Chemical Principles

ZUMDAHL · DECOSTE

Periodic Table of the Elements

Noble gases ↓ 18 8A	2 He	10 Ne	18 Ar	36 Kr	54 Xe	86 Rn	118 Uuo	71 Lu
Nob gase Halogens 18 8A	→ 1 ₹	6 Ц	17 CI	35 Br	53 I	85 At	117 Uus	70 Yb
	16 6A	∞ 0	16 S	34 Se	52 Te	84 Po	116 Lv	69 Tm
	15 5A	۲ N	15 P	33 AS	51 Sb	83 Bi	115 Uup	68 Er
	14 4A	C v	14 Si	32 Ge	50 Sn	82 Pb	114 Fl	67 Ho
	13 3A	5 B	13 Al	31 Ga	49 In	81 TI	113 Uut	66 Dy
	·		12	30 Zn	48 Cd	80 Hg	112 Cn	65 Tb
			Ξ	29 Cu	47 Ag	79 Au	111 Rg	64 Gd
			10	28 Ni	46 Pd	78 Pt	110 Ds	63 Eu
			•	27 Co	45 Rh	77 Ir	109 Mt	62 Sm
			8 n metals	26 Fe	44 Ru	76 Os	108 Hs	61 Pm
			7 8 Transition metals	25 Mn	43 Tc	75 Re	107 Bh	60 Nd
			້	24 Cr	42 Mo	74 W	106 Sg	59 Pr
			w	23 V	41 Nb	73 Ta	105 Db	58 Ce
			4	22 Ti	40 Zr	72 Hf	104 Rf	nides
als			~	21 Sc	39 Y	57 La*	$^{89}{ m Ac}^{\dagger}$	*Lanthanides
Alkaline earth metals	5 ⊳ ←	4 Be	12 Mg	20 Ca	38 Sr	56 Ba	88 Ra	
1 60 1	1 H	3 Li	11 Na	\mathbf{K}	37 Rb	55 Cs	87 Fr	

Alkali metals

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103 Lr

102 No

101 Md

100 Fm

99 Es

98 Cf

97 Bk

⁹⁶ Cm

95 Am

94 Pu

93 Np

92 U

91 Pa

90 Th

[†]Actinides

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
•		0	۲)) آر		(0			:		
Actinium	AC	89	[77/]3	Germanium	e D	32	/2.59	Potassium	¥	T9	39.T0
Aluminum	A	13	26.98	Gold	Au	79	197.0	Praseodymium	Pr	59	140.9
Americium	Am	95	[243]	Hafnium	Hf	72	178.5	Promethium	Pm	61	[145]
Antimony	Sb	51	121.8	Hassium	Hs	108	[265]	Protactinium	Ра	91	[231]
Argon	Ar	18	39.95	Helium	He	2	4.003	Radium	Ra	88	226
Arsenic	As	33	74.92	Holmium	Ч	67	164.9	Radon	Rn	86	[222]
Astatine	At	85	[210]	Hydrogen	I	Ч	1.008	Rhenium	Re	75	186.2
Barium	Ba	56	137.3	Indium	Ц	49	114.8	Rhodium	Rh	45	102.9
Berkelium	Bk	97	[247]	lodine	_	53	126.9	Roentgenium	Rg	111	[272]
Beryllium	Be	4	9.012	Iridium	느	77	192.2	Rubidium	Rb	37	85.47
Bismuth	Bi	83	209.0	Iron	Fe	26	55.85	Ruthenium	Ru	44	101.1
Bohrium	Bh	107	[264]	Krypton	Kr	36	83.80	Rutherfordium	Rf	104	[261]
Boron	В	5	10.81	Lanthanum	La	57	138.9	Samarium	Sm	62	150.4
Bromine	Br	35	79.90	Lawrencium	Lr	103	[260]	Scandium	Sc	21	44.96
Cadmium	Cd	48	112.4	Lead	Pb	82	207.2	Seaborgium	Sg	106	[263]
Calcium	Ca	20	40.08	Livermorium	۲۷	116	[293]	Selenium	Se	34	78.96
Californium	Cf	98	[251]	Lithium	:1	£	6.9419	Silicon	Si	14	28.09
Carbon	U	9	12.01	Lutetium	Lu	71	175.0	Silver	Ag	47	107.9
Cerium	Ce	58	140.1	Magnesium	Mg	12	24.31	Sodium	Na	11	22.99
Cesium	Cs	55	132.90	Manganese	Mn	25	54.94	Strontium	Sr	38	87.62
Chlorine	Ū	17	35.45	Meitnerium	Mt	109	[268]	Sulfur	S	16	32.07
Chromium	C	24	52.00	Mendelevium	pW	101	[258]	Tantalum	Та	73	180.9
Cobalt	CO	27	58.93	Mercury	Hg	80	200.6	Technetium	Tc	43	[98]
Copernicium	Cu	112	[285]	Molybdenum	Mo	42	95.94	Tellurium	Те	52	127.6
Copper	Cu	29	63.55	Neodymium	PN	60	144.2	Terbium	Tb	65	158.9
Curium	Cm	96	[247]	Neon	Ne	10	20.18	Thallium	Π	81	204.4
Darmstadtium	Ds	110	[271]	Neptunium	Np	93	[237]	Thorium	ТҺ	90	232.0
Dubnium	Db	105	[262]	Nickel	ïZ	28	58.69	Thulium	Tm	69	168.9
Dysprosium	Dy	66	162.5	Niobium	ЧN	41	92.91	Tin	Sn	50	118.7
Einsteinium	Es	66	[252]	Nitrogen	z	7	14.01	Titanium	Ξ	22	47.88
Erbium	Ц	68	167.3	Nobelium	No	102	[259]	Tungsten	N	74	183.9
Europium	Eu	63	152.0	Osmium	Os	76	190.2	Uranium	D	92	238.0
Fermium	Fm	100	[257]	Oxygen	0	∞	16.00	Vanadium	>	23	50.94
Flerovium	Ē	114	[289]	Palladium	Pd	46	106.4	Xenon	Xe	54	131.3
Fluorine	ш	6	19.00	Phosphorus	٩	15	30.97	Ytterbium	γb	70	173.0
Francium	노	87	[223]	Platinum	Pt	78	195.1	Yttrium	≻	39	88.91
Gadolinium	Gd	64	157.3	Plutonium	Pu	94	[244]	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Polonium	Ро	84	[209]	Zirconium	Zr	40	91.22
- - -											

