy Change Due to Mixing of Ideal Gases 90 • Entropy Change Due to Phase Transitions 91 • Entropy Change Due to Heating 92
- 4.5 The Third Law of Thermodynamics 95
 - Third Law or Absolute Entropies 96 • Entropy of Chemical Reactions 97 • The Meaning of Entropy 98
- 4.6 Gibbs Energy 101
 - The Meaning of Gibbs Energy 103
- 4.7 Standard Molar Gibbs Energy of Formation ($\Delta_f \bar{G}^\circ$) 105
- 4.8 Dependence of Gibbs Energy on Temperature and Pressure 107
 - Dependence of G on Temperature 107 • Dependence of G on Pressure 108
- 4.9 Phase Equilibria 110
 - The Clapeyron and the Clausius-Clapeyron Equations 112 • Phase Diagrams 115 • The Phase Rule 117
- 4.10 Thermodynamics of Rubber Elasticity 117
- Problems 121

CHAPTER 5 Solutions 127

- 5.1 Concentration Units 127
 - Percent by Weight 127 • Mole Fraction 128 • Molarity (M) 128 • Molality (m) 128
- 5.2 Partial Molar Quantities 129
 - Partial Molar Volume 129 • Partial Molar Gibbs Energy 131 • The Meaning of Chemical Potential 131
- 5.3 The Thermodynamics of Mixing 132
- 5.4 Binary Mixtures of Volatile Liquids 134
 - Raoult's Law 135 • Henry's Law 137
- 5.5 Real Solutions 139
 - The Solvent Component 139 • The Solute Component 141
- 5.6 Colligative Properties 142
 - Vapor-Pressure Lowering 143 • Boiling-Point Elevation 143 • Freezing-Point Depression 146 • Osmotic Pressure 148
- 5.7 Electrolyte Solutions 154
 - A Molecular View of the Electrolyte Solution Process 154 • Thermodynamics of Ions in Solution 157 • Enthalpy, Entropy, and Gibbs Energy of Formation of Ions in Solution 159
- 5.8 Ionic Activity 160
 - Debye-Hückel Theory of Electrolytes 164 • The Salting-In and Salting-Out Effects 167
- 5.9 Colligative Properties of Electrolyte Solutions 170
 - The Donnan Effect 172
- 5.10 Biological Membranes 175
 - Membrane Transport 177
- Appendix 5.1 Notes on Electrostatics 182
- Problems 186

CHAPTER 6 Chemical Equilibrium 193

- 6.1 Chemical Equilibrium in Gaseous Systems 193
 - Ideal Gases 193 • A Closer Look at Equation 6.7 197
 - A Comparison of $\Delta_r G^\circ$ with $\Delta_r G$ 199 • Real Gases 200
- 6.2 Reactions in Solutions 201
- 6.3 Heterogeneous Equilibria 203
- 6.4 The Influence of Temperature, Pressure, and Catalysts on the Equilibrium Constant 205
 - The Effect of Temperature 205 • The Effect of Pressure 208
 - The Effect of a Catalyst 208
- 6.5 Binding of Ligands and Metal Ions to Macromolecules 209
 - One Binding Site per Macromolecule 210 • n Equivalent Binding Sites per Macromolecule 211 • Experimental Studies of Binding Equilibria 213
- 6.6 Bioenergetics 217
 - The Standard State in Biochemistry 218 • ATP—The Currency of Energy 220 • Principles of Coupled Reactions 222 • Glycolysis 223
 - Some Limitations of Thermodynamics in Biology 228
- Problems 230

CHAPTER 7 Electrochemistry 235

- 7.1 Electrochemical Cells 235
- 7.2 Single Electrode Potentials 236
- 7.3 Thermodynamics of Electrochemical Cells 238
 - The Nernst Equation 242 • Temperature Dependence of EMF 244
- 7.4 Types of Electrochemical Cells 245
 - Concentration Cells 245 • Fuel Cells 245
- 7.5 Applications of EMF Measurements 246
 - Determination of Activity Coefficients 246 • Determination of pH 247
- 7.6 Biological Oxidation 248
 - The Chemiosmotic Theory of Oxidative Phosphorylation 252
- 7.7 Membrane Potential 255
 - The Goldman Equation 258 • The Action Potential 258
- Problems 262

