## **Contents**

**Periodic Table** *Inside front cover* 

Engine

106

	List of Numerical Tables in Appendix A Inside front cover
	Information Tables Inside back cover
	Preface xv
	Acknowledgments xvii
Part 1	Thermodynamics and the Macroscopic Description of Physical Systems 1
Chapter 1	The Behavior of Gases and Liquids 3  1.1 Introduction 4  1.2 Systems and States in Physical Chemistry 12  1.3 Real Gases 21  1.4 The Coexistence of Phases and the Critical Point 27
Chapter 2	Work, Heat, and Energy: The First Law of Thermodynamics 39
	2.1 Work and the State of a System 40
	2.2 Heat 51
	2.3 Internal Energy: The First Law of Thermodynamics 55
	2.4 Calculation of Amounts of Heat and Energy Changes 60
	<ul> <li>2.5 Enthalpy 74</li> <li>2.6 Calculation of Enthalpy Changes of Processes without Chemical Reactions 81</li> </ul>
	2.7 Calculation of Enthalpy Changes of a Class of Chemical Reactions 86
	2.8 Calculation of Energy Changes of Chemical Reactions 94
Chapter 3	The Second and Third Laws of Thermodynamics: Entropy 105
	3.1 The Second Law of Thermodynamics and the Carnot Heat

Contents

Part 2	Dyn	amics 381	
Chapter 9	Gas l	Kinetic Theory: The Molecular Theory of Dilute Gases at	
	Equi	librium 383	
	9.1	Macroscopic and Microscopic States of Macroscopic	
		Systems 384	
	9.2	A Model System to Represent a Dilute Gas 386	
	9.3	The Velocity Probability Distribution 394	
	9.4	The Distribution of Molecular Speeds 405	
	9.5	The Pressure of a Dilute Gas 411	
	9.6	Effusion and Wall Collisions 416	
	9.7	The Model System with Potential Energy 418	
	9.8	The Hard-Sphere Gas 422	
	9.9	The Molecular Structure of Liquids 434	
Chapter 10	Tran	ransport Processes 441	
	10.1	The Macroscopic Description of Nonequilibrium	
		States 442	
	10.2	1	
	10.3	, <u>1</u>	
		Sphere Gases 460	
	10.4	1	
	10.5	Electrical Conduction in Electrolyte Solutions 475	
Chapter 11	The l	Rates of Chemical Reactions 485	
	11.1	The Macroscopic Description of Chemical Reaction	
		Rates 486	
	11.2		
	11.3		
	11.4		
		Equilibrium 507	
	11.5	A Simple Reaction Mechanism: Two Consecutive	
		Steps 510	
	11.6	1 &	
	11.7	The Experimental Study of Fast Reactions 515	
Chapter 12		nical Reaction Mechanisms I: Rate Laws and	
		nanisms 523	
	12.1	Reaction Mechanisms and Elementary Processes in	
		Gases 524	
	12.2	Elementary Processes in Liquid Solutions 527	
	12.3	The Temperature Dependence of Rate Constants 533	
	12.4	Reaction Mechanisms and Rate Laws 540	
	12.5	Chain Reactions 556	
Chapter 13		nical Reaction Mechanisms II: Catalysis and Miscellaneous	
	Topic		
	13.1	Catalysis 566	
	13.2	Competing Mechanisms and the Principle of Detailed	
	100	Balance 583	
	13.3	Autocatalysis and Oscillatory Chemical Reactions 585	
	13.4	The Reaction Kinetics of Polymer Formation 589	

