

FRANCIS MARION MILLER

CHEMISTRY

STRUCTURE AND DYNAMICS

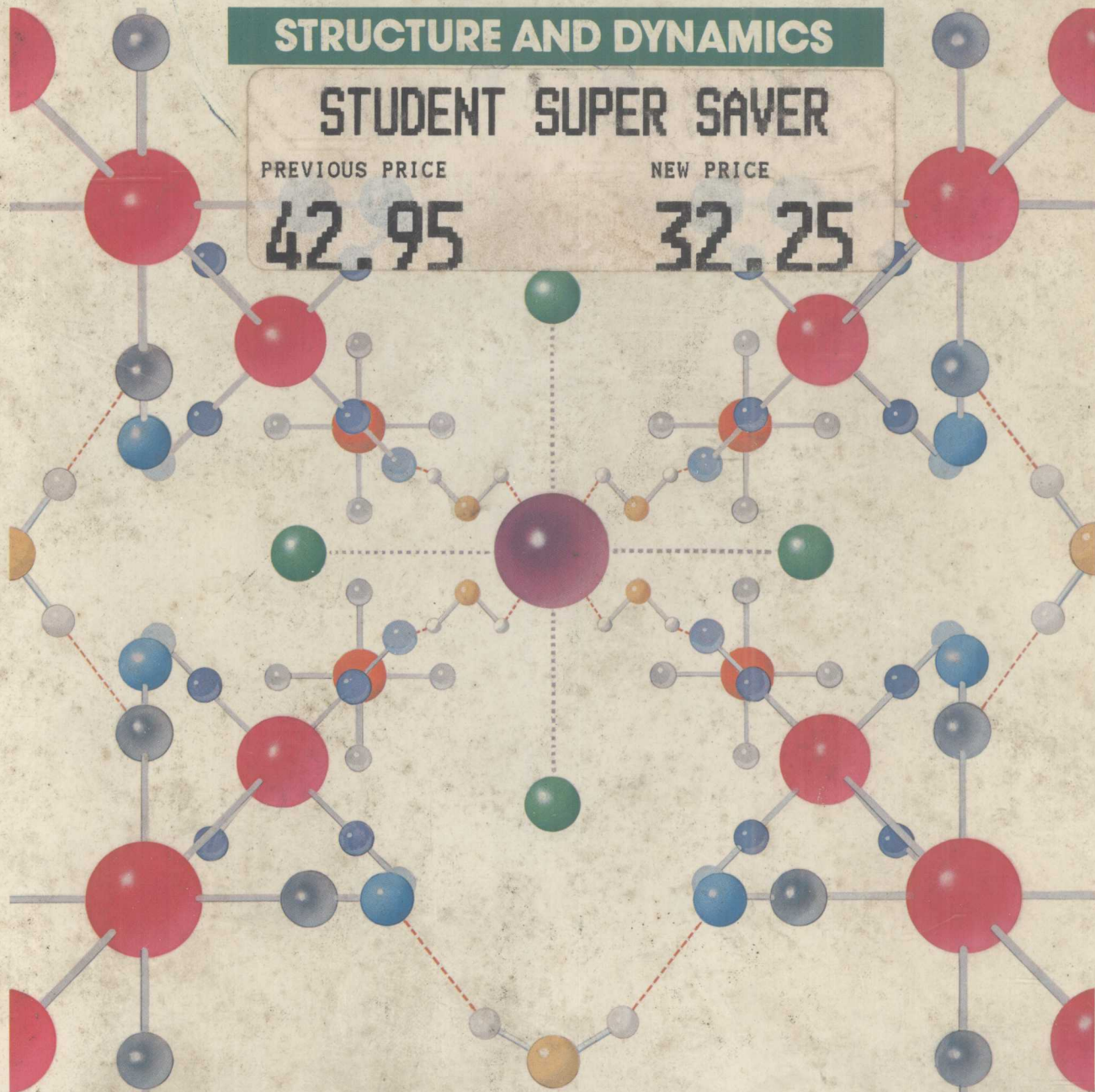
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STRUCTURE AND DYNAMICS

FRANCIS MARION MILLER

Professor of Chemistry
Northern Illinois University

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**CHEMISTRY:
STRUCTURE
AND DYNAMICS**

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TO C.W.M.

