

# CONTENTS

---

## PART ONE

### *Macroscopic Systems* 1

---

#### CHAPTER 1

### *Description of Macroscopic Systems* 3

- 1-1 The Nature of Thermodynamics 3
- 1-2 The Thermodynamicist's Picture of the World 4  
*J. Willard Gibbs* 11
- 1-3 A Process Is an Event in which a Property of a System Changes 12
- 1-4 Definitions of Heat and Work 15
- 1-5 Mathematical Description of a System with a Single Independent Variable 18
- 1-6 Mathematical Description of a System with Two or More Variables 21
- 1-7 Exact Differentials Represent Small Changes in Properties in a Process; Inexact Differentials Represent Small Changes of Heat and Work 24
- 1-8 The Thermodynamicist's Description of Nature: A Summary 28

#### CHAPTER 2

### *Energy and the First Law of Thermodynamics* 37

- 2-1 The First Law of Thermodynamics Relates Heat, Work, and Energy 37
- 2-2 Molecular Interpretation of Energy Changes 41
- 2-3 Heat, Energy Change, Enthalpy Change, and Heat Capacity Are Readily Measured Quantities 46
- 2-4 An Example:  $W$  and  $Q$  for an Ideal Gas Expansion  
*Benjamin Thompson, Count Rumford* 51
- 2-5 Enthalpy Changes: A General Principle 58
- 2-6 Thermochemistry Relates Heat to the Enthalpy Change of Chemical Reactions 59

●	2-7	Molecular Interpretation of Enthalpy Changes	66
◐	2-8	Transition Enthalpies and Heat Capacities	68
◐	2-9	The Unusual Thermal Properties of Water	70
○	2-10	Mathematical Principles: Integrals, Logarithms, and Exponentials	75

## CHAPTER 3

*Entropy and the Second Law of Thermodynamics* 85

○	3-1	Spontaneous Changes Imply the Need for a Second Law	85
○	3-2	The Second Law of Thermodynamics <i>William Thomson, Baron Kelvin</i>	87 92
●	3-3	$\frac{1}{T}$ Is an Integrating Factor for $dQ_{\text{rev}}$	95
○	3-4	The Spontaneity Criterion	95
○	3-5	The Boltzmann Equation Relates the Degeneracy of a State to its Entropy	98
○	3-6	General Principles and Examples of Spontaneous Processes	99
●	3-7	The Efficiency of a Heat Engine Is Less than One	104
○	3-8	The First and Second Laws Combined	109
○	3-9	Calculation of Entropy Changes	112
○	3-10	The Third Law of Thermodynamics	114
◐	3-11	Entropy and Life	118

## CHAPTER 4

*Free Energy and Equilibrium* 123

○	4-1	The Gibbs and Helmholtz Free Energies	124
○	4-2	The Free Energy Spontaneity Criterion	126
○	4-3	What Is Free Energy?	129
○	4-4	Free Energy and the Principle of Equilibrium	133
○	4-5	Free Energies of Ideal Gases and Ideal Solutions	135
○	4-6	The Chemical Potential <i>Percy W. Bridgman</i>	140 144
○	4-7	Chemical Equilibrium	148
○	4-8	Standard Free-Energy Changes	154
○	4-9	The Temperature Dependence of $\Delta G$ and $K$	158
○	4-10	A Summary of the Methods for Determining $\Delta G^\circ$	162

⬢	4-11	Hydrophobic Bonding Results from Minimization of the Free Energy	164
⬡	4-12	Phase Equilibria	168
⬡	4-13	Phase Diagrams	171
⬡	4-14	The Clausius-Clapeyron Equation Gives the Slope of Lines on a $P$ - $T$ Phase Diagram	174
⬢	4-15	Transitions in Biological Macromolecules and Molecular Aggregates	176

## CHAPTER 5

*Biological Applications of Thermodynamics* 187

⬡	5-1	Solar Energy	187
		<i>J. D. Bernal and Max Delbrück</i>	188
⬢	5-2	The $\text{CO}_2$ - $\text{O}_2$ Cycle of the Biosphere	193
⬢	5-3	Coupled Reactions and Group Transfer Potentials; Endergonic Reactions Are Coupled to Exergonic Reactions by an Enzyme	196
⬢	5-4	Metabolic and Thermodynamic Strategies of Bicycle Racing	202