Table of Atomic Masses*

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Steven S. Zumdahl

University of Illinois

Donald J. DeCoste

8TH EDITION

University of Illinois



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Contents

Learning to Think Like a Chemist xv About the Authors xxi

1 Chemists and Chemistry

- **1.1** Thinking Like a Chemist 3
- A Real-World Chemistry Problem 3
 Chemistry Explorers Alison Williams's Focus: The Structure of Nucleic Acids 4
 Chemistry Explorers Stephanie Burns: Chemist, Executive 5

1

- 1.3 The Scientific Method 7Chemical Insights Critical Units! 9
- 1.4 Industrial Chemistry 10 Chemical Insights A Note-able Achievement 11
- 1.5 Polyvinyl Chloride (PVC): Real-World Chemistry 12 Key Terms 14 For Review 14

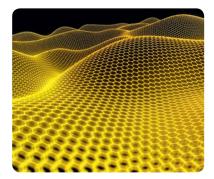
2 Atoms, Molecules, and Ions 15

- 2.1 The Early History of Chemistry 16
- 2.2 Fundamental Chemical Laws 17
- 2.3 Dalton's Atomic Theory 19
- 2.4 Cannizzaro's Interpretation 21 Chemical Insights Seeing Atoms 22
- 2.5 Early Experiments to Characterize the Atom 24Chemical Insights Marie Curie: Founder of Radioactivity 26
- 2.6 The Modern View of Atomic Structure: An Introduction 29
- 2.7 Molecules and Ions 30
- 2.8 An Introduction to the Periodic Table 34
- **2.9** Naming Simple Compounds 35

Chemical Insights Hassium Fits Right In 36

Chemical Insights Playing Tag 42

Key Terms 45 For Review 45 Discussion Questions and Exercises 46



3 Stoichiometry 47

3.1	Atomic Masses 48
	Chemical Insights "Whair" Do You Live? 49
3.2	The Mole 51
3.3	Molar Mass 53
	Chemical InsightsMeasuring the Masses of Large Molecules or Making Elephants Fly55
3.4	Conceptual Problem Solving 55
3.5	Percent Composition of Compounds 57
3.6	Determining the Formula of a Compound 59
3.7	Chemical Equations 65
3.8	Balancing Chemical Equations 67
3.9	Stoichiometric Calculations: Amounts of Reactants and Products
3.10	Calculations Involving a Limiting Reactant 71
3.11	Solving a Complex Problem 78
	Key Terms 82



4 Types of Chemical Reactions and Solution Stoichiometry 84

69

4.1 Water, the Common Solvent 85

For Review 82

4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes 87

Discussion Questions and Exercises 83

- 4.3 The Composition of Solutions 90
- **4.4** Types of Chemical Reactions 96
- 4.5 Precipitation Reactions 96
- 4.6 Describing Reactions in Solution 101
- 4.7 Selective Precipitation 102
 Chemical Insights Chemical Analysis of Cockroaches 103
- 4.8 Stoichiometry of Precipitation Reactions 104
- 4.9 Acid–Base Reactions 107
- 4.10 Oxidation–Reduction Reactions 113
- 4.11 Balancing Oxidation–Reduction Equations 117
- 4.12 Simple Oxidation-Reduction Titrations 124

Key Terms 126 For Review 126 Discussion Questions and Exercises 127



5 Gases 128

5.1	Early Experiments 129
5.2	The Gas Laws of Boyle, Charles, and Avogadro 130
5.3	The Ideal Gas Law 133
5.4	Gas Stoichiometry 137
5.5	Dalton's Law of Partial Pressures 139
	Chemical Insights The Chemistry of Air Bags 141
5.6	The Kinetic Molecular Theory of Gases 143
	Chemical Insights Separating Gases 144
5.7	Effusion and Diffusion 151
5.8	Collisions of Gas Particles with the Container Walls 154
5.9	Intermolecular Collisions 156
5.10	Real Gases 159
	Chemistry Explorers Kenneth Suslick Practices Sound Chemistry
5.11	Characteristics of Several Real Gases 162
5.12	Chemistry in the Atmosphere 162
	Chemical Insights The Importance of Oxygen 165
	Key Terms 167
	For Review 167
	Discussion Questions and Exercises 168

6 Chemical Equilibrium 169

- 6.1 The Equilibrium Condition 171
 6.2 The Equilibrium Constant 173
 6.3 Equilibrium Expressions Involving Pressures
 6.4 The Concept of Activity 178
 6.5 Heterogeneous Equilibria 179
 6.6 An Involving States Equilibria 179
- **6.6** Applications of the Equilibrium Constant 180
- 6.7 Solving Equilibrium Problems 184
- 6.8 Le Châtelier's Principle 188
- 6.9 Equilibria Involving Real Gases 194 Key Terms 195 For Review 195 Discussion Questions and Exercises 196



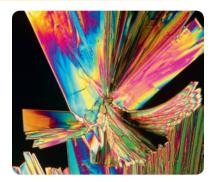


161

176

7 Acids and Bases 197

- 7.1 The Nature of Acids and Bases 198
- 7.2 Acid Strength 200
- 7.3 The pH Scale 204
- 7.4 Calculating the pH of Strong Acid Solutions 205
- 7.5 Calculating the pH of Weak Acid Solutions 206
- 7.6 Bases 212 Chemical Insights Amines 216
- 7.7 Polyprotic Acids 217
- 7.8 Acid–Base Properties of Salts 225
- **7.9** Acid Solutions in Which Water Contributes to the H⁺ Concentration 232
- **7.10** Strong Acid Solutions in Which Water Contributes to the H⁺ Concentration 237
- 7.11 Strategy for Solving Acid–Base Problems: A Summary 237 Key Terms 238 For Review 238 Discussion Questions and Exercises 240a