In producing this textbook, we have made every effort to provide you with a book that will assist your instructor in bringing the science of chemistry to you as smoothly and effectively as possible. As you begin your study, I want to point out some of the book's features, along with some suggestions about how to use it to the greatest advantage.

You should begin your study of each chapter by examining the *outline* to obtain an overview of the chapter's contents. A good approach then is to scan the chapter to gain a general grasp of the material. You should include the *chapter summary* in this first reading. Whenever possible, read the chapter as soon as it is assigned and before the material is discussed in the lecture.

You are now ready for a careful reading of the chapter, taking time to study the worked-out *examples*, which provide further illustration of the ideas explained in the text. A worthwhile tactic is to attempt to answer the question in the example before looking at the solution. When you have worked through the chapter thoroughly, again read the summary, because in many cases the ideas and relationships of the chapter are stated there in a slightly different way, providing you with another perspective of the material.

To check your mastery of the material in the chapter, make certain that you are able to satisfy each item in the *chapter mastery checklist*. Do this in an active way by carrying out each operation and verifying your answer. This can be done both with the examples in the chapter and with the *exercises* at the end of the chapter. These exercises are grouped by topic, and those with colored numbers have answers in the appendix. You can best acquire a thorough competence in the topic by working a number of these exercises.

Also included at the end of each chapter is a list of *suggested readings*. These articles were chosen to provide you with interesting and informative supplementary material related to the discussions in the chapter.

A useful feature of this text is the *glossary*. Where possible, terms here are defined with somewhat different words from those used in the chapters. The glossary items include reference to the section of the book where a term is introduced. Therefore, if at a later point in your study you find that you are uncertain about the meaning of a word or the statement of a law, the glossary will provide a ready source of the definition and a reference to the more complete explanation in the body of the book.

Your study of chemistry with this text does not require a high level of mathematics. However, mathematics is part of the language of chemistry, and a lack of familiarity with that language can become a barrier to success in understanding chemistry. Appendix A is a *review of mathematics*, included to assist you in your recollection of the operations of algebra, exponential numbers, logarithms, and graphing. Examine it now, and then refer to it any time you are not completely certain of a mathematical operation.

I hope that you are eager to begin your study of chemistry and that this course is an enjoyable and rewarding experience for you.

Francis Marion Miller

**TO THE
STUDENT**

Chemistry: Structure and Dynamics is a text for a two-semester general chemistry course for science majors. The book assumes no previous knowledge of chemistry or of calculus. Nevertheless, it is designed to provide students whose background includes a year or more of high school chemistry with stimulation and some new material.

The objective of a general chemistry course for science majors is preparation for such advanced courses as organic chemistry, analytical chemistry, physical chemistry, and biochemistry. Students emerging from the course should have firm ideas of molecular structure, acids and bases, equilibrium, the energetics of physical and chemical changes, and fundamental descriptive chemistry. At the same time, the course should enhance the student's ability to analyze a problem and proceed logically toward a solution; the student should develop an understanding of scientific methodology.

The decision to write this text was based on the conviction that the most coherent and unified presentation of the subject matter usually considered in the general chemistry course for science majors is based on two principles:

- 1 The topic of energy and enthalpy changes must be introduced early and the energy changes accompanying physical and chemical changes emphasized wherever possible.
- 2 The physical and chemical properties of elements and compounds must be correlated thoroughly with the structure and polarity of the substances under consideration.

Following the first principle, I have examined energy rather thoroughly in Chapter 4 in terms of the first law of thermodynamics, thermochemistry, enthalpy changes, radiant energy, and electrical energy. Students are thus prepared for the ideas of molecular energies in gas behavior (Chapter 5), electron energy levels (Chapter 6), ionization energies and electron affinities (Chapter 7), bond energies (Chapter 9), the energy changes associated with phase changes (Chapters 10 and 12), enthalpy cycles and the dissociation of acids and bases (Chapter 13), activation energies (Chapter 14), the second and third laws of thermodynamics (Chapter 18), electrochemical energy changes (Chapter 19), radiant energy changes (Chapter 20), and a variety of energy considerations associated with descriptive chemistry (Chapter 21 *et seq.*).

