# CONTENTS

# Preface, v

# 1 INTRODUCTION

- 1.1 GENERAL AND HISTORICAL, 1
- 1.2 DEFINITIONS OF SOME CHEMICAL TERMS, 2
- 1.3 THE PURITY OF COMPOUNDS, 4
- 1.4 CHEMICAL SYMBOLS, FORMULAS, AND EQUATIONS, 4

#### 2 ELECTRONIC STRUCTURES OF ATOMS

- 2.1 INTRODUCTION, 7
- 2.2 QUANTIZATION OF ELECTRICITY, 8
- 2.3 THE POSITIVE IONS (POSITIVE RAYS), 10
- 2.4 THE RUTHERFORD-BOHR NUCLEAR THEORY OF THE ATOM, 10
- 2.5 THE NATURE OF LIGHT, 13
- 2.6 SPECTRA OF ELEMENTS, 17
- 2.7 QUANTIZATION OF THE ENERGY OF AN ELECTRON ASSOCIATED WITH A NUCLEUS, 18
- 2.8 MODIFICATION OF THE BOHR THEORY, 22
- 2.9 THE ELECTRON-HOW SHALL WE THINK ABOUT IT?, 23
- 2.10 THE DISTRIBUTION OF ELECTRONS IN QUANTUM LEVELS, 24
- 2.11 THE ENERGIES OF THE QUANTUM LEVELS, 26
- 2.12 ELECTRON SPIN, 28
- 2.13 AUFBAU, 29
- 2.14 WHAT DO THE QUANTUM NUMBERS REPRESENT?, 34
- 2.15 REPRESENTATIONS OF THE SHAPES OF ATOMIC ORBITALS, 34
- 2.16 PARAMAGNETISM, 35

#### 3 CHEMICAL PERIODICITY

- 3.1 FORMULAS AND VALENCE, 41
- 3.2 NOMENCLATURE, 41
- 3.3 CHEMICAL PERIODICITY BEFORE MENDELEEV, 43
- 3.4 MENDELEEV; MEYER, 44
- 3.5 THE PERIODIC LAW AND THE PERIODIC TABLE. TYPES OF ELEMENTS,  $46\,$
- 3.6 THE PERIODICITY OF CHEMICAL PROPERTIES, 51
- 3.7 ATOMIC STRUCTURE AND PERIODIC PROPERTIES OF ATOMS, 54

## 4 M ATOMIC AND MOLECULAR WEIGHTS. THE MOLE

- 4.1 THE LAW OF CONSERVATION OF MATTER, 63
- 4.2 THE LAW OF DEFINITE PROPORTIONS, 63
- 4.3 THE ATOMIC THEORY, 64
- 4.4 THE LAW OF COMBINING VOLUMES; THE AVOGADRO HYPOTHESIS, 65
- 4.5 APPROXIMATE MOLECULAR WEIGHTS OF GASES. THE MOLE, 66
- 4.6 ATOMIC WEIGHTS FROM MOLECULAR WEIGHTS; THE CANNIZZARO METHOD, 69
- 4.7 MOLECULAR FORMULAS, 71
- 4.8 EMPIRICAL FORMULAS; IONIC SOLIDS, 73
- 4.9 MASS SPECTROSCOPY; ISOTOPES; ACCURATE ATOMIC WEIGHTS, 75

# 5 STOICHIOMETRY-THE ARITHMETIC OF CHEMISTRY

- 5.1 CHEMICAL EQUATIONS, 83
- 5.2 QUANTITATIVE INFORMATION FROM CHEMICAL EQUATIONS, 84
- 5.3 CONVERSION AND SELECTIVITY (YIELD), 89

## 6 ■ THE FIRST LAW OF THERMODYNAMICS; THERMOCHEMISTRY

- 6.1 CONSERVATION OF ENERGY, 95
- 6.2 THE FIRST LAW OF THERMODYNAMICS, 95
- 6.3 THERMOCHEMISTRY, 99
- 6.4 HESS'S LAW, 101
- 6.5 BOND DISSOCIATION ENERGY, 102
- 6.6 THE INTERCONVERTIBILITY OF MATTER AND ENERGY, 105