CHAPTER 8 Acids and Bases 267

- 8.1 Definitions of Acids and Bases 267
- 8.2 Acid-Base Properties of Water 268
 - pH—A Measure of Acidity 269
- 8.3 Dissociation of Acids and Bases 270
 - The Relationship Between the Dissociation Constant of an Acid and Its Conjugate Base 275 • Salt Hydrolysis 275
- 8.4 Diprotic and Polyprotic Acids 276
- 8.5 Buffer Solutions 280
 - The Effect of Ionic Strength and Temperature on Buffer Solutions 283
 - Preparing a Buffer Solution with a Specific pH 284
 - Buffer Capacity 285
- 8.6 Acid-Base Titrations 286
 - Acid-Base Indicators 287
- 8.7 Amino Acids 289
 - Dissociation of Amino Acids 290 • The Isoelectric Point (pI) 291
 - Titration of Proteins 292
- 8.8 Maintaining the pH of Blood 293

CHAPTER 9 Chemical Kinetics 311

- 9.1 Reaction Rates 311
- 9.2 Reaction Order 312
 - Zero-Order Reactions 313 • First-Order Reactions 314
 - Second-Order Reactions 318 • Determination of Reaction Order 323
- 9.3 Molecularity of a Reaction 324
 - Unimolecular Reactions 325 • Bimolecular Reactions 327
 - Termolecular Reactions 327
- 9.4 More Complex Reactions 328
 - Reversible Reactions 328 • Consecutive Reactions 330
 - Chain Reactions 332
- 9.5 The Effect of Temperature on Reaction Rates 332
 - The Arrhenius Equation 333
- 9.6 Potential Energy Surfaces 335
- 9.7 Theories of Reaction Rates 336
 - Collision Theory 336 • Transition-State Theory 338
 - Thermodynamic Formulation of Transition-State Theory 340
- 9.8 Isotope Effects in Chemical Reactions 343
- 9.9 Reactions in Solution 346
- 9.10 Fast Reactions in Solution 347
 - The Flow Method 349 • The Relaxation Method 349
- 9.11 Oscillating Reactions 353
- Problems 356

CHAPTER 10 Enzyme Kinetics 363

- 10.1 General Principles of Catalysis 363
 - Enzyme Catalysis 364
- 10.2 The Equations of Enzyme Kinetics 367
 - Michaelis-Menten Kinetics 367 • Steady-State Kinetics 368
 - The Significance of K_M and V_{max} 370
- 10.3 Chymotrypsin: A Case Study 372
- 10.4 Multisubstrate Systems 375
 - The Sequential Mechanism 376 • The Nonsequential or “Ping-Pong” Mechanism 376
- 10.5 Enzyme Inhibition 377
 - Reversible Inhibition 377 • Irreversible Inhibition 384
- 10.6 Allosteric Interactions 385
 - Oxygen Binding to Myoglobin and Hemoglobin 385 • The Hill Equation 387 • The Concerted Model 390 • The Sequential Model 391 • Conformational Changes in Hemoglobin Induced by Oxygen Binding 392
- 10.7 The Effect of pH on Enzyme Kinetics 393
- Problems 398

CHAPTER 11 Quantum Mechanics and Atomic Structure 401

- 11.1 The Wave Theory of Light 401
- 11.2 Planck's Quantum Theory 403
- 11.3 The Photoelectric Effect 405

11.4	Bohr's Theory of the Hydrogen Emission Spectrum	407
11.5	de Broglie's Postulate	410
11.6	The Heisenberg Uncertainty Principle	414
11.7	The Schrödinger Wave Equation	416
11.8	Particle in a One-Dimensional Box	418
	• Electronic Spectra of Polyenes	423
11.9	Quantum-Mechanical Tunneling	424
11.10	The Schrödinger Wave Equation for the Hydrogen Atom	426
11.11	Many-Electron Atoms and the Periodic Table	432
	• Electronic Configurations	433
	• Variations in Periodic Properties	437
	Problems	441

CHAPTER 12 The Chemical Bond 447

12.1	Lewis Structures	447
12.2	Valence Bond Theory	448
12.3	Hybridization of Atomic Orbitals	450
12.4	Electronegativity and Dipole Moment	455
	• Electronegativity	455
	• Dipole Moment	456
12.5	Molecular Orbital Theory	458
12.6	Diatomic Molecules	460
	• Homonuclear Diatomic Molecules of the Second-Period Elements	460
	• Heteronuclear Diatomic Molecules of the Second-Period Elements	463
12.7	Resonance and Electron Delocalization	465
	• The Peptide Bond	467
12.8	Coordination Compounds	469
	• Crystal Field Theory	470
	• Molecular Orbital Theory	475
	• Valence Bond Theory	476
12.9	Coordination Compounds in Biological Systems	477
	• Iron	477
	• Copper	480
	• Cobalt, Manganese, and Nickel	480
	• Zinc	481
	• Toxic Heavy Metals	482
	Problems	485