In agreement with the second principle, after the introduction of the basic ideas of molecular geometry (Chapter 8), the consequences of molecular shape and polarity are invoked at every appropriate opportunity: structure and physical properties (Chapter 10), solubilities and properties of solutions (Chapter 12), structure and chemical reactivity (Chapter 13), and throughout the discussions of descriptive chemistry in the last third of the book.

An objective constantly in mind during the writing of this book was to produce a text that would be of maximum usefulness to the student reader. I have made every effort to achieve the highest possible degree of readability, to avoid jargon while introducing the vocabulary of chemistry, and to provide clear, precise, and meaningful definitions of new terms. The illustrations have been planned and executed with care. To make troublesome concepts as accessible as possible I have chosen to present the development of the foundations

TO THE INSTRUCTOR

of chemistry as it actually occurred. I have made a consistent effort to show how chemistry is done, rather than to hand down facts. Where feasible, experimental methods are discussed. To show that the ideas of chemistry are reasonable and have developed in a logical manner, I have examined how scientific models relate to observed facts. Practical applications with which the student is likely to be familiar have been included wherever possible.

I have paid particular attention to the development of topics with which students often have difficulty gaining an effective level of understanding. Believing that repetition is one helpful technique, I have introduced troublesome ideas early and considered them frequently to achieve maximum familiarity. Equilibrium, including LeChatelier's principle, and entropy are first examined in relation to changes of state (Chapters 10 and 12). The factors affecting acid-base strength are discussed in detail in Chapter 13 as background for the quantitative consideration of aqueous acid-base equilibria in Chapter 16. Oxidation-reduction is first encountered in Chapter 8, where oxidation states are examined, and is reconsidered briefly in Chapter 13 along with other reaction types. In the electrochemistry chapter (Chapter 19), the student uses the ion-electron method for balancing redox equations in connection with half-cell reactions.

Many years of teaching chemistry have provided me with convincing evidence that students gain a functional comprehension of a new idea more quickly if the concept is developed logically from first principles than if the topic is summarized in a superficial manner. I believe that I have attained the proper balance between telling students more than they need to know in an introductory course and presenting an idea or equation without an explanation of its origin. As the result, students can at least appreciate the way in which the idea or equation was developed, and not simply be told "it can be shown that. . . ."

As the title indicates, I have divided the book on a general basis into an initial development of chemical structure followed by a consideration of chemical dynamics. However, keeping the needs of laboratory programs in mind, stoichiometry, molar concentration, and reactions in solution are covered in Chapter 3, and the behavior of gases in Chapter 5. This organization permits a logical development of the subject matter, as well as the use of a wide variety of laboratory experiments during the first half of the semester.

The book employs several approaches not generally found in general chemistry texts. In Chapter 2 the foundation for discussing the mole concept and stoichiometry is developed on the basis of Dalton's atomic theory and Gay-Lussac's law of combining volumes, prior to considering the ideal gas law. Bond dissociation energies are examined in the coverage of covalent bonds (Chapter 9) rather than in the thermodynamics chapter. I have introduced the essential features of descriptive chemistry in Chapter 13, immediately following the discussions of bonding and physical properties. Here the types of chemical reactions, acids and bases, and reactivity trends are surveyed as preparation for the consideration of kinetics, equilibrium, and thermodynamics and for elaboration in later chapters.

The goal of the science of chemistry is to explain the behavior of matter and, on a more immediate level, to correlate descriptive chemistry. I have attempted to provide a theoretical background adequate to permit maximum correlation and minimum student distress in the coverage of descriptive chemistry. The detailed chemistry of the nonmetals (Chapters 22 and 23), metals (Chapter 25), and coordination complexes (Chapter 26) is delayed until a solid foundation has been established in the areas of kinetics, equilibrium, thermodynamics, and electrochemistry. The coverage of the behavior of metals and nonmetals is more extensive than can be handled in some courses, permitting the selection and presentation of the topics desired. Consistent with the effort to present a nonfragmented picture of chemistry, I have included carbon chemistry with that of the other nonmetals, while taking due note of the importance of the field of organic chemistry.