8 Applications of Aqueous Equilibria 241

- 8.1 Solutions of Acids or Bases Containing a Common Ion 242
- 8.2 Buffered Solutions 244
- 8.3 Exact Treatment of Buffered Solutions 252
- 8.4 Buffer Capacity 254
- 8.5 Titrations and pH Curves 257
- 8.6 Acid–Base Indicators 270
- 8.7 Titration of Polyprotic Acids 275
- 8.8 Solubility Equilibria and the Solubility Product 278
- 8.9 Precipitation and Qualitative Analysis 286
 Chemistry Explorers Yi Lu Researches the Role of Metals in Biological Systems 290
- 8.10 Complex Ion Equilibria 291

Key Terms297For Review297Discussion Questions and Exercises298



9 Energy, Enthalpy, and Thermochemistry 299

9.1	The Nature of Energy 300
	Chemical Insights Bees Are Hot 303
9.2	Enthalpy 306
9.3	Thermodynamics of Ideal Gases 307
9.4	Calorimetry 314
9.5	Hess's Law 320
	Chemical Insights Firewalking: Magic or Science? 322
9.6	Standard Enthalpies of Formation 323
9.7	Present Sources of Energy 329
	Chemical Insights Fracking: What Is It? 331
	Chemical Insights Hiding Carbon Dioxide 333
9.8	New Energy Sources 335
	Chemical Insights Geoengineering 336
	Chemical Insights Farming the Wind 338
	Key Terms 342
	For Review 342



10 Spontaneity, Entropy, and Free Energy 344

10.1	Spontaneous	Processes	345
------	-------------	-----------	-----

- 10.2 The Isothermal Expansion and Compression of an Ideal Gas 353
- 10.3 The Definition of Entropy 359 Chemical Insights Entropy: An Organizing Force? 361

Discussion Questions and Exercises 343

- **10.4** Entropy and Physical Changes 362
- 10.5 Entropy and the Second Law of Thermodynamics 364
- **10.6** The Effect of Temperature on Spontaneity 365
- 10.7 Free Energy 368
- **10.8** Entropy Changes in Chemical Reactions 371
- 10.9 Free Energy and Chemical Reactions 374
- 10.10 The Dependence of Free Energy on Pressure 379
- **10.11** Free Energy and Equilibrium 382
- 10.12 Free Energy and Work 388
- 10.13 Reversible and Irreversible Processes: A Summary 390
- **10.14** Adiabatic Processes 391

Key Terms 395 For Review 395 Discussion Questions and Exercises 396



11 Electrochemistry 397

- **11.1** Galvanic Cells 398
- 11.2 Standard Reduction Potentials 401
- 11.3 Cell Potential, Electrical Work, and Free Energy 406
- 11.4 Dependence of the Cell Potential on Concentration 409 Chemical Insights Electrochemical Window Shades 416
- **11.5** Batteries
 417

 Chemical Insights Fuel Cells—Portable Energy
 420
- **11.6** Corrosion 421 Chemical Insights Refurbishing the Lady 422
- 11.7
 Electrolysis
 425

 Chemical Insights
 The Chemistry of Sunken Treasure
 428
- **11.8** Commercial Electrolytic Processes 429

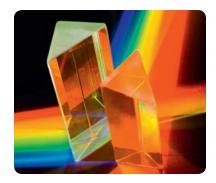
Key Terms 434 For Review 434 Discussion Questions and Exercises 435



12 Quantum Mechanics and Atomic Theory 436

- 12.1 Electromagnetic Radiation 437 Chemical Insights New-Wave Sunscreens 439
- **12.2** The Nature of Matter 440
- 12.3 The Atomic Spectrum of Hydrogen 445
- 12.4 The Bohr Model 446 Chemical Insights Fireworks 450
- 12.5 The Quantum Mechanical Description of the Atom 452 Chemical Insights Electrons as Waves 454
- **12.6** The Particle in a Box 455
- 12.7 The Wave Equation for the Hydrogen Atom 461 Chemical Insights 0.035 Femtometer Is a Big Deal 462
- 12.8 The Physical Meaning of a Wave Function 464
- 12.9 The Characteristics of Hydrogen Orbitals 465
- **12.10** Electron Spin and the Pauli Principle 470
- 12.11 Polyelectronic Atoms 470
- **12.12** The History of the Periodic Table 472
- **12.13** The Aufbau Principle and the Periodic Table 475 **Chemical Insights** The Chemistry of Copernicium 476
- **12.14** Further Development of the Polyelectronic Model 481
- 12.15
 Periodic Trends in Atomic Properties
 484

 Chemical Insights
 Why Is Mercury a Liquid?
 488
- 12.16 The Properties of a Group: The Alkali Metals 492
 Chemical Insights Lithium: Behavior Medicine 494
 Key Terms 496
 For Review 496
 Discussion Questions and Exercises 497



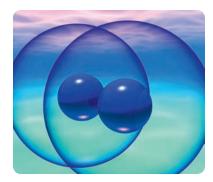
13 Bonding: General Concepts 498

13.1	Types of Chemical Bonds 499
	Chemical Insights No Lead Pencils 502
13.2	Electronegativity 503
13.3	Bond Polarity and Dipole Moments 505
13.4	Ions: Electron Configurations and Sizes 509
13.5	Formation of Binary Ionic Compounds 512
13.6	Partial Ionic Character of Covalent Bonds 516
13.7	The Covalent Chemical Bond: A Model 517
13.8	Covalent Bond Energies and Chemical Reactions 521
13.9	The Localized Electron Bonding Model 524
13.10	Lewis Structures 524
13.11	Resonance 529
13.12	Exceptions to the Octet Rule 530
13.13	Molecular Structure: The VSEPR Model 540
	Chemical Insights Chemical Structure and Communication: Semiochemicals 548
	Chemical Insights Smelling and Tasting Electronically 550
	Key Terms 553
	For Review 553
	Discussion Questions and Exercises 554



