

Contents

Preface *v*

1 The Nature and Properties of Matter 1

- 1-1 Matter and Chemistry 1
- 1-2 Mass and Energy 2
- 1-3 The International System of Units 3
- 1-4 Temperature 5
- 1-5 Kinds of Matter 7
- 1-6 The Physical Properties of Substances 11
- 1-7 The Chemical Properties of Substances 12
- 1-8 The Scientific Method 13

2 The Atomic and Molecular Structure of Matter 16

- 2-1 Hypotheses, Theories, and Laws 16
- 2-2 The Atomic Theory 17
- 2-3 Modern Methods of Studying Atoms and Molecules 19
- 2-4 The Arrangement of Atoms in a Crystal 20
- 2-5 The Description of a Crystal Structure 21
- 2-6 Crystal Symmetry; the Crystal Systems 27
- 2-7 The Molecular Structure of Matter 27

3 The Electron, the Nuclei of Atoms, and the Photon 39

- 3-1 The Nature of Electricity 40
- 3-2 The Discovery of the Electron 45
- 3-3 The Discovery of X-rays and Radioactivity 53
- 3-4 The Nuclei of Atoms 56
- 3-5 The Birth of the Quantum Theory 58
- 3-6 The Photoelectric Effect and the Photon 63
- 3-7 The Diffraction of X-rays by Crystals 70
- 3-8 Electron Wave Character and Electron Spin 74
- 3-9 What Is Light? What Is an Electron? 80
- 3-10 The Uncertainty Principle 82

4 Elements and Compounds.

Atomic and Molecular Masses 87

- 4-1 The Chemical Elements 88
- 4-2 The Neutron. The Structure of Nuclei 91
- 4-3 Chemical Reactions 95
- 4-4 Nuclidic Masses and Atomic Weights 95
- 4-5 Avogadro's Number. The Mole 96
- 4-6 Examples of Weight-relation Calculations 97
- 4-7 Determination of Atomic Weights by
the Chemical Method 99
- 4-8 Determination of Atomic Weights by Use of
the Mass Spectrograph 100
- 4-9 Determination of Nuclidic Masses by Nuclear
Reactions 103
- 4-10 The Discovery of the Correct Atomic Weights.
Isomorphism 104

5 Atomic Structure and the Periodic Table of the Elements 108

- 5-1 The Bohr Theory of the Hydrogen Atom 108
- 5-2 Excitation and Ionization Energies 115
- 5-3 The Wave-mechanical Description of Atoms 120
- 5-4 The Periodic Table of the Elements 133
- 5-5 Electron Energy as the Basis of the Periodic Table 138
- 5-6 The History of the Periodic Table 143

6 The Chemical Bond 148

- 6-1 The Nature of Covalence 148
- 6-2 The Structure of Covalent Compounds 152
- 6-3 The Direction of Valence Bonds in Space 157
- 6-4 Tetrahedral Bond Orbitals 161
- 6-5 Bond Orbitals with Large p Character 164
- 6-6 Molecules and Crystals of the Nonmetallic
Elements 165
- 6-7 Resonance 170
- 6-8 Ionic Valence 172
- 6-9 The Partial Ionic Character of Covalent Bonds 179
- 6-10 The Electronegativity Scale of the Elements 183
- 6-11 Heats of Formation and Relative Electronegativity
of Atoms 186
- 6-12 The Electroneutrality Principle 192
- 6-13 The Sizes of Atoms and Molecules.
Covalent Radii and van der Waals Radii 195
- 6-14 Oxidation Numbers of Atoms 198

7 The Nonmetallic Elements and Some of Their Compounds 205

- 7-1 The Elementary Substances 206
- 7-2 Hydrides of Nonmetals. Hydrocarbons 219

7-3	Hydrocarbons Containing Double Bonds and Triple Bonds	229	<i>ix</i>
7-4	Aromatic Hydrocarbons. Benzene	231	
7-5	Ammonia and Its Compounds	235	
7-6	Other Normal-valence Compounds of the Nonmetals	238	
7-7	Some Transargononic Single-bonded Compounds	244	
7-8	The Argonons	247	