## CHAPTER 6

*Chemical and Biochemical Kinetics* 212

⬡	6-1	Rates, Not Energy Differences, Control the Course of Biochemical Reactions	212
⬡	6-2	What Kineticists Do—A Summary	213
⬡	6-3	A Reaction Mechanism Consists of a Set of Elementary Steps	217
⬡	6-4	An Equilibrium Constant Equals a Ratio of Rate Constants	219
⬡	6-5	The Principle of Microscopic Reversibility Requires that a Reaction Have the Same Intermediates in Forward and Reverse Directions	220
⬡	6-6	How Reaction Mechanisms Are Inferred	221
⬡	6-7	First-Order Reactions Follow an Exponential Time Course	226
⬢	6-8	Radioactive Decay Is a First-Order Reaction	227
		<i>Marya Skłodowska—Marie Curie</i>	230
⬡	6-9	Second-Order Rate Laws Can Be Integrated	233
⬢	6-10	DNA Renaturation Is a Second-Order Reaction	234
⬡	6-11	Elementary Rate Constants Depend on the Energy and Entropy of Activation	237

●	6-12	In a Diffusion-Limited Process, Reaction Occurs at Every Collision	245
◻	6-13	Experimental Methods for Measuring Reaction Rates Cover a Wide Range of Times	247
●	6-14	Relaxation Kinetics Relies on Small Perturbations of Reactions at Equilibrium	249
●	6-15	Proton Transfer Reactions Are Important in Biochemistry	251
◻	6-16	Enzymes Profoundly Affect Reaction Rates and Reaction Rate Laws	253
◻	6-17	The Special Catalytic Power of Enzymes	258




## PART TWO

<i>Solutions and Electrochemistry</i>	269
---------------------------------------	-----

## CHAPTER 7












<i>Solutions</i>	271
------------------	-----

◻	7-1	Macromolecules Form Genuine Solutions	271
◻	7-2	Solution Concentrations	272
◻	7-3	Partial Molar Quantities Allow One to Represent the Properties of a Solution in Terms of Properties of its Components	273
◻	7-4	The Gibbs-Duhem Equation Relates the Chemical Potentials of Solute and Solvent	277
◻	7-5	Ideal Solutions and Raoult's Law	281
◻	7-6	Henry's Law	285
◻	7-7	Real Solutions: A Summary <i>Hermann von Helmholtz</i>	290 291
●	7-8	Fugacity and Real Gases	293
●	7-9	Real Solutions, Activity, and the Activity Coefficient	296
●	7-10	Measurement of Activity Coefficients	300
◻	7-11	Physical Interpretation of Activity Coefficients	302
◻	7-12	Activity and Chemical Equilibrium	305
●	7-13	The Virial Expansion	306
◻	7-14	Polydispersity in Macromolecular Solutions	308
●	7-15	Colligative Properties	310

	7-16	Membrane Equilibria and Osmotic Pressure	314
	7-17	Equilibrium Sedimentation	320
	7-18	Sedimentation Equilibrium in Multicomponent Systems	323








## CHAPTER 8

*Electrolyte Solutions* 331

	8-1	Coulomb's Law Determines Electrostatic Forces	331
	8-2	Ohm's Law States that the Electric Current Is Proportional to the Potential Difference, or to the Electric Field	334
	8-3	Why Do Electrolytes Dissolve in Water?	335
	8-4	Thermodynamics of Ion Solvation	337
	8-5	Coulomb's Law and the Dielectric Constant Give the Free Energy, Entropy, and Enthalpy of Interaction between a Pair of Ions in Solution	340
	8-6	The Conductivity of Aqueous Solutions	343
	8-7	The Mobility of an Ion Depends on its Transport Velocity	346
		<i>Michael Faraday</i>	348
	8-8	Chemical Potential of Electrolytes	350
	8-9	Ionic Strength	353
	8-10	A Summary of the Debye-Hückel Theory	353
	8-11	Calculation of Ionic Activity Coefficients by the Debye-Hückel Theory	358

