

Contents

PREFACE XIII

INTRODUCTION

The Nature of Physical Laws 1

1 The Gas Laws 5

- 1.1 Attractive Forces Between Ions, Molecules, and Atoms 5
- 1.2 Temperature and the Zeroth Law of Thermodynamics 13
- 1.3 The Perfect Gas Law or Ideal Gas Equation 15
- 1.4 Another Route to the Perfect Gas Law: The Kinetic Equation for Gases 21
- 1.5 Other Relationships Derivable from the Kinetic Equation for Gases 24
- 1.6 An Equation of State for Real (Nonideal) Gases: The van der Waals Equation 26
- 1.7 Dalton's Law of Partial Pressures 30
- 1.8 The Barcroft-Warburg Manometric Method as an Application of the Gas Laws 31

2 The Laws of Thermodynamics and an Introduction to the Free Energy Concept 38

- 2.1 The First Law of Thermodynamics 39
Definitions. The statement of the First Law. Illustrations of the First Law.

- 2.2 The Enthalpy, H 54
Thermochemistry.
- 2.3 The Second Law of Thermodynamics 65
The entropy concept and a search for a new state function. Statements of the Second Law of Thermodynamics. Entropy and probability. Calculating the entropy change. The entropy change and predicting the direction of spontaneity.
- 2.4 Absolute Entropies and the Third Law of Thermodynamics 81
- 2.5 The Free Energy 83
The Gibbs-Helmholtz Equation. The free energy of formation.
- 2.6 Thermodynamic Studies on the Structure of Water 91

3 Chemical Equilibrium in Heterogeneous and Homogeneous Systems 102

- 3.1 The Chemical Potential 102
- 3.2 The Ideal Solution 106
Definition of an ideal solution. The chemical potential of a component of an ideal solution. The free energy of mixing. The entropy of mixing.
- 3.3 Principles Governing Heterogeneous Equilibria 113
The Phase Rule. The Clausius-Clapeyron Equation.
- 3.4 The Colligative Properties of Solutions 119
Raoult's Law. Freezing point lowering and boiling point elevation. Osmotic pressure. Measurement of the colligative properties. The Donnan effect. Dialysis.
- 3.5 Free Energy and Chemical Equilibrium 138
Expression for the chemical potential in dilute solutions. The general equilibrium expression. K_p and K_c . Equilibrium calculations involving gases. Spontaneous change in biochemical systems.
- 3.6 The Effect of Temperature on Chemical Equilibrium 148
- 3.7 Sedimentation Equilibrium 153
- 3.8 Metabolism and Free Energy 160
Transfer reactions in which the energy of ATP is conserved. Reactions involving utilization of the free energy of ATP. Tandem reactions. Calculations involving ΔG° and $\Delta G'$. The use of K_{app} .

4 Solutions of Electrolytes 179

- 4.1 General Considerations of Strong and Weak Electrolytes 179
Weak electrolytes. Strong electrolytes.
- 4.2 Acid-Base Equilibria: Practical Considerations and Calculations 186
The titration curve. Summary.
- 4.3 Indicators of pH 208
Theory of indicators. Sources of error in the use of indicators.
- 4.4 Acid-Base Equilibria in the Dissociation of Amino Acids 211
Amino acids as Bronsted acids. Titration curves. Miscellaneous uses of amino acid pK'_a values.

- 4.5 Theoretical Considerations Involving Polyprotic Species 216
Microscopic and macroscopic dissociation constants. The hydrolysis of ATP.
- 4.6 “Salting-in” and “Salting-out” of Polar Molecules 223
- 4.7 The Formation of Coordination Compounds 226
- 4.8 Cellulose Ion Exchangers for Protein Purification 238

5 Electrochemical Cells 245

- 5.1 Electrical and Chemical Work 246
- 5.2 The Galvanic Cell and Cell Conventions 248
- 5.3 Temperature Dependence of $\mathcal{E}^\circ$ 253
- 5.4 Types of Half-Cells 255
The reference cell or standard cell. Reference electrodes. The concentration cell. Fuel cells. The oxygen electrode.
- 5.5 The Determination of pH 265
Normal calomel electrode and hydrogen electrode. Quinhydrone electrode and normal calomel electrode.
- 5.6 Oxidation-Reduction in Biological Systems 268
- 5.7 Electrochemical Potentials and Ion Movement Through Membranes 270

6 Kinetics 279

- 6.1 Writing the Rate Equation 280
- 6.2 Reaction Order and Molecularity: Definitions 282
- 6.3 Several Forms of the First-Order Rate Equation 284
- 6.4 The Second-Order Rate Equation 289
- 6.5 The Third-Order Rate Equation 293
- 6.6 The Zero Order Rate Equation 294
- 6.7 Complex Reactions 296
- 6.8 Kinetics of Enzyme-Catalyzed Reactions 299
Rate equations. The significance of K_m and $V_{\max}$. The Michaelis-Menten Equation and enzyme mechanisms. General velocity equation. Enzyme inhibition. Analysis of enzyme mechanisms by use of product inhibition patterns.
- 6.9 Fast Reactions 317
Flow methods. Relaxation methods. Relaxation times.
- 6.10 The Arrhenius Equation: The Effect of Temperature on Reaction Rate 323

7 Electromagnetic Radiation and Matter 340

- 7.1 Emission Spectra 346
- 7.2 Dispersion of Radiation 347
- 7.3 Absorption of Light 348
Beer-Lambert Law. Infrared Spectroscopy. Visible-Ultraviolet Spectroscopy.

- 7.4 Optical Activity 375
- 7.5 Fluorescence 383
- 7.6 Photochemistry 386
- 7.7 Bioluminescence 388
- 7.8 Light Scattering by Small Particles 389
- 7.9 Spectroscopy Utilizing Flame Sources 393

8 The Principles of Nuclear Chemistry and Some Biological Applications 402

- 8.1 Disintegration of Radioactive Elements: Nuclear Equations 403
- 8.2 Kinetics of Nuclear Disintegrations 408
- 8.3 Nuclear Fission and Reactors 409
- 8.4 Particle Accelerators 412
- 8.5 The Measurement of Radioactivity 413
- 8.6 Biological Research Applications 415
*Tracer studies. Isotope dilution. Nuclear activation analysis. Dating.
Other applications.*

9 Systems of Large Particles: Macromolecular Solutions and Colloidal Dispersions 426

- 9.1 Surface Energy 428
Adsorption isotherms. Adsorption on surfaces.
- 9.2 Allosteric Interaction 436
- 9.3 Molecular Weight Distributions 439
- 9.4 Angular Dependence of Light Scattering from Large Molecules 442
*Radius of gyration for a uniform sphere. Radius of gyration for rods.
Radius of gyration for random coils. Scattering at higher angles.*
- 9.5 The Transport Properties of Macromolecular Systems 452
*Frictional coefficient. Diffusion. Sedimentation velocity. Electrophoresis.
Viscosity. Flow birefringence.*
- 9.6 Helix-Coil Transitions 474

APPENDIX A

Mathematics 486

APPENDIX B

Symbols and Notation 526

APPENDIX C

Fundamental Constants 528

APPENDIX D

International Atomic Weights 529

APPENDIX E

Answers to Odd-numbered Problems 531

INDEX 541