8 Oxygen Compounds of Nonmetallic Elements 257

8-1	The Oxycompounds of the Halogens	258
8-2	Oxycompounds of Sulfur, Selenium, and Tellurium	267
8-3	Oxycompounds of Phosphorus, Arsenic, Antimony, and Bismuth	278
8-4	Oxycompounds of Nitrogen	283
8-5	Oxycompounds of Carbon	289
8-6	Molecules containing Bivalent Carbon. Free Radicals	293
8-7	Unstable and Highly Reactive Molecules	298

9 Gases: Quantum Mechanics and Statistical Mechanics 306

9-1	The Perfect-gas Equation	308
9-2	Quantum Mechanics of a Monatomic Gas	317
9-3	The Wave Equation	321
9-4	The Kinetic Theory of Gases	323
9-5	The Distribution Law for Molecular Velocities	325
9-6	The Boltzmann Distribution Law	329
9-7	Deviations of Real Gases from Ideal Behavior	334

10 Chemical Thermodynamics 343

10-1	Heat and Work. Energy and Enthalpy	343
10-2	The First Law of Thermodynamics	345
10-3	Heat Capacity. Heats of Fusion, Vaporization, and Transition	347
10-4	Entropy. The Probable State of an Isolated System	350
10-5	The Absolute Entropy of a Perfect Gas	354
10-6	Reversible and Irreversible Changes in State	355
10-7	The Efficiency of a Heat Engine	357
10-8	Change in Entropy of Any System with Temperature	359
10-9	The Third Law of Thermodynamics	360
10-10	The Heat Capacity of Diatomic Gases	364
10-11	Quantum States of the Rigid Rotator	365
10-12	The Rotational Entropy of Diatomic Gases	366
10-13	Quantum States of the Harmonic Oscillator	369
10-14	Vibrational States of Diatomic Molecules	370
10-15	Energy, Heat Capacity, and Entropy of a Harmonic Oscillator	371
10-16	The Quantum Theory of Low-temperature Heat Capacity of Crystals	374

11 Chemical Equilibrium 381

- 11-1 The Thermodynamic Condition for Chemical Equilibrium 381
- 11-2 The Vapor Pressure of a Liquid or Crystal 384
- 11-3 Entropy of Transition, Fusion, and Vaporization 387
- 11-4 Van der Waals Forces. Melting Points and Boiling Points 393
- 11-5 Chemical Equilibrium in Gases 400
- 11-6 Change of Equilibrium with Temperature 406
- 11-7 Equilibrium in Heterogeneous Systems 407
- 11-8 Le Chatelier's Principle 408
- 11-9 The Phase Rule—a Method of Classifying All Systems in Equilibrium 410
- 11-10 The Conditions under Which a Reaction Proceeds to Completion 413

12 Water 420

- 12-1 The Composition of Water 420
- 12-2 The Water Molecule 425
- 12-3 The Properties of Water 426
- 12-4 The Hydrogen Bond—the Cause of the Unusual Properties of Water 428
- 12-5 The Entropy of Ice 433
- 12-6 The Importance of Water as an Electrolytic Solvent 434
- 12-7 Heavy Water 438
- 12-8 Deviation of Water and Some Other Liquids from Hildebrand's Rule 438
- 12-9 The Dense Forms of Ice 439
- 12-10 The Phase Diagram of Water 443

13 The Properties of Solutions 447

- 13-1 Types of Solutions. Nomenclature 448
- 13-2 Solubility 449
- 13-3 The Dependence of Solubility on the Nature of Solute and Solvent 452
- 13-4 Solubility of Salts and Hydroxides 453
- 13-5 The Solubility-Product Principle 454
- 13-6 The Solubility of Gases in Liquids: Henry's Law 457
- 13-7 The Freezing Point and Boiling Point of Solutions 458
- 13-8 The Vapor Pressure of Solutions: Raoult's Law 461
- 13-9 The Osmotic Pressure of Solutions 464
- 13-10 The Escaping Tendency and the Chemical Potential 465
- 13-11 The Properties of Ionic Solutions 470
- 13-12 Colloidal Solutions 475