## CHAPTER 9

*Electrochemical Equilibria* 367

	9-1	Oxidation-Reduction Reactions and Electrochemical Cells	367
	9-2	The Electromotive Force and Free-Energy Change of Electrochemical Cells	371
	9-3	Half-Cells and Standard Electrode Potentials	374
	9-4	Calculation of a Half-Cell Potential from Two Other Half-Cell Potentials	379
	9-5	A Biochemical Example: The Terminal Oxidation Chain	381
	9-6	Ionic Effects on Membrane Equilibria	384
	9-7	Osmotic Pressure and the Sodium Pump	392

## PART THREE

*Microscopic Systems*

399

## CHAPTER 10

*Principles of Quantum Mechanics*

401

○	10-1	Waves, Particles, and Quanta	402
		<i>Max Planck and Albert Einstein</i>	409
○	10-2	The Schrödinger Wave Equation Describes de Broglie Waves	419
○	10-3	A Particle Confined to a Box Has Quantized Energy Levels	427
○	10-4	The Harmonic Oscillator Is a Model for Molecular Vibration	432
○	10-5	The Rigid Rotor Is a Model for Molecular Rotation	441
○	10-6	The Hydrogen-Atom Wave Functions, Derived from Schrödinger's Equation, Are the Basis for Theories of Chemical Bonding	447
●	10-7	Angular Momentum Is Quantized	456

## CHAPTER 11

*Chemical Bonds*

468

○	11-1	Covalent Bonds Form Because of the Decrease in the Electrostatic Potential Energy of Electrons that Accompanies Coupling of Atoms	469
○	11-2	Molecular Orbitals Describe the Motions of Electrons in Molecules	471
●	11-3	Determination of Constants in a MO LCAO Wavefunction	474
○	11-4	Molecular Orbitals for Diatomic Molecules <i>In the Matter of J. Robert Oppenheimer</i>	480
○	11-5	Polyatomic Molecules	489
○	11-6	Charge-Distribution Properties of Molecules	496
○	11-7	Noncovalent Forces Are Described by Potential-Energy Functions	503

## CHAPTER 12

	<i>Principles of Spectroscopy</i>	516
○	12-1 Biochemists Use Spectroscopy to Monitor Changes at the Atomic Level: An Example	516
○	12-2 The Interaction of Light with Matter: An Overview	520
○	12-3 Energy Changes in Chemical Systems Are of Several Types: The Example of Water	526
○	12-4 The Electromagnetic Spectrum Detects Energy Changes in Chemical Systems: A Hypothetical Experiment	529
○	12-5 The Classical Mechanical Description of Absorption and Dispersion	535
○	12-6 Quantum Mechanical Description of Polarization and Absorption	546
	<i>John Strutt, Lord Rayleigh</i>	547

## CHAPTER 13













	<i>Biochemical Spectroscopy</i>	562
○	13-1 The Spectrum of Raman Scattered Light Reveals Vibrational Quantum States of the Sample	562
○	13-2 Vibrational (Infrared) Spectroscopy	566
○	13-3 Visible and Ultraviolet (UV) Spectroscopy Detect Excitations of Electrons	576
○	13-4 Fluorescence Is Rapid Re-emission of Absorbed Radiation	582
○	13-5 Optical Rotatory Dispersion and Circular Dichroism Reveal Asymmetric Arrangements of Chemical Groups	589
	<i>Louis Pasteur</i>	590
○	13-6 Nuclear Magnetic Resonance Is a Versatile Spectroscopic Tool Characterized by Sensitivity and High Resolution	604
●	13-7 Nuclear Relaxation and Fourier Transform NMR	617
●	13-8 Nuclear Magnetic Resonance Can Be Used to Measure Kinetics	623
○	13-9 Electron Spin Resonance (ESR) Detects Unpaired Electrons	627
◐	13-10 Light Scattering Allows Determination of Macromolecular Size and Shape	630