## 7 TYPES OF CHEMICAL BONDS

- 7.1 INTRODUCTION, 110
- 7.2 WHAT TYPE OF ATTRACTIVE FORCES HOLD ATOMS TOGETHER IN CHEMICAL BONDS?, 110
- 7.3 LEWIS SYMBOLS, 111
- 7.4 THE IONIC BOND, 112
- 7.5 THE COVALENT BOND, 114
- 7.6 THE MULTIPLE BONDS, 116
- 7.7 PROPERTIES OF IONIC AND COVALENT COMPOUNDS, 117
- 7.8 POLAR COVALENT BONDS; ELECTRONEGATIVITY, 118
- 7.9 EXCEPTIONS TO THE OCTET RULE, 120
- 7.10 FORMAL CHARGE AND OXIDATION NUMBER, 122
- 7.11 PERIODICITY OF CHEMICAL BONDING, 127

## 8 THE COVALENT BOND

- 8.1 THE MOLECULAR ORBITAL, 133
- 8.2 SIGMA (σ) BONDS AND PI (π) BONDS, 134
- 8.3 BINARY COVALENT MOLECULES AND IONS, 135
- 8.4 HYBRIDIZATION OF ATOMIC ORBITALS, 136
- 8.5 MULTIPLY BONDED MOLECULES, 140
- 8.6 HYBRID ORBITAL NUMBER, 144
- 8.7 RELATIVE ENERGY LEVELS OF THE s-p TYPE OF HYBRID ORBITAL, 145
- 8.8 RESONANCE AND DELOCALIZED p ELECTRONS, 145

## 9 THE SHAPES AND SYMMETRY OF MOLECULES

- 9.1 INTRODUCTION, 150
- 9.2 HYBRIDIZATION OF ORBITALS OF ATOMS WITH MORE THAN AN OCTET OF VALENCE ELECTRONS, 150
- 9.3 PRINCIPAL FACTORS DETERMINING MOLECULAR SHAPE, 152
- 9.4 PRINCIPAL EFFECT OF A LONE PAIR OF ELECTRONS, 154
- 9.5 MOLECULES WHOSE CENTRAL ATOMS USE UNHYBRIDIZED p ORBITALS, 157
- 9.6 SHAPES OF MULTIPLE-BONDED MOLECULES, 157
- 9.7 MOLECULAR SYMMETRY, 158
- 9.8 MOLECULAR DISSYMMETRY, 162

# 10 INTERMOLECULAR FORCES

- 10.1 INTRODUCTION, 166
- 10.2 DIPOLE-DIPOLE INTERACTION, 166
- 10.3 ION-DIPOLE ATTRACTIONS, 168
- 10.4 HYDROGEN BONDING, 168
- 10.5 LONDON FORCES, 171
- 10.6 LONDON FORCES AND MOLECULAR SHAPE, 171

#### 11 GASES

- 11.1 THE STATES OF AGGREGATION OF MOLECULES IN MATTER, 174
- 11.2 THE PROPERTIES OF GASES, 174
- 11.3 BOYLE'S LAW, 175

- 11.4 THE LAW OF CHARLES AND GAY-LUSSAC; ABSOLUTE TEMPERATURE, 177
- 11.5 AVOGADRO'S LAW, 179
- 11.6 THE GAS LAW; THE MOLE; GAS DENSITIES, 179
- 11.7 DALTON'S LAW OF PARTIAL PRESSURES, 182
- 11.8 THE PRESSURE OF A GAS CONFINED BY A LIQUID, 184
- 11.9 GAS VOLUME CORRECTIONS IN STOICHIOMETRY, 186
- 11.10 IDEAL GASES. THE KINETIC MOLECULAR HYPOTHESIS, 187
- 11.11 DEVIATIONS FROM IDEAL BEHAVIOR, 189