14 Acids and Bases 481

- 14-1 Hydronium-ion (Hydrogen-ion) Concentration 482

14-2	The Equilibrium between Hydrogen Ion and Hydroxide Ion in Aqueous Solution	485
14-3	Indicators	486
14-4	Equivalent Weights of Acids and Bases	488
14-5	Weak Acids and Bases	490
14-6	The Titration of Weak Acids and Bases	493
14-7	Buffered Solutions	497
14-8	The Strengths of the Oxygen Acids	499
14-9	The Solution of Carbonates in Acid; Hard Water	503
14-10	The Precipitation of Sulfides	505
14-11	Nonaqueous Amphiprotic Solvents	506
15	Oxidation-Reduction Reactions. Electrolysis	512
15-1	The Electrolytic Decomposition of Molten Salts	513
15-2	The Electrolysis of an Aqueous Salt Solution	517
15-3	Oxidation-Reduction Reactions	520
15-4	Quantitative Relations in Electrolysis	523
15-5	The Electromotive-force Series of the Elements	525
15-6	Equilibrium Constants for Oxidation-Reduction Couples	530
15-7	The Dependence of the Electromotive Force of Cells on Concentration	535
15-8	Primary Cells and Storage Cells	536
15-9	Electrolytic Production of Elements	539
15-10	The Reduction of Ores. Metallurgy	543
16	The Rate of Chemical Reactions	551
16-1	Factors Influencing the Rate of Reactions	552
16-2	The Rate of a First-order Reaction at Constant Temperature	555
16-3	Reactions of Higher Order	561
16-4	Mechanism of Reactions. Dependence of Reaction Rate on Temperature	564
16-5	Catalysis	568
16-6	Kinetics of Enzyme Reactions	569
16-7	Chain Reactions	572
17	The Nature of Metals and Alloys	577
17-1	The Metallic Elements	578
17-2	The Structure of Metals	578
17-3	The Nature of the Transition Metals	580
17-4	The Metallic State	582
17-5	Metallic Valence	585
17-6	The Free-electron Theory of Metals	588
17-7	The Nature of Alloys	590
17-8	Experimental Methods of Studying Alloys	596
17-9	Interstitial Solid Solutions and Substitutional Solid Solutions	603
17-10	Physical Metallurgy	604

18 Lithium, Beryllium, Boron, and Silicon and Their Congeners 612

- 18-1 The Electronic Structures of Lithium, Beryllium,
Boron, and Silicon and Their Congeners 613
- 18-2 Radius Ratio, Ligancy, and the Properties of
Substances 614
- 18-3 The Alkali Metals and Their Compounds 621
- 18-4 The Alkaline-earth Metals and Their Compounds 625
- 18-5 Boron 628
- 18-6 The Boranes. Electron-deficient Substances 629
- 18-7 Aluminum and Its Congeners 632
- 18-8 Silicon and Its Simpler Compounds 636
- 18-9 Silicon Dioxide 637
- 18-10 Sodium Silicate and Other Silicates 639
- 18-11 The Silicate Minerals 640
- 18-12 Glass 643
- 18-13 Cement 644
- 18-14 The Silicones 645
- 18-15 Germanium 646
- 18-16 Tin 648
- 18-17 Lead 650

19 Inorganic Complexes and the Chemistry of the Transition Metals 654

- 19-1 The Nature of Inorganic Complexes 654
- 19-2 Tetrahedral, Octahedral, and Square Bond Orbitals 655
- 19-3 Ammonia Complexes 659
- 19-4 Cyanide Complexes 662
- 19-5 Complex Halides and Other Complex Ions 663
- 19-6 Hydroxide Complexes 665
- 19-7 Sulfide Complexes 666
- 19-8 The Quantitative Treatment of Complex
Formation 667
- 19-9 Polydentate Complexing Agents 670
- 19-10 The Structure and Stability of Carbonyls and Other
Covalent Complexes of the Transition Metals 671
- 19-11 Polynuclear Complexes 674

20 Iron, Cobalt, Nickel, and the Platinum Metals 678

- 20-1 The Electronic Structures and Oxidation States of
Iron, Cobalt, Nickel, and the Platinum Metals 679
- 20-2 Iron 681
- 20-3 Steel 686
- 20-4 Compounds of Iron 690
- 20-5 Cobalt 692
- 20-6 Nickel 692
- 20-7 The Platinum Metals 693