The book's scope is comprehensive, allowing the selection and presentation of material most suitable for the course and the students. Beyond the core of subject matter usually covered in two semesters, the text includes several topics that can be treated completely or partially on an optional basis: radiant energy and spectroscopy (Chapter 20), atmospheric chemistry (Chapter 21), geochemistry and metallurgy (Chapter 24), and nuclear chemistry (Chapter 27). These topics can also be presented at earlier points in the course if desired. The *Instructor's Manual* includes alternate topic sequences.

I have attempted to handle the use of SI units on a rational basis. To unify the ideas of energy changes and interconvertibility, enthalpy changes, ionization energies, electron affinities, bond energies, etc., are all expressed in units of joules. I use nanometers as the unit for bond length and ultraviolet and visible radiation wavelength. However, I have retained the traditional units of atmospheres, liters, and milliliters, since these units currently provide a more significant description of quantities than do pascals or cubic meters.

To assist student achievement in the course, all important mathematical operations and nonquantitative evaluations are illustrated and explained in step-by-step solutions of in-chapter examples. A summary, including key terms, appears at the end of each chapter, along with a checklist to determine chapter mastery. A complete glossary is located at the end of the book. Exercises at the ends of chapters are abundant and cover a range of difficulty. The appendices contain a review of mathematical operations, units, physical constants, and the more involved derivations of equations. Answers to selected exercises (those whose numbers appear in color in the exercise sets) are provided at the end of the book. The *Instructor's Manual* contains answers to the remaining exercises, and the *Solutions Manual* provides solutions to all the exercises.

A valuable aid to students seeking another perspective and additional practice with problem solving will be found in *Coping with Chemistry*, the study guide prepared by Carl Trindle of the University of Virginia for use with this volume.

An effort of this magnitude requires the assistance and cooperation of many people. My colleagues Gordon Kresheck, Roy Mason, Morley Russell, Joe Vaughn, and Malcolm Weiss graciously provided comments and sugges-

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I hope that you will find this text well-suited to your needs and that it will be of significant assistance to your students in their study of chemistry. Your comments regarding its features and your recommendations for its improvement will be most welcome.

Francis Marion Miller

**PART ONE
STRUCTURE**

Chapter 1	Introduction	1
1.1	The Roots of Chemical Science <i>The Greek Philosophers The Alchemists</i>	2
1.2	The Phlogiston Theory	4
1.3	The Discovery of Oxygen	5
1.4	Scientific Method	6
1.5	Scientific Measurements <i>Length Area and Volume Mass Density Temperature</i>	8
1.6	Significant Figures	14
1.7	Unit Factors in Calculations	18
Chapter 2	Matter	24
2.1	Law of Constant Composition	25
2.2	Mixtures and Pure Substances <i>Separation of Mixtures</i>	25
2.3	Compounds and Elements	28
2.4	Law of Multiple Proportions	29
2.5	The Atomic Theory	30
2.6	Symbols for the Elements	30
2.7	Atomic Masses (Weights) <i>Law of Combining Volumes of Gases Avogadro's Hypothesis Molecular Masses</i>	32
2.8	Molecular Formulas <i>Elemental Analysis</i>	36
2.9	Names of Compounds	39
Chapter 3	Chemical Equations and Stoichiometry	43
3.1	Chemical Equations	43
3.2	Stoichiometry	44
3.3	The Mole	45
3.4	Stoichiometric Calculations <i>Mole Relationships Relationships Based on Equations</i>	46
3.5	Reactions in Solution <i>Concentration Solution Stoichiometry Titrations</i>	55
Chapter 4	Energy	64
4.1	Mechanical Energy <i>Kinetic and Potential Energy State Functions</i>	64
4.2	Heat	66