14 Covalent Bonding: Orbitals 555

- 14.1 Hybridization and the Localized Electron Model 556
- 14.2 The Molecular Orbital Model 568
- 14.3 Bonding in Homonuclear Diatomic Molecules 572
- 14.4 Bonding in Heteronuclear Diatomic Molecules 578
- 14.5 Combining the Localized Electron and Molecular Orbital Models 579Chemical Insights The Always Interesting NO 581
- 14.6 Orbitals: Human Inventions 582
- 14.7 Molecular Spectroscopy: An Introduction 584
- 14.8 Electronic Spectroscopy 585
- 14.9 Vibrational Spectroscopy 587
- 14.10 Rotational Spectroscopy 590
- 14.11 Nuclear Magnetic Resonance Spectroscopy 593
 Chemical Insights NMR and Oenology 596
 Key Terms 598
 For Review 598
 Discussion Questions and Exercises 599



15 Chemical Kinetics 600

15.1 **Reaction Rates** 601 **Chemical Insights** Femtochemistry 604 15.2 Rate Laws: An Introduction 605 15.3 Determining the Form of the Rate Law 607 15.4 The Integrated Rate Law 611 15.5 Rate Laws: A Summary 620 15.6 Reaction Mechanisms 622 Chemical Insights Ultracold Reactions 623 Chemical Insights Seeing Reaction Mechanisms 626 15.7 The Steady-State Approximation 628 15.8 A Model for Chemical Kinetics 631 **15.9** Catalysis 636 Chemical Insights TiO₂—One of Nature's Most Versatile Materials 637 **Chemical Insights** Enzymes: Nature's Catalysts 640 Chemical Insights Hot, New Enzymes 643 Key Terms 645 For Review 645 Discussion Questions and Exercises 647



16 Liquids and Solids 648

16.1 Intermolecular Forces 650 16.2 The Liquid State 652 **Chemical Insights** Getting a Grip 653 Chemical Insights Smart Fluids 655 **16.3** An Introduction to Structures and Types of Solids Chemical Insights Conch Clues 658 Chemistry Explorers Dorothy Crowfoot Hodgkin: Pioneering Crystallographer 660 **16.4** Structure and Bonding in Metals 662 Chemical Insights Closest Packing of M & Ms 664

Chemical Insights Seething Surfaces 665

- 16.5 Carbon and Silicon: Network Atomic Solids 670
 Chemical Insights Graphene—Miracle Substance? 672
 Chemical Insights Superconductivity 674
 Chemical Insights Gorilla Glass 676
 Chemical Insights Gallium Arsenide Lasers 678
- 16.6 Molecular Solids 680
- 16.7 Ionic Solids 681
- 16.8 Structures of Actual Ionic Solids 685
- 16.9 Lattice Defects 686
- 16.10 Vapor Pressure and Changes of State 687



656

16.11 Phase Diagrams 694
Chemical Insights Making Diamonds at Low Pressures: Fooling Mother Nature 696
16.12 Nanotechnology 699
Chemical Insights Smaller Can Be Better 700
Chemical Insights Nanogenerators: Power from Motion 701
Key Terms 703
For Review 703
Discussion Questions and Exercises 704a

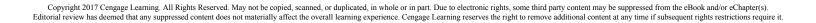
17 Properties of Solutions 705

17.1	Solution Composition 706
17.2	The Thermodynamics of Solution Formation 707
	Chemical Insights Miracle Solvents 710
17.3	Factors Affecting Solubility 711
	Chemical Insights Ionic Liquids? 715
	Chemical Insights The Lake Nyos Tragedy 716
17.4	The Vapor Pressures of Solutions 716
17.5	Boiling-Point Elevation and Freezing-Point Depression 721
17.6	Osmotic Pressure 724
17.7	Colligative Properties of Electrolyte Solutions 728
17.8	Colloids 730
	Chemical Insights Organisms and Ice Formation 731
	Key Terms 732
	For Review 732
	Discussion Questions and Exercises 733

18 The Representative Elements 734

- **18.1** A Survey of the Representative Elements 735
- 18.2 The Group 1A Metals 739
- 18.3 The Chemistry of Hydrogen 741
- **18.4** The Group 2A Elements 743
- 18.5 The Group 3A Elements 745
- **18.6** The Group 4A Elements 747
 - Chemical Insights Beethoven: Hair Is the Story 748
- 18.7 The Group 5A Elements 749
- 18.8 The Chemistry of Nitrogen 750
 Chemical Insights An Explosive Discovery 753
 Chemical Insights Nitrous Oxide: Laughing Gas That Propels Whipped Cream and Cars 757
- 18.9 The Chemistry of Phosphorus 758
- 18.10 The Group 6A Elements 760







18.11 The Chemistry of Oxygen 761
18.12 The Chemistry of Sulfur 763
18.13 The Group 7A Elements 765
18.14 The Group 8A Elements 769

Chemical Insights Automatic Sunglasses 770
Key Terms 772
For Review 772
Exercises 774

19 Transition Metals and Coordination Chemistry 775

19.1 The Transition Metals: A Survey 776 Chemical Insights The Lanthanides: Critical Elements 777 **19.2** The First-Row Transition Metals 782 Chemical Insights Titanium Makes Great Bicycles 784 **19.3** Coordination Compounds 788 **19.4** Isomerism 792 **Chemical Insights** Alfred Werner: Coordination Chemist 795 Chemical Insights The Importance of Being cis 796 Chemical Insights Chirality: Why Is It Important? 798 19.5 Bonding in Complex Ions: The Localized Electron Model 799 The Crystal Field Model 800 19.6 The Molecular Orbital Model 19.7 806 Chemical Insights Transition Metal Ions Lend Color to Gems 808 19.8 The Biological Importance of Coordination Complexes 809

Key Terms 813 For Review 813 Discussion Questions and Exercises 814

20 The Nucleus: A Chemist's View 815

- 20.1 Nuclear Stability and Radioactive Decay 816 Chemical Insights Does Antimatter Matter? 820 **20.2** The Kinetics of Radioactive Decay 820 Chemical Insights Stellar Nucleosynthesis 822 20.3 Nuclear Transformations 824 20.4 Detection and Uses of Radioactivity 826 20.5 Thermodynamic Stability of the Nucleus 830
- 20.6 Nuclear Fission and Nuclear Fusion 833 Chemical Insights Nuclear Physics: An Introduction 837
- 20.7 Effects of Radiation 838 Key Terms 840
 - For Review 840 Exercises 840a