X Contents

	13.5 13.6	Nonequilibrium Electrochemistry 595 Experimental Molecular Study of Chemical Reaction Mechanisms 608	
Part 3	The	Molecular Nature of Matter 617	
Chapter 14		sical Mechanics and the Old Quantum Theory 619	
	14.1		
	14.2		
	14.3 14.4		
Chapter 15	The I	Principles of Quantum Mechanics. I. De Broglie Waves and	
Chapter 10		chrodinger Equation 653	
	15.1		
	15.2		
	15.3	The Particle in a Box and the Free Particle 663	
	15.4	The Quantum Harmonic Oscillator 674	
Chapter 16		Principles of Quantum Mechanics. II. The Postulates of	
	•	ntum Mechanics 683	
	16.1		
	16.2	The Third Postulate. Mathematical Operators and Mechanical Variables 684	
	16.3	The Operator Corresponding to a Given Variable 688	
	16.4	1	
	16.5	The Uncertainty Principle of Heisenberg 711	
	16.6	Postulate 5. Measurements and the Determination of the State of a System 717	
		The of a bystem 717	
Chapter 17		Electronic States of Atoms. I. The Hydrogen Atom 725	
	17.1	, ,	
	17.2	The Relative Schrodinger Equation. Angular	
	17.3	Momentum 729	
	17.3	The Radial Factor in the Hydrogen Atom Wave Function.  The Energy Levels of the Hydrogen Atom  736	
	17.4	• •	
	17.5	Expectation Values in the Hydrogen Atom 749	
	17.6	The Time-Dependent Wave Functions of the Hydrogen Atom	753
	17.7	The Intrinsic Angular Momentum of the Electron.	
		"Spin" 755	
Chapter 18	The I	${f Electronic States  of Atoms.  II.  The  Zero-Order  Approximation}$	n
	for M	Iultielectron Atoms 763	
	18.1	The Helium-Like Atom 764	
	18.2	The Indistinguishability of Electrons and the Pauli Exclusion Principle 766	
	18.3	The Ground State of the Helium Atom in Zero Order 768	
	18.4	Excited States of the Helium Atom 772	
	18.5	Angular Momentum in the Helium Atom 774	

ntents xi

	18.6	The Lithium Atom 781
	18.7	Atoms with More Than Three Electrons 784
Chapter 19		Electronic States of Atoms. III. Higher-Order
		roximations 789
	19.1	The Variation Method and Its Application to the Helium
	19.2	Atom 790 The Self-consistent Field Method 796
	19.3	The Perturbation Method and Its Application to the Ground State of the Helium Atom 799
	19.4	Excited States of the Helium Atom. Degenerate Perturbation
	17.4	Theory 803
	19.5	The Density Functional Method 805
	19.5	Atoms with More Than Two Electrons 806
	17.0	Atoms with More Than Two Electrons
Chapter 20	The F	Electronic States of Diatomic Molecules 823
	20.1	The Born-Oppenheimer Approximation and the Hydrogen
		Molecule Ion 824
	20.2	LCAOMOs. Approximate Molecular Orbitals That Are Linear
		Combinations of Atomic Orbitals 833
	20.3	Homonuclear Diatomic Molecules 838
	20.4	Heteronuclear Diatomic Molecules 851
Chapter 21	The E	Electronic Structure of Polyatomic Molecules 867
Chapter 21	21.1	•
	21.1	a .
	21.3	The CH <sub>4</sub> , NH <sub>3</sub> , and H <sub>2</sub> O Molecules
	21.3	and the $sp^3$ Hybrid Orbitals 873
	21.4	Molecules with Multiple Bonds 878
	21.5	The Valence-Bond Description of Polyatomic Molecules 881
	21.6	Delocalized Bonding 885
	21.7	The Free-Electron Molecular Orbital Method 892
	21.8	Applications of Symmetry to Molecular Orbitals 894
	21.9	Groups of Symmetry Operators 896
	21.10	More Advanced Treatments of Molecular Electronic
		Structure. Computational Chemistry 904
~	_	
Chapter 22		slational, Rotational, and Vibrational States of Atoms and
	Mole	
	22.1	The Translational States of Atoms 916
	22.2	The Nonelectronic States of Diatomic Molecules 919
	22.3 22.4	Nuclear Spins and Wave Function Symmetry 930 The Rotation and Vibration of Polyatomic
	22.4	Molecules 933
	22.5	The Equilibrium Populations of Molecular States 942
	22.3	The Equinorium Topulations of Molecular States 942
Chapter 23	Optic	al Spectroscopy and Photochemistry 949
	23.1	Emission/AbsorptionSpectroscopy and Energy Levels 950
	23.2	The Spectra of Atoms 959
	23.3	Rotational and Vibrational Spectra of Diatomic
		Molecules 961
	23.4	Electronic Spectra of Diatomic Molecules 972