CONTENTS

4.3	Heat, Work, and Energy Transfer	68
	<i>Temperature</i>	
4.4	The First Law of Thermodynamics	71
4.5	Calorimetry	72
4.6	Enthalpy	73
	<i>Enthalpy and States of Matter Standard Enthalpy Change Hess's Law Standard Enthalpy of Formation</i>	
4.7	Radiant Energy	82
	<i>The Wave Nature of Radiant Energy Diffraction of Radiation The Particle Nature of Radiant Energy</i>	
4.8	Electrical Energy	90
4.9	Energy Resources and Utilization	90
Chapter 5	Gases	97
5.1	The Bulk Properties of Gases	97
5.2	Atmospheric Pressure	98
5.3	The Pressure-Volume Relationship of Gases	100
5.4	The Temperature-Volume Relationship of Gases	102
5.5	Kinetic Energy of Gas Molecules	105
5.6	The Ideal Gas Law	106
	<i>Molar Volume Gas Density Molar Masses Gas Stoichiometry Partial Pressures</i>	
5.7	The Kinetic-Molecular Theory	116
	<i>Molecular Velocities Mean Free Path Effusion of Gases</i>	
5.8	Real Gases	121
Chapter 6	Atomic Structure	127
6.1	The Electron	128
6.2	Protons and Neutrons	131
6.3	Radioactivity	132
6.4	The Nuclear Atom	132
6.5	X Rays and Atomic Number	133
6.6	The Mass Spectrometer	134
6.7	Electron Structure of the Atom	137
	<i>Emission Spectra The Hydrogen Spectrum</i>	
6.8	The Bohr Model for the Hydrogen Atom	140
6.9	Matter Waves	145
6.10	The Uncertainty Principle	147
6.11	Wave Mechanics	148
6.12	The Quantum Mechanical Hydrogen Atom	149
6.13	Quantum Numbers	151
6.14	Orbital Energies	155
6.15	The Spin Quantum Number	156

6.16	Multielectron Atoms	157
6.17	Electron Configurations of the Elements	158
6.18	Scientific Models	162
Chapter 7	Periodic Relationships of the Elements	167
7.1	Mendeleev's Periodic Table	167
7.2	The Periodic Table Today	171
7.3	The Periodic Variation of Properties	173
7.4	Atomic Size	174
7.5	Ionization Energy	178
7.6	Electron Affinity	183
7.7	Electronegativity	184
7.8	Metals and Nonmetals	186
7.9	The Position of Hydrogen in the Periodic Table	187
Chapter 8	The Chemical Bond	191
8.1	The Ionic Bond	191
8.2	The Covalent Bond <i>Lewis Structures—The Octet Rule Inadequacies of the Octet Rule and Lewis Structures Resonance</i>	195
8.3	Molecular Geometry—Electron-Pair Repulsion	202
8.4	Oxidation-Reduction <i>Oxidation State Oxidizing Agents and Reducing Agents Balancing Oxidation-Reduction Equations</i>	207
8.5	Nomenclature <i>Binary Compounds Polyatomic Anions Acids</i>	212
Chapter 9	Theories of the Covalent Bond	220
9.1	The Valence Bond Model <i>Bond Polarity Hybrid Orbitals Multiple Bonds Resonance</i>	220
9.2	The Molecular Orbital Model <i>First Period Homonuclear Diatomic Molecules Second Period Homonuclear Diatomic Molecules Heteronuclear Diatomic Molecules</i>	236
9.3	The Metallic Bond	246
9.4	Average Bond Energies	249
Chapter 10	Molecular Structure and the States of Matter: Liquids	255
10.1	Gases, Liquids, and Solids	255
10.2	Polarities of Molecules <i>Polar Covalent Molecules Hydrogen Bonds London Forces</i>	256
10.3	Liquids	265

Intermolecular Attractions in Liquids | Vapor Pressure | Le Chatelier's Principle | Enthalpy of Vaporization | Freezing of Liquids

10.4	Phase Changes <i>Phase Diagrams</i>	279
------	----------------------------------------	-----

Chapter 11 The Solid State 289

11.1	Crystal Structure <i>Crystal Systems Close-Packed Structures Ionic Crystal Structures Solid Covalent Compounds Network Covalent Crystals Properties of Crystalline Solids</i>	289
11.2	Liquid Crystals	304
11.3	Crystal Lattice Defects	305

Chapter 12 Properties of Mixtures: Solutions and Colloids 310

12.1	Gaseous Solutions <i>Solutions of Gases in Liquids</i>	310
12.2	Solutions of Solids in Liquids <i>The Solution Process Enthalpy of Solution Solubility Structure and Solubility</i>	313
12.3	Expressions of Concentration <i>Mass Percent Parts per Million and Parts per Billion Mole Fraction Molality Molarity</i>	322
12.4	Solution Stoichiometry	329
12.5	Properties of Solutions of Solids in Liquids <i>Vapor Pressure Boiling Point Elevation Freezing Point Depression Osmotic Pressure Molar Mass Determination Solutions of Ionic Solutes in Liquids</i>	330
12.6	Solutions of Liquids in Liquids <i>Vapor Pressure Distillation</i>	340
12.7	Solid Solutions	343
12.8	Colloidal Suspensions	344