21 Organic and Biochemical Molecules 841

21.1	Alkanes: Saturated Hydrocarbons 842 Chemical Insights Chemistry in the Garden 843
21.2	Alkenes and Alkynes 851
21.3	Aromatic Hydrocarbons 853
21.4	Hydrocarbon Derivatives 855
21.5	Polymers 862
	Chemical Insights Wallace Hume Carothers 868
	Chemical Insights Heal Thyself 870
21.6	Natural Polymers 871
	Chemical Insights Tanning in the Shade 878
	Key Terms 887
	For Review 887
	Exercises 888



Appendix 1 Mathematical Procedures A1

- A1.1 Exponential Notation A1
- A1.2 Logarithms A3
- A1.3 Graphing Functions A4
- A1.4 Solving Quadratic Equations A5
- A1.5 Uncertainties in Measurements A7
- A1.6 Significant Figures A12

Appendix 2 Units of Measurement and Conversions Among Units A14

- A2.1 Measurements A14
- A2.2 Unit Conversions A15
- Appendix 3 Spectral Analysis A16
- Appendix 4 Selected Thermodynamic Data A19
- Appendix 5 Equilibrium Constants and Reduction Potentials A22
- Appendix 6 Deriving the Integrated Rate Laws A25
 - A6.1 First-Order Rate Laws A25
 - A6.2 Second-Order Rate Laws A26
 - A6.3 Zero-Order Rate Laws A26

Glossary A27 Answers to Selected Exercises A40 Index A79

Learning to Think Like a Chemist

Chemistry is a fascinating and important subject that is challenging to teach and even more challenging to learn. Making this complex subject accessible to students without distortion is the challenge of the chemical educator, especially at the introductory level. *Chemical Principles*, Eighth Edition, provides a rigorous but understandable introduction to chemistry. It emphasizes conceptual understanding, the importance of models, and thoughtful problem solving.

Chemical Principles is based on our experiences at the University of Illinois teaching an accelerated general chemistry course for chemical sciences majors and other students who require a rigorous introductory course. These students typically have excellent credentials and a genuine aptitude for chemistry but only limited understanding of the fundamental concepts of chemistry. Although they may know how to solve stoichiometry and gas problems when they arrive in our courses, these students typically lack a thorough appreciation for the chemical principles that underlie these applications. This is not because they had inadequate preparation in high school; instead, we believe it results from the nature of chemistry itself—a subject that requires several passes before real mastery can take place.

Our mission in writing this text was to produce a book that does not assume that students already know how to think like chemists. These students will eventually do complicated and rigorous thinking, but they must be brought to that point gradually. Thus this book covers the advanced topics (in gases, atomic theory, thermodynamics, and so on) that one expects in a course for chemical sciences majors, but it starts with the fundamentals and then builds to the level required for more complete understanding. Chemistry is not the result of an inspired vision. It is the product of countless observations and many attempts, using logic and trial and error, to account for these observations. In this book we develop key chemical concepts in the same way—to show the observations first and then discuss the models that have been constructed to explain the observed behavior. We hope students will practice "thinking like a chemist" by carefully studying the observations to see if they can follow the thought process, rather than just jumping ahead to the equation or model that will follow.

In *Chemical Principles*, Eighth Edition, we take advantage of the excellent math skills that these students typically possess. As a result, there are fewer worked-out examples than would be found in most mainstream books. The end-of-chapter problems cover a wide range—from drill exercises to difficult problems, some of which would challenge the average senior chemistry major. Thus instructors can tailor the problem assignments to the level appropriate for their students.

This text maintains a student-friendly approach without being patronizing. In addition, to demonstrate the importance of chemistry in real life, we have incorporated throughout the book a number of applications and recent advances in essay form.

New to This Edition

We continue to be pleased that the previous editions of the text have been well received. In response to comments from users, however, we have made some significant changes for the eighth edition.

- We have expanded Section 3.4 "Conceptual Problem Solving" to increase the emphasis on the importance of having students think their way through a problem.
- We have increased the discussion of how to use our problem-solving approach in the examples in Chapters 3 through 5 to model for the students the types of questions they should be asking and answering when solving problems.
- All examples have been checked and revised as needed, with titles being added.
- In the new Section 3.11, "Solving a Complex Problem," we discuss at length a complex problem (that is, one which requires the students to utilize knowledge and understanding of many concepts). We also consider an alternative solution to show students that there is always more than one method to solve a complex problem.
- A more rigorous discussion of the mathematics involved in relating the number of microstates to the concept of entropy is included in Section 10.1.
- *Critical Thinking* questions have been added throughout the text to emphasize the importance of conceptual learning.
- Several *Chemical Insights and Chemistry Explorers* features have been added or revised.
- Calculus-based derivations of integrated rate laws for zero-, first-, and second-order reactions have been added in Appendix 6.
- New end-of-chapter questions and problems have been added throughout the text.
- *ChemWork* problems have been added to the end-of-chapter problems throughout the text. These problems test the students' understanding of core concepts from each chapter. Students who solve a particular problem with no assistance can proceed directly to the answer. However, students who need help can get assistance through a series of online hints. The online procedure for assisting students is modeled after the way a teacher would help with homework problems in his or her office. The hints are usually in the form of interactive questions that guide students through the problem-solving process. Students cannot receive the correct answer from the computer; rather, it encourages students to continue working through the hints to arrive at the answer. *ChemWork* problems in the text can be worked using the online system or as pencil-and-paper problems.
- All end-of-chapter questions and problems have been checked, rewritten, and updated as needed to comply with OWL v.2.
- The art program has been modified and updated as needed.