#### 12 AGGREGATED STATES OF MATTER

- 12.1 CRYSTALLINE SOLIDS; METHODS OF INVESTIGATION, 196
- 12.2 THE SPACE LATTICE; THE UNIT CELL, 196
- 12.3 THE TETRAHEDRON; THE OCTAHEDRON, 201
- 12.4 LIQUIDS; GLASSES, 201
- 12.5 CHANGES OF STATE, 204
- 12.6 SPONTANEOUS CHANGE; ENTROPY, 206
- 12.7 LIQUID-GAS INTERCONVERSION; VAPOR PRESSURE, 208
- 12.8 CRITICAL CONSTANTS, 209
- 12.9 BOILING, MELTING, AND FREEZING POINTS, 210
- 12.10 COLLOIDS; ADSORBENTS, 212

#### 13 SOLUTIONS

- 13.1 INTRODUCTION, 217
- 13.2 LIQUID SOLUTIONS, 217
- 13.3 SATURATION: GASES IN LIQUIDS, 218
- 13.4 SATURATION: SOLIDS IN LIQUIDS OR LIQUIDS IN LIQUIDS, 220
- 13.5 DEPENDENCE OF SOLUBILITY ON TEMPERATURE, 220
- 13.6 SUPERSATURATION, 221
- 13.7 SOLUBILITY AND MOLECULAR STRUCTURE, 222
- 13.8 DETERGENCY, 223
- 13.9 SOLID SOLUTIONS, 225
- 13.10 MEASURES OF COMPOSITION FOR SOLUTIONS, 226
- 13.11 VAPOR PRESSURES OF SOLUTIONS; RAOULT'S LAW, 232
- 13.12 VAPOR PRESSURE DEPRESSION, 234
- 13.13 BOILING-POINT ELEVATION AND FREEZING-POINT DEPRESSION, 234
- 13.14 DETERMINATION OF MOLECULAR WEIGHTS, 237

## 14 CHEMICAL EQUILIBRIUM

- 14.1 INTRODUCTION, 243
- 14.2 EQUILIBRIUM IN GASES; THE EQUILIBRIUM CONSTANT, 245
- 14.3 CHANGE OF K WITH FORM OF EQUATION, 247
- 14.4 COMBINATION OF EQUILIBRIA, 248
- 14.5 PRINCIPLE OF LE CHATELIER, 249
- 14.6 HETEROGENEOUS EQUILIBRIUM, 251
- 14.7 EQUILIBRIUM IN SOLUTIONS, 253
- 14.8 EQUILIBRIUM CALCULATIONS, 255

# 15 IONIC SOLUTIONS

- 15.1 ELECTRICAL CONDUCTANCE, 260
- 15.2 COLLIGATIVE PROPERTIES OF SOLUTIONS OF ELECTROLYTES, 261
- 15.3 IONIC CONDUCTION, 262
- 15.4 SOLVATION OF IONS, 263
- 15.5 COVALENT ELECTROLYTES, 264
- 15.6 NET IONIC EQUATIONS, 264
- 15.7 BALANCING OXIDATION-REDUCTION EQUATIONS BY THE ION-ELECTRON METHOD, 266
- 15.8 ELECTRODE PROCESSES, 269
- 15.9 ELECTROLYSIS OF FUSED SALTS, 270
- 15.10 FARADAY'S LAWS, 271
- 15.11 STRONG ELECTROLYTES, 274
- 15.12 CONDUCTANCES OF INDIVIDUAL IONS, 275
- 15.13 WEAK ELECTROLYTES, 276
- 15.14 DEGREE OF DISSOCIATION, 277

# 16 ■ GALVANIC CELLS AND THE DRIVING FORCE OF CHEMICAL REACTIONS

- 16.1 INTRODUCTION, 282
- 16.2 ELECTRICITY FROM A CHEMICAL REACTION, 283
- 16.3 A GALVANIC CELL WITH ONE SOLUTION, 284
- 16.4 ELECTRICAL WORK; ELECTROMOTIVE FORCE, 285
- 16.5 MEASUREMENT OF ELECTROMOTIVE FORCE, 286
- 16.6 FREE ENERGY AND ENTROPY, 287
- 16.7 SALT BRIDGES; CONVENTIONAL NOTATION FOR CELLS, 290
- 16.8 THE EFFECT OF CONCENTRATION ON EMF; NERNST EQUATION, 291
- 16.9 HALF-CELL POTENTIALS; THE HYDROGEN HALF-CELL, 293
- 16.10 EMF, K, AND AG, 297
- 16.11 PREDICTING THE DIRECTION OF A REACTION, 299
- 16.12 STRENGTHS OF OXIDIZING AND REDUCING AGENTS, 300
- 16.13 SOME PRACTICAL CELLS, 301
- 16.14 CORROSION, 303