21 Copper, Zinc, and Gallium and Their Congeners 697

xiii

- 21-1 The Electronic Structures and Oxidation States of
Copper, Silver, and Gold 698
- 21-2 The Properties of Copper, Silver, and Gold 699
- 21-3 The Compounds of Copper 701
- 21-4 The Compounds of Silver 703
- 21-5 Photochemistry and Photography 704
- 21-6 The Compounds of Gold 711
- 21-7 Color and Mixed Oxidation States 712
- 21-8 The Properties and Uses of Zinc, Cadmium, and
Mercury 712
- 21-9 Compounds of Zinc and Cadmium 713
- 21-10 Compounds of Mercury 715
- 21-11 Gallium, Indium, and Thallium 719

22 Titanium, Vanadium, Chromium, and Manganese and Their Congeners 722

- 22-1 The Electronic Structures of Titanium, Vanadium,
Chromium, and Manganese and Their Congeners 722
- 22-2 Titanium, Zirconium, Hafnium, and Thorium 723
- 22-3 Vanadium, Niobium, Tantalum, and Protactinium 725
- 22-4 Superconductivity 727
- 22-5 Chromium 729
- 22-6 The Congeners of Chromium 733
- 22-7 Manganese 736
- 22-8 Acid-forming and Base-forming Oxides and Hydroxides
739
- 22-9 The Congeners of Manganese 740

23 Organic Chemistry 743

- 23-1 The Nature and Extent of Organic Chemistry 743
- 23-2 Petroleum and the Hydrocarbons 744
- 23-3 Alcohols and Phenols 749
- 23-4 Aldehydes and Ketones 753
- 23-5 The Organic Acids and Their Esters 755
- 23-6 Amines and Other Organic Compounds of Nitrogen 759
- 23-7 Carbohydrates, Sugars, Polysaccharides 764
- 23-8 Fibers and Plastics 765

24 Biochemistry 767

- 24-1 The Nature of Life 767
- 24-2 The Structure of Living Organisms 769
- 24-3 Amino Acids and Proteins 770
- 24-4 Nucleic Acids. The Chemistry of Heredity 781
- 24-5 Metabolic Processes. Enzymes and Their Action 789
- 24-6 Vitamins 791
- 24-7 Hormones 796
- 24-8 Chemistry and Medicine 791

25 The Chemistry of the Fundamental Particles 802

- 25-1 The Classification of the Fundamental Particles 803
- 25-2 The Discovery of the Fundamental Particles 805
- 25-3 The Forces between Nucleons. Strong Interactions 809
- 25-4 The Structure of Nucleons 813
- 25-5 Leptons and Antileptons 814
- 25-6 Mesons and Antimesons 819
- 25-7 Baryons and Antibaryons 819
- 25-8 The Decay Reactions of the Fundamental Particles 819
- 25-9 Strangeness (Xenicity) 822
- 25-10 Resonance Particles and Complexes 824
- 25-11 The Structure of the Fundamental Particles.
Quarks 825
- 25-12 Positronium, Muonium, Mesonic Atoms 829

26 Nuclear Chemistry 831

- 26-1 Natural Radioactivity 833
- 26-2 The Age of the Earth 837
- 26-3 Artificial Radioactivity 837
- 26-4 The Kinds of Nuclear Reactions 839
- 26-5 The Use of Radioactive Elements as Tracers 841
- 26-6 Dating Objects by Use of Carbon 14 843
- 26-7 The Properties of Nuclides 845
- 26-8 The Shell Model of Nuclear Structure 854
- 26-9 The Helion-Triton Model 856
- 26-10 Nuclear Fission and Nuclear Fusion 859

Appendixes

- I. Units of Measurement 865
- II. Values of Some Physical and Chemical Constants 868
- III. Symmetry of Molecules and Crystals 869
- IV. X-rays and Crystal Structure 881
- V. Hydrogenlike Orbitals 895
- VI. Russell-Saunders States of Atoms Allowed by
the Pauli Exclusion Principle 898
- VII. Hybrid Bond Orbitals 906
- VIII. Bond Energy and Bond-dissociation Energy 912
- IX. The Vapor Pressure of Water
at Different Temperatures 916
- X. An Alternative Derivation
of the Boltzmann Distribution Law 917
- XI. The Boltzmann Distribution Law
in Classical Mechanics 919
- XII. The Entropy of a Perfect Gas 921
- XIII. Electric Polarizabilities and
Electric Dipole Moments 924
- XIV. The Magnetic Properties of Substances 928
- XV. Values of Thermodynamic Properties of Some
Substances at 25°C and 1 atm 939
- XVI. Selected Readings 942