## PART FOUR

*Bridging the Macroscopic and Microscopic* 647




## CHAPTER 14

*Statistical Mechanics* 649

-  14-1 Statistical Mechanics Provides the Connection between Molecular and Macroscopic Properties 649  
 14-2 Entropy Is a Measure of Disorder or Degeneracy 651  
 14-3 The Probability of a Quantum State Is Proportional to  $\exp(-\epsilon_n/kT)$  654  
 14-4 Calculation of the Total Energy 659  
 14-5 The Classical Principle of Equipartition of Energy 664  
 14-6 Quantum-Mechanical Effects Influence the Energy and Heat Capacity 665  
 14-7 A Statistical-Mechanical Interpretation of Heat, Work, Entropy, and Information 668  
 14-8 The System Partition Function Is a Product of Molecular Partition Functions 670  
*Leo Szilard* 672  
 14-9 Free Energy and the Partition Function 676  
 14-10 Calculating the Probability of Complex Molecular States 678  
 14-11 A Biological Application: Multiple Equilibria 682  
 14-12 Flexible Polymers Have a Statistical Distribution of Conformations 686

## CHAPTER 15

*Transport Processes* 700

-  15-1 Transport Processes Involve a Flow of Matter or Energy 700  
 15-2 How the Transport Velocity Differs from the Molecular Velocity 702  
 15-3 The Forces that Drive Transport Can Be Obtained by Differentiating a Potential Energy or a Free Energy 704



○	15-4	The First Law of Diffusion States that the Flux Is Proportional to the Concentration Gradient	705
○	15-5	Diffusion Can Be Thought of as a Random Walk	707
○	15-6	The Second Law of Diffusion Results when Conservation of Mass Is Included	708
●	15-7	Measurement of Light Scattering Fluctuations Can Be Used to Determine the Diffusion Coefficient	710
○	15-8	Sedimentation Velocity in the Ultracentrifuge	715
○	15-9	Diffusion and Sedimentation Velocity Measurements Can Be Combined to Determine Molecular Weights	718
○	15-10	The Frictional Coefficient Depends on Molecular Size and Shape	718
◐	15-11	The Sedimentation Behavior of DNA	724
○	15-12	Viscosity Is a Measure of the Resistance to Bulk Flow	725
◐	15-13	Polymer Normal Modes: The Retardation Time Is Sensitive to Molecular Weight	733
○	15-14	Electrophoresis Is Transport Driven by an Electric Field	735
●	15-15	Onsager's Generalization of the Phenomenological Transport Equations	739

## PART FIVE

## *Symmetry and Molecular Structure* 747

---









 CHAPTER 16

		<i>Symmetry</i>	749
○	16-1	Symmetry Operations and Elements	751
○	16-2	Symmetry about a Point <i>Johannes Kepler</i>	753 769
●	16-3	Group Theory Describes Symmetry Concisely	772
◐	16-4	Self-Assembly and the Structure of Spherical Viruses	775
◐	16-5	Symmetry along a Line—Helices	779
○	16-6	Symmetry in a Plane and in Three Dimensions: Designs and Crystals	784

## CHAPTER 17

*X-ray Diffraction and the Determination  
of Molecular Structure*

798

- |  |      |   |            |
|--|------|---|------------|
|  | 17-1 | Outline of the Determination of Protein Structure<br>by X-ray Crystallography                                       | 798        |
|  | 17-2 | Diffraction Occurs by Interference of Waves   | 802        |
|  | 17-3 | Determination of Crystal Parameters, Molecular<br>Weight, and Molecular Symmetry                                    | 817        |
|  | 17-4 | The Intensity of Diffraction  | 821        |
|  | 17-5 | Fourier Showed that Periodic Objects Can Be<br>Represented as a Sum of Waves<br><i>Jean-Baptiste Joseph Fourier</i> | 827<br>832 |
|  | 17-6 | The Patterson Function  | 835        |
|  | 17-7 | The Heavy-Atom and Fourier Methods  | 837        |
|  | 17-8 | Isomorphous Replacement   | 839        |

*References for Biographical Sketches*

847

*Index*

849