Organization

The early chapters in this book deal with chemical reactions. Stoichiometry is covered in Chapters 3 and 4, with special emphasis on reactions in aqueous solutions. The properties of gases are treated in Chapter 5, followed by coverage of gas phase equilibria in Chapter 6. Acid–base equilibria are covered in Chapter 7, and Chapter 8 deals with additional aqueous equilibria. Thermodynamics is covered in two chapters: Chapter 9 deals with thermochemistry and the first law of thermodynamics; Chapter 10 treats the topics associated with the second law of thermodynamics. The discussion of electrochemistry follows in Chapter 11. Atomic theory and quantum mechanics are covered in

Chapter 12, followed by two chapters on chemical bonding and modern spectroscopy (Chapters 13 and 14). Chemical kinetics is discussed in Chapter 15, followed by coverage of solids and liquids in Chapter 16 and the physical properties of solutions in Chapter 17. A systematic treatment of the descriptive chemistry of the representative elements is given in Chapter 18 and of the transition metals in Chapter 19. Chapter 20 covers topics in nuclear chemistry, and Chapter 21 provides an introduction to organic chemistry and to the most important biomolecules.

Flexibility of Topic Order

We recognize that the order of the chapters in this text may not fit the order of the topics in your course. Therefore, we have tried to make the order as flexible as possible. In the courses that we have taught using the text, we have successfully used it in a very different order from the one the text follows. We would encourage you to use it in whatever order that serves your purposes.

Instructors have several options for arranging the material to complement their syllabi. For example, the section on gas phase and aqueous equilibria (Chapters 6–8) could be moved to any point later in the course. The chapters on thermodynamics can be separated: Chapter 9 can be used early in the course with Chapter 10 later. In addition, the chapters on atomic theory and bonding (Chapters 12–14) can be used near the beginning of the course. In summary, an instructor who wants to cover atomic theory early and equilibrium later might prefer the following order of chapters: 1–5, 9,

Two approaches for teaching atomic theory earlier and equilibrium later in the course

11 5 5	I Contraction of the second seco
APPROACH 1	APPROACH 2
Chapter 1 Chemists and Chemistry	Chapter 1 Chemists and Chemistry
Chapter 2 Atoms, Molecules, and Ions	Chapter 2 Atoms, Molecules, and Ions
Chapter 3 Stoichiometry	Chapter 3 Stoichiometry
Chapter 4 Types of Chemical Reactions and Solution Stoichiometry	Chapter 4 Types of Chemical Reactions and Solution Stoichiometry
Chapter 5 Gases	Chapter 5 Gases
Chapter 9 Energy, Enthalpy, and Thermochemistry	Chapter 9 Energy, Enthalpy, and Thermochemistry
Chapter 12 Quantum Mechanics and Atomic Theory	Chapter 12 Quantum Mechanics and Atomic Theory
Chapter 13 Bonding: General Concepts	Chapter 13 Bonding: General Concepts
Chapter 14 Covalent Bonding: Orbitals	Chapter 14 Covalent Bonding: Orbitals
Chapter 10 Spontaneity, Entropy, and Free Energy	Chapter 6 Chemical Equilibrium
Chapter 11 Electrochemistry	Chapter 7 Acids and Bases
Chapter 6 Chemical Equilibrium	Chapter 8 Applications of Aqueous Equilibria
Chapter 7 Acids and Bases	Chapter 10 Spontaneity, Entropy, and Free Energy
Chapter 8 Applications of Aqueous Equilibria	Chapter 11 Electrochemistry
Chapter 15 Chemical Kinetics	Chapter 15 Chemical Kinetics
Chapter 16 Liquids and Solids	Chapter 16 Liquids and Solids
Chapter 17 Properties of Solutions	Chapter 17 Properties of Solutions
Chapter 18 The Representative Elements	Chapter 18 The Representative Elements
Chapter 19 Transition Metals and Coordination Chemistry	Chapter 19 Transition Metals and Coordination Chemistry
Chapter 20 The Nucleus: A Chemist's View	Chapter 20 The Nucleus: A Chemist's View
Chapter 21 Organic and Biochemical Molecules	Chapter 21 Organic and Biochemical Molecules

12, 13, 14, 10, 11, 6, 7, 8, 15–21. An alternative order might be: 1–5, 9, 12, 13, 14, 6, 7, 8, 10, 11, 15–21. The point is that the chapters on atomic theory and bonding (12–14), thermodynamics (9, 10), and equilibrium (6, 7, 8) can be moved around quite easily. In addition, the kinetics chapter (Chapter 15) can be covered at any time after bonding. It is also possible to use Chapter 20 (on nuclear chemistry) much earlier—after Chapter 12, for example—if desired.

Mathematical Level

This text assumes a solid background in algebra. All of the mathematical operations required are described in Appendix One or are illustrated in workedout examples. A knowledge of calculus is not required for use of this text. Differential and integral notions are used only where absolutely necessary and are explained when they are used.

Supporting Materials

Please visit http://www.cengage.com/chemistry/zumdahl/chemprin8e for more information about student and instructor resources for this book and about custom versions.

Acknowledgments

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STEVEN S. ZUMDAHL received his B.S. degree in Chemistry from Wheaton College (Illinois) in 1964 and his Ph.D. in Chemistry from the University of Illinois, Urbana, in 1968.

In over 35 years of teaching he has been a faculty member at the University of Colorado, Boulder; Parkland College (Illinois); and the University of Illinois, where he served as Professor and Associate Head and Director of Undergraduate Programs in Chemistry until he became Professor Emeritus in 2003. In 1994 Dr. Zumdahl received the National Catalyst Award from the Chemical Manufacturers Association in recognition of his contribution to chemical education in the United States.

Professor Zumdahl is known at the University of Illinois for his rapport with students and for his outstanding teaching ability. During his

tenure at the University, he received the University of Illinois Award for Excellence in Teaching, the Liberal Arts and Sciences College Award for Distinguished Teaching, and the School of Chemical Sciences Teaching Award (five times).

Dr. Z., as he is known to his students, greatly enjoys "mechanical things," including bicycles and cars. He collects and restores classic automobiles, having a special enthusiasm for vintage Corvettes and Packards.

DONALD J. DECOSTE is Associate Director of General Chemistry at the University of Illinois, Urbana-Champaign, and has been teaching chemistry at the high school and college levels for over 25 years. He earned his B.S. degree in Chemistry and Ph.D. from the University of Illinois, Urbana-Champaign.