PART TWO DYNAMICS

Chapter 13 Structure and Chemical Reactivity 355

13.1	Direct Combination of Elements <i>The Formation of Ionic Compounds The Formation of Covalent Compounds Decomposition Reactions</i>	355
13.2	Ion-Combining Reactions	360
13.3	Oxidation-Reduction Reactions	362

13.4	Acids and Bases	363
	<i>Arrhenius Definition of Acids and Bases Brønsted-Lowry Definition of Acids and Bases Lewis Definition of Acids and Bases Strengths of Acids and Bases Aqueous Solutions of Salts Oxides Amphoterism</i>	
13.5	Reactivity Trends	379
	<i>Hydrides Chlorides</i>	
Chapter 14	Chemical Kinetics	386
14.1	Rates of Reactions	387
14.2	Collision Theory	390
14.3	Concentration Effects	392
	<i>Rate Equations Integrated Rate Equations Half-Life</i>	
14.4	Temperature Effects	405
14.5	Transition State Theory	408
14.6	Reaction Mechanism	410
14.7	Catalysis	417
Chapter 15	Chemical Equilibrium	428
15.1	Concentration Effects in Equilibria	428
	<i>Equilibrium Constant Expressions Kinetics and Equilibrium Equilibrium Constants</i>	
15.2	Equilibrium Calculations	435
15.3	Applications of Le Chatelier's Principle	441
	<i>Effect of Concentration Changes Effect of Pressure Changes Effect of Temperature Changes Effect of Catalysts The Haber Process</i>	
15.4	Heterogeneous Equilibria	451
Chapter 16	Ionic Equilibria: Aqueous Acids and Bases	457
16.1	Dissociation Constant Expressions	457
16.2	The Dissociation of Water	460
16.3	The pH Scale	462
	<i>pOH and pK_w pK_a</i>	
16.4	Polyprotic Acids	466
16.5	Weak Bases	467
16.6	Conjugate Acid-Base Relationships	469
16.7	Aqueous Solutions of Salts	470
16.8	Common Ion Effect	473
16.9	Buffers	476
16.10	Acid-Base Titrations	481
16.11	Indicators	486
16.12	Summary of Acid-Base Equilibria	487

Chapter 17	Ionic Equilibria: Solubility and Complex Ions	496
17.1	Solubility Equilibria <i>Solubility Product Constants K_{sp} and Precipitation Common Ions and Solubility</i>	496
17.2	Complex Ion Equilibria	505
17.3	Qualitative Analysis	509
Chapter 18	Chemical Thermodynamics	515
18.1	The First Law Revisited	515
18.2	Reversible and Irreversible Processes	517
18.3	Exothermic and Endothermic Processes	519
18.4	Spontaneous Processes	519
18.5	Entropy <i>Entropy and Reversibility Mathematical Definition of Entropy</i>	520
18.6	Free Energy	528
18.7	Free Energy and Equilibrium <i>Free Energy Change under Nonstandard Conditions</i>	532
18.8	Experimental Determination of Thermodynamic Functions	538
18.9	The Third Law of Thermodynamics	539
18.10	Standard Free Energies of Formation	541
18.11	The Second Law and Human Activity	543
Chapter 19	The Interconversion of Chemical and Electrical Energy	549
19.1	Voltaic Cells	550
19.2	Balancing Oxidation-Reduction Equations	554
19.3	Cell Potentials	558
19.4	Electrode Potentials	561
19.5	Free Energy Changes in Voltaic Cells	568
19.6	Cell Potentials and Equilibrium Constants	569
19.7	Concentration Effects in Voltaic Cells <i>Measurement of Ionic Concentrations</i>	570
19.8	Commercial Voltaic Cells <i>Fuel Cells</i>	576
19.9	Electrolysis <i>Quantitative Electrolysis Commercial Uses of Electrolysis</i>	581
Chapter 20	The Interactions between Radiant Energy and Matter	595
20.1	The Absorption of Radiant Energy	597
20.2	Absorption Spectra <i>Rotational Spectra Vibrational Spectra Electronic Spectra</i>	598