## 17 ACIDS AND BASES

- 17.1 EARLY DEFINITIONS, 309
- 17.2 BRÖNSTED-LOWRY CONCEPT OF ACID-BASE REACTIONS, 310
- 17.3 AMPHOTERISM; AUTOPROTOLYSIS (SELF-IONIZATION), 314
- 17.4 TYPES OF PROTOLYTIC REACTION, 315
- 17.5 LEWIS ACID-BASE CONCEPT, 320
- 17.6 SOME EXAMPLES OF LEWIS ACIDS, 320
- 17.7 INDUSTRIAL APPLICATIONS OF ACID-BASE REACTIONS, 321
- 17.8 PREPARATION OF ACIDS, 324

#### 18 CALCULATIONS OF IONIC EQUILIBRIUM

- 18.1 THE IONIZATION OF WATER, 327
- 18.2 pH AND pOH, 328
- 18.3 ACIDIC, BASIC, AND NEUTRAL SOLUTIONS, 329
- 18.4 IONIZATION OF WEAK ACIDS, 329
- 18.5 IONIZATION OF WEAK BASES, 336
- 18.6 CONJUGATE ACID-BASE PAIRS, 337
- 18.7 POLYPROTIC ACIDS, 337
- 18.8 WEAK ACID (OR BASE) IN THE PRESENCE OF STRONG ACID (OR BASE), 339
- 18.9 BUFFER SOLUTIONS, 341
- 18.10 INDICATORS AND TITRATION, 343
- 18.11 SOLUBILITY PRODUCT, 345
- 18.12 EFFECT OF pH ON SOLUBILITY, 351
- **18.13 COMPLEX IONS, 352**

## 19 CHEMICAL KINETICS

- 19.1 INTRODUCTION, 357
- 19.2 CONDITIONS AFFECTING REACTION RATES, 358
- 19.3 THEORY OF REACTION RATES, 363
- 19.4 MECHANISM OF REACTION FROM RATE EQUATION, 371
- 19.5 CHAIN MECHANISM, 375

## 20 THE CHEMISTRY OF THE REPRESENTATIVE ELEMENTS

- 20.1 INTRODUCTION, 382
- 20.2 ALLOTROPY AND PERIODICITY, 382
- 20.3 REACTIVITY OF HYDRIDES, 384
- 20.4 THE PERIODICITY OF PROPERTIES OF THE OXIDES, 387
- 20.5 STRUCTURE OF OXYANIONS, 391
- 20.6 THE CHEMISTRY OF SOME COMMON OXIDES AND OXYANIONS, 392
- 20.7 PEROXIDES, 401
- 20.8 PERIODICITY OF PROPERTIES OF THE HALIDES; DIFFERENCES IN OXIDATION STATES, 402
- 20.9 PROPERTIES OF SULFIDES, 405
- 20.10 COMPOUNDS OF NOBLE GASES, 407

## 21 THE CHEMISTRY OF THE TRANSITION ELEMENTS

- 21.1 DEFINITION; GROUPS AND TRIADS, 412
- 21.2 METALLIC BEHAVIOR, 412
- 21.3 OXIDATION STATES AND BONDING, 413
- 21.4 COLOR, 415
- 21.5 INTERSTITIAL COMPOUNDS, 417
- 21.6 OXIDES AND OXYIONS, 418
- 21.7 COMPLEX FORMATION, 420
- 21.8 COORDINATION NUMBER OR LIGANCY, 420
- 21.9 WERNER'S COORDINATION THEORY, 421
- 21.10 COORDINATION NUMBER AND SHAPE, 421
- 21.11 BONDING IN TRANSITION METAL COMPLEXES, 422
- 21.12 CRYSTAL FIELD THEORY, 423
- 21.13 CARBONYL COMPLEXES, 427
- 21.14 GEOMETRICAL ISOMERISM, 428
- 21.15 STABILITY OF COMPLEX IONS, 429