At UIUC he teaches courses in introductory chemistry and the teaching of chemistry and has developed chemistry courses for nonscience majors, preservice secondary teachers, and preservice elementary teachers. He has received the LAS Award for Excellence in Undergraduate Teaching by Instructional Staff Award, the Provost's Excellence in Undergraduate Teaching Award, and the School of Chemical Sciences Teaching Award four times.

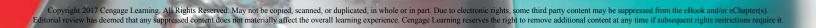
Don has led workshops for secondary teachers and graduate student teaching assistants, discussing the methods and benefits of getting students more actively involved in class. When not involved in teaching and advising, Don enjoys spending time with his wife and three children.

xxi

chapter **1** Chemists and Chemistry

- **1.1** Thinking Like a Chemist
- **1.2** A Real-World Chemistry Problem
- **1.3** The Scientific Method

- 1.4 Industrial Chemistry
- **1.5** Polyvinyl Chloride (PVC): Real-World Chemistry
- ► Solutions are often analyzed by titration. Tek Images/Science Source



hemistry. It is a word that evokes various, and often dramatic, responses. It is a word that is impossible to define concisely, because the field is so diverse and its practitioners perform such an incredible variety of jobs. Chemistry mainly deals with situations in which the nature of a substance is changed by altering its composition; entirely new substances are synthesized, or the properties of existing substances are enhanced.

There are many misconceptions about the practitioners of chemistry. Many people picture a chemist as a solitary figure who works in a laboratory and does not talk to anyone else for days at a time. Nothing could be further from the truth. Many chemists do indeed work in laboratories, but rarely by themselves. A typical day for a modern chemist would be spent as a member of a team solving a particular problem important to his or her company. This team might consist of chemists from various specialties, chemical engineers, development specialists, and possibly even lawyers. Figure 1.1 ▼ represents the people and organizations with which typical laboratory chemists might expect to interact in the course of their jobs.

On the other hand, many persons trained as chemists do not perform actual laboratory work but may work as patent lawyers, financial analysts, plant managers, salespeople, personnel managers, and so on. Also, it is quite common for a person trained as a chemist to have many different jobs during a career.

In Chapters 2 through 21 of this text we will concentrate on the formal discipline of chemistry—its observations, theories, and applications. The goal of Chapter 1 is to introduce some of the important aspects of chemistry not typically discussed in connection with learning chemistry. The chapter includes an introduction to the world of commercial chemistry and provides a couple



Typical chemists interact with a great variety of other people while doing

Figure 1.1

their jobs. (Center photo: Photograph Courtesy of Argonne National Laboratory) of specific examples of the types of problems confronting the practitioners of the "chemical arts." We begin by considering the chemical scientist as a problem solver.

1.1 Thinking Like a Chemist

Much of your life, both personal and professional, will involve problem solving. Most likely, the more creative you are at solving problems, the more effective and successful you will be. Chemists are usually excellent problem solvers because they get a lot of practice. Chemical problems are frequently very complicated—there is usually no neat and tidy solution. Often it is difficult to know where to begin. In response to this dilemma, a chemist makes an educated guess (formulates a hypothesis) and then tests it to see if the proposed solution correctly predicts the observed behavior of the system. This process of trial and error is virtually a way of life for a chemist. Chemists rarely solve a complex problem in a straightforward, elegant manner. More commonly, they poke and prod the problem and make progress only in fits and starts.

It's very important to keep this in mind as you study chemistry. Although "plug and chug" exercises are necessary to familiarize you with the relationships that govern chemical behavior, your ultimate goal should be to advance beyond this stage to true problem solving. Unfortunately, it is impossible to give a formula for becoming a successful problem solver. Creative problem solving is a rather mysterious activity that defies simple analysis. However, it is clear that practice helps. That's why we will make every attempt in this text to challenge you to be creative with the knowledge of chemistry you will be acquiring. Although this process can be frustrating at times, it is definitely worth the struggle-both because it is one of the most valuable skills you can develop and because it helps you test your understanding of chemical concepts. If your understanding of these concepts is not sufficient to allow you to solve problems involving "twists" that you have never encountered before, your knowledge is not very useful to you. The only way to develop your creativity is to expose yourself to new situations in which you need to make new connections. A substantial part of creative problem solving involves developing the confidence necessary to think your way through unfamiliar situations. You must recognize that the entire solution to a complex problem is almost never visible in the beginning. Typically, one tries first to understand pieces of the problem and then puts those pieces together to form the solution.

1.2 A Real-World Chemistry Problem

As discussed, the professional chemist is primarily a problem solver—one who daily confronts tough, but fascinating, situations that must be understood. To illustrate, we will consider an important current problem that requires chemical expertise to solve: the crumbling of the paper in many of the books published in the past century. The pages of many of these books are literally falling apart. To give some perspective on the magnitude of the problem, if the books in the New York Public Library were lined up, they would stretch for almost 100 miles. Currently, about 40 miles of these books are quietly crumbling to dust.

Because of the magnitude of this problem, the company that develops a successful preservation process will reap considerable financial rewards, in addition to performing an important service to society. Assume that you work for a company that is interested in finding a method for saving the crumbling paper in books and that you are put in charge of your company's efforts to develop such a process. What do you know about paper? Probably not much. So the first step is to go to the library to learn all you can about paper. Because



Acid-damaged paper.

CHEMICAL EXPLORERS

Alison Williams's Focus: The Structure of Nucleic Acids

Alison Williams started her scientific career as a high school student when she worked part-time at the Ohio State Agricultural Research and Development Center in Wooster, Ohio. She subsequently received her undergraduate degree from Wesleyan University, and then her master's degree and Ph.D. in biophysical chemistry. Dr. Williams has taught at Swarthmore College, Wesleyan University, Princeton University, Barnard College, and is now at Oberlin College.