	23.5 23.6 23.7 23.8	Fluorescence, Phosphorescence, and Photoch Raman Spectroscopy 985 Other Types of Spectroscopy 991	emistry 979	
Chapter 24	Magi 24.1 24.2 24.3 24.4 24.5	Magnetic Fields and Magnetic Dipoles Electronic and Nuclear Magnetic Dipoles Electron Spin Resonance Spectroscopy Nuclear Magnetic Resonance Spectroscopy Fourier Transform NMR Spectroscopy	1002 1006 1010 1014 1024	
Part 4		Reconciliation of the Macroscopic arories of Matter 1037	nd Molecular	
Chapter 25	_	librium Statistical Mechanics I. The Probab ibution for Molecular States 1039	oility	
	25.1	The Quantum Statistical Mechanics of a S	Simple Model	
		System 1040	1	
	25.2	The Probability Distribution for a Dilute Gas	s 1047	
	25.3	The Probability Distribution and the Molec	cular Partition	
		Function 1055		
	25.4	The Calculation of Molecular Partition Fund	etions 1064	
Chapter 26	Equilibrium Statistical Mechanics. II. Statistical			
		modynamics 1081	Car 1092	
	26.1 26.2	The Statistical Thermodynamics of a Dilute Working Equations for the Thermodynamic Dilute Gas 1089		
	26.3	Chemical Equilibrium in Dilute Gases	1101	
	26.4	The Activated Complex Theory of Bimolecu	ular Chemical	
		Reaction Rates in Dilute Gases 1106		
	26.5	Miscellaneous Topics in Statistical		
		Thermodynamics 1116		
Chapter 27	Equil	librium Statistical Mechanics. III. Ensembl	es 1121	
	27.1	The Canonical Ensemble 1122		
	27.2	Thermodynamic Functions in the Canonical Ensemble 1128		
	27.3	The Dilute Gas in the Canonical Ensemble	1130	
	27.4			
	27.5	Thermodynamic Functions in the Classical C	Canonical	
	27.6	Ensemble 1141 The Classical Statistical Mechanics of Den	usa Gasas and	
	27.0	Liquids 1147	ise Gases and	
Chapter 28	The S	Structure of Solids, Liquids, and Polymers	1153	
	28.1	The Structure of Solids 1154		
	28.2	•	_	
	28.3	•	ls 1171	
	28.4	Electrical Resistance in Solids 1179		

28.5	The Structure of Liquids 1184
28.6	Approximate Theories of Transport Processes in
	Liquids 1188
28.7	Polymer Conformation 1194
28.8	Polymers in Solution 1198
28.9	Rubber Elasticity 1200
28.1	0 Nanomaterials 1205
	U 1000
App	endices 1209
A.	Tables of Numerical Data 1209
B.	Some Useful Mathematics 1235
C.	A Short Table of Integrals 1257
D.	Some Derivations of Formulas and Methods 1261
E.	Classical Mechanics 1267
F.	Some Mathematics Used in Quantum Mechanics 1275
G.	The Perturbation Method 1283
H.	The Hiickel Method 1289
[.	Matrix Representations of Groups 1293
J.	Symbols Used in This Book 1303
K.	Answers to Numerical Exercises and Odd-Numbered
	Numerical Problems 1309

## Additional Reading 1351

**Index** 1361