#### 22 ORGANIC CHEMISTRY

- 22.1 WHAT IS ORGANIC CHEMISTRY?, 433
- 22.2 THE BONDING OF CARBON, 434
- 22.3 ALKANE HYDROCARBONS; ISOMERISM AND HOMOLOGY, 435
- 22.4 THE SHAPES OF ALKANE MOLECULES. CONFORMATION, 437
- 22.5 CHEMICAL PROPERTIES OF THE ALKANES, 438
- 22.6 ALKENES AND ALKYNES; UNSATURATED HYDROCARBONS; GEOMETRICAL ISOMERISM. 440
- 22.7 CYCLOALKANES, 442
- 22.8 DIENES; BENZENE AND AROMATIC COMPOUNDS, 443
- 22.9 FUNCTIONAL GROUP DERIVATIVES, 447
- 22.10 REACTIONS OF COVALENT BONDS, 451
- 22.11 DECOMPOSITION, 451
- 22.12 DISPLACEMENT OR SUBSTITUTION REACTIONS, 452
- 22.13 REARRANGEMENTS, 455

#### 23 METALS AND METALLURGY

- 23.1 THE PROPERTIES OF METALS, 460
- 23.2 THE METALLIC BOND; THE BAND THEORY OF METALS, 461
- 23.3 METALLIC PROPERTIES IN TERMS OF THE BAND THEORY, 464
- 23.4 INSULATORS AND SEMICONDUCTORS, 464
- 23.5 SOURCES OF METALS, 465
- 23.6 THE WINNING OF METALS FROM ORES: GENERAL CONSIDERATIONS, 467
- 23.7 PRELIMINARY PHYSICAL TREATMENT, 467
- 23.8 PHYSICAL CONCENTRATION, 468
- 23.9 CHEMICAL LEACHING, 469
- 23.10 ROASTING, 469
- 23.11 REDUCTION, 470
- 23.12 ELECTROMETALLURGY, 472
- 23.13 REFINING; ELECTROLYTIC METHODS, 472
- 23.14 REFINING; NONELECTROLYTIC METHODS, 474

#### 24 NUCLEAR CHEMISTRY

- 24.1 RADIOACTIVITY, 477
- 24.2 NUCLEAR ENERGY, 479
- 24.3 THE STABILITY OF NUCLEI, 480
- 24.4 NUCLEAR REACTIONS, 482
- 24.5 RATE OF RADIOACTIVE DECAY PROCESSES; HALF-LIFE, 488
- 24.6 RADIOCHEMISTRY, 489

## 25 POLYMERS

- 25.1 BACKGROUND AND DEFINITIONS, 495
- 25.2 THE DECOMPOSITION OF NATURAL HIGH POLYMERS; MONOMERIC UNITS (MERS), 496

- 25.3 THE PRODUCTION OF SYNTHETIC HIGH POLYMERS; C-POLYMERIZATION, 499
- 25.4 A-POLYMERIZATION, 499
- 25.5 THE ORIENTATION OF MONOMERIC UNITS IN MACROMOLECULES, 501
- 25.6 CRYSTALLINITY OF POLYMERS, 505
- 25.7 IONIC POLYMERS, 506
- 25.8 PROPERTIES OF POLYMERS, 507

# 26 BIOCHEMISTRY

- 26.1 INTRODUCTION, 514
- 26.2 THE ROLE OF THE CELL, 515
- 26.3 BIOCHEMICALS, 516
- 26.4 BIOCHEMICAL PROCESSES IN THE CELL, 524
- **26.5 EPILOGUE, 526**
- APPENDIX 1: Definitions and Review of Physical Concepts, 529
- APPENDIX 2: Review of Some Mathematical Operations, 543
- APPENDIX 3: Nomenclature, 550
- APPENDIX 4: Fundamental Constants, 558
- APPENDIX 5: Vapor Pressure of Water, 559
- APPENDIX 6: Abbreviations, 560
- APPENDIX 7: Logarithms—Natural and Common, 561

Index, 565