CHAPTER 13 Intermolecular Forces 489

13.1	Intermolecular Interactions	489
13.2	The Ionic Bond	490
13.3	Types of Intermolecular Forces	492
	• Dipole-Dipole Interaction	492
	• Ion-Dipole Interaction	494
	• Ion-Induced Dipole and Dipole-Induced Dipole Interactions	495
	• Dispersion, or London, Forces	497
	• Repulsive and Total Interactions	498
	• The Role of Dispersion Forces in Sickle-Cell Anemia	500
13.4	Hydrogen Bonding	502
13.5	The Structure and Properties of Water	505
	• The Structure of Ice	505
	• The Structure of Water	506
	• Some Physiochemical Properties of Water	507
13.6	Hydrophobic Interaction	508
	Problems	511

CHAPTER 14 Spectroscopy 513

14.1	Vocabulary	513
	• Absorption and Emission	513
	• Units	513
	• Regions of the	

	Spectrum	514	•	Line Width	514	•	Resolution	517
			•	Intensity	518	•	Selection Rules	519
			•	Signal-to-Noise Ratio	521			
			•	The Beer-Lambert Law	521			
14.2	Microwave Spectroscopy	522						
14.3	Infrared Spectroscopy	527						
			•	Simultaneous Vibrational and Rotational Transitions	532			
14.4	Electronic Spectroscopy	534						
			•	Organic Molecules	535	•	Transition Metal Complexes	537
			•	Molecules that Undergo Charge-Transfer Interactions	537			
			•	Application of the Beer-Lambert Law	538			
14.5	Nuclear Magnetic Resonance	539						
			•	The Boltzmann Distribution	542	•	Chemical Shifts	542
			•	Spin-Spin Coupling	544	•	NMR and Rate Processes	545
			•	NMR of Nuclei Other than ^1H	546	•	Fourier-Transform NMR	547
			•	Magnetic Resonance Imaging (MRI)	551			
14.6	Electron Spin Resonance	552						
14.7	Fluorescence and Phosphorescence	554						
			•	Fluorescence	554	•	Phosphorescence	556
14.8	Lasers	557						
			•	Properties and Applications of Laser Light	560			
14.9	Optical Rotatory Dispersion and Circular Dichroism	562						
			•	Molecular Symmetry and Optical Activity	562	•	Polarized Light and Optical Rotation	563
			•	Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD)	566			
	Problems	570						

CHAPTER 15 Photochemistry and Photobiology 575

15.1	Introduction	575						
			•	Thermal Versus Photochemical Reactions	575	•	Primary Versus Secondary Processes	576
			•	Quantum Yields	576	•	Measurement of Light Intensity	578
			•	Action Spectrum	579			
15.2	Photosynthesis	580						
			•	The Chloroplast	580	•	Chlorophyll and Other Pigment Molecules	581
			•	The Reaction Center	581			
			•	Photosystems I and II	583	•	Dark Reactions	586
15.3	Vision	586						
			•	Structure of Rhodopsin	588	•	Mechanism of Vision	588
			•	Rotation About the C=C Bond	589			
15.4	Biological Effects of Radiation	591						
			•	Sunlight and Skin Cancer	591	•	Photomedicine	592
	Problems	598						

CHAPTER 16 Macromolecules 599

16.1	Methods for Determining Size, Shape, and Molar Mass of Macromolecules	599						
			•	Molar Mass of Macromolecules	599	•	Sedimentation in the Ultracentrifuge	600
			•	Viscosity	607	•	Electrophoresis	608
16.2	Structure of Synthetic Polymers	613						
			•	Configuration and Conformation	613	•	The Random-Walk Model	614
16.3	Structure of Proteins and DNA	616						
			•	Proteins	616	•	DNA	621

16.4 Protein Stability 624

- Hydrophobic Interaction 625 • Denaturation 626 • Protein Folding 629

Problems 635

Appendix 1 Review of Mathematics 639

Appendix 2 Thermodynamic Data 651

Glossary 655

Answers to Even-Numbered Computational Problems 665

Index 669