20.3	Fluorescence and Phosphorescence	607
20.4	Photochemical Reactions	610
	<i>Photography Photosynthesis Photoelectrolysis Other Photochemical Reactions</i>	
Chapter 21	Atmospheric Chemistry	618
21.1	Atmospheric Composition	618
21.2	Atmospheric Density	620
21.3	Atmospheric Temperatures	622
21.4	Atmospheric Ionization	625
21.5	Atmospheric Pollution	626
	<i>Stratospheric Pollution Tropospheric Pollution</i>	
21.6	Control of Atmospheric Pollution	635
Chapter 22	Chemistry of the Nonmetals. I	640
22.1	Hydrogen	640
	<i>Preparation Reactivity</i>	
22.2	Group 8A, The Noble Gases	643
	<i>Occurrence Reactivity</i>	
22.3	Group 7A, The Halogens	646
	<i>Preparation Reactivity Metal Halides, MX_n Hydrogen Halides, HX Nonmetal Halides, AX_n Interhalogen Compounds, XX'_n Halogen Oxides, XO_n Oxohalogen Acids, HXO_n</i>	
22.4	Group 6A, The Chalcogens	657
	<i>Occurrence and Preparation Reactivity Metal Chalcogenides, MA_n Hydrogen Chalcogenides, H_2A_n Chalcogen Oxides, AO_2 and AO_3 Oxochalcogen Acids, H_2AO_3 and H_2AO_4</i>	
Chapter 23	Chemistry of the Nonmetals. II	672
23.1	Group 5A, The Nitrogen Family	672
	<i>Occurrence and Preparation Structure and Reactivity Nitrides and Phosphides, M_3Q Hydrides, QH_3 Halides, QX_3 and QX_5 Oxides Oxoacids</i>	
23.2	Group 4A, Carbon and Silicon	687
	<i>Occurrence, Preparation and Reactivity Carbides and Silicides Oxides and Oxoacids Sulfur, Halogen, and Nitrogen Compounds Hydrides</i>	
28.3	Group 3A, Boron	707
	<i>Borides Halides Boric Acid Hydrides</i>	
Chapter 24	Geochemistry and Metallurgy	714
24.1	Geochemistry	714
	<i>Minerals Rocks</i>	

24.2	Metallurgy	724
	<i>Preliminary Treatment of Ores Reduction of Ores Refining Metals</i>	
24.3	Corrosion	736
Chapter 25	Chemistry of the Metals	742
25.1	Physical Properties	743
25.2	Properties of Cations	748
25.3	Representative Metals	751
	<i>Group 1A Metals, the Alkali Metals Group 2A Metals, the Alkaline Earth Metals Group 3A Metals Group 4A Metals</i>	
25.4	Transition Metals	760
25.5	Inner Transition Metals	763
25.6	Important Transition Metals	764
	<i>Chromium Manganese Iron The Coinage Metals—Copper, Silver and Gold Zinc, Cadmium and Mercury</i>	
Chapter 26	Coordination Complexes	773
26.1	The Nature of Coordination Complexes	773
	<i>Ligands Nomenclature Coordination Number and Geometry Isomerism in Coordination Complexes Color of Coordination Complexes</i>	
26.2	Bonding in Coordination Complexes	781
	<i>Valence Bond Theory Crystal Field Theory Ligand Field Theory</i>	
26.3	Reactions of Coordination Complexes	790
Chapter 27	Nuclear Chemistry	797
27.1	The Nature of Radioactive Radiation	797
27.2	Detection of Radioactive Emissions	798
	<i>Radioactive Tracers</i>	
27.3	Natural Radioactive Decay Series	801
27.4	Kinetics of Radioactive Disintegration	804
	<i>Dating</i>	
27.5	Nuclear Structure and Stability	808
	<i>Neutron/Proton Ratio Binding Energies Nuclear Structure Nuclear Emissions</i>	
27.6	Nuclear Transformations	815
	<i>Particle Accelerators Synthetic Elements</i>	
27.7	Nuclear Fission	820
	<i>The Fission Reaction Nuclear Reactors</i>	
27.8	Nuclear Fusion	825
27.9	Biological Effects of Radiation	826