Dr. Williams's primary interest is to understand the thermodynamic and kinetic behavior of nucleic acid structure. Nucleic acids, in the form of the huge polymers DNA and RNA, are central to the genetic machinery of cells. In 2012, Dr. Williams was appointed as Director of the Multicultural Resource Center (MRC) and Associate Dean of Academic Diversity at Oberlin College in Ohio. At Oberlin, Dr. Williams works on curricular and faculty diversity initiatives with emphasis on student inclusion and faculty support.



Alison Williams.

paper manufacturing is a mature industry, a great deal of information is available. Research at the library will show that paper is made of cellulose obtained from wood pulp and that the finished paper is "sized" to give it a smooth surface that prevents ink from "fuzzing." The agent typically used for sizing is alum $[Al_2(SO_4)_3]$, which is the cause of the eventual decomposition of the paper. This happens as follows: In the presence of moisture, the Al^{3+} ions from alum become hydrated, forming $Al(H_2O)_6^{3+}$. The $Al(H_2O)_6^{3+}$ ion acts as an acid because the very strong Al^{3+} —O bond causes changes in the O—H bonds of the attached water molecules, thus allowing H⁺ ions to be produced by the following reaction:

$$Al(H_2O)_6^{3+} \Longrightarrow [Al(OH)(H_2O)_5]^{2+} + H^{-1}$$

Therefore, paper sized with alum contains significant numbers of H⁺ ions. This is important because the H⁺ assists in the breakdown of the polymeric cellulose structure of paper. Cellulose is composed of glucose molecules ($C_6H_{12}O_6$) bonded together to form long chains. A segment of cellulose is shown in Fig. 1.2 \triangleright . When the long chains of glucose units in cellulose are broken into shorter pieces, the structural integrity of the paper fails and it crumbles.

Although library research helps you to understand the fundamentals of the problem, now the tough part (and the most interesting part) begins. Can you find a creative solution to the problem? Can the paper in existing books be treated to stop the deterioration in a way that is economical, permanent, and safe?

The essence of the problem seems to be the H⁺ present in the paper. How can it be removed or at least rendered harmless?

Your general knowledge of chemistry tells you that some sort of base (a substance that reacts with H^+) is needed. One of the most common and least expensive bases is sodium hydroxide. Why not dip the affected books in a solution of sodium hydroxide and remove the H^+ by the reaction: $H^+ + OH^- \rightarrow H_2O$? This seems to be a reasonable first idea, but as you consider it further and discuss it with your colleagues, several problems become apparent:

1. The NaOH(*aq*) is a strong base and is therefore quite corrosive. It will destroy the paper by breaking down the cellulose just as acid does.

Stephanie Burns: Chemist, Executive

CHEMICAL EXPLORERS

Stephanie Burns was always interested in science, even as a little girl. This interest intensified over the years until she obtained a Ph.D. in organic chemistry from Iowa State University, where she specialized in the organic chemistry of silicon. Her career path led her to a job with Dow Corning Company, where she developed useful products containing silicon. Eventually her career path led to several positions involving product development, marketing, and business management. Her outstanding performance in these positions resulted in her appointment as an executive vice president. In early 2003, Dr. Burns, at age 48, was promoted to President and Chief Operating Officer for Dow Corning. In 2004 she became Chief

Executive Officer, and in 2006 she was elected Chairman. She has repeatedly been on Forbes's list of the 100 most powerful women.

Dr. Burns says "there was no magic" in reaching the position of Chairman and Chief Executive Officer of Dow Corning. "I'm driven by the science and technology of the company. It's in my blood," she says. Burns says her top priority is to encourage her company's scientists to develop innovative products and expand business built on silicon-based chemistry.



Stephanie Burns.

- 2. The book bindings will be destroyed by dipping the books in water, and the pages will stick together after the books dry.
- 3. The process will be very labor-intensive, requiring the handling of individual books.

Some of these difficulties can be addressed. For example, a much weaker base than sodium hydroxide could be used. Also, the pages could be removed from the binding, soaked one at a time, dried, and then rebound. In fact, this process is used for some very rare and valuable books, but the labor involved makes it very expensive—much too expensive for the miles of books in the

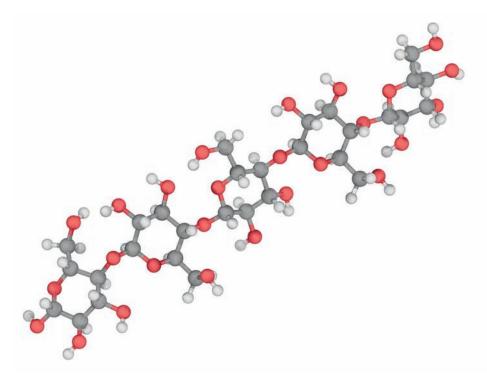


Figure 1.2

The polymer cellulose, which consists of β -D-glucose monomers. (Source: Laguna Design/Science Source)

New York Public Library. Obviously, this process is not what your company is seeking.

You need to find a way to treat large numbers of books without disassembling them. How about using a gaseous base? The books could be sealed in a chamber and the gaseous base allowed to permeate them. The first candidate that occurs to you is ammonia, a readily available gaseous base that reacts with H^+ to form NH_4^+ :

$$NH_3 + H^+ \longrightarrow NH_4^-$$

This seems like a very promising idea, so you decide to construct a pilot treatment chamber. To construct this chamber, you need some help from coworkers. For example, you might consult a chemical engineer for help in the design of the plumbing and pumps needed to supply ammonia to the chamber. You might also consult a mechanical engineer about the appropriate material to use for the chamber and then discuss the actual construction of the chamber with machinists and other personnel from the company's machine shop. In addition, you probably would consult a safety specialist and possibly a toxicologist about the hazards associated with ammonia.

Before the chamber is built, you also have to think carefully about how to test the effectiveness of the process. How could you evaluate, in a relatively short time, how well the process protects paper from deterioration? At this stage, you would undoubtedly do more library research and consult with other experts, such as a paper chemist your company hires as an outside consultant.

Assume now that the chamber has been constructed and that the initial tests look encouraging. At first the H^+ level is greatly reduced in the treated paper. However, after a few days the H^+ level begins to rise again. Why? The fact that ammonia is a gas at room temperature (and pressure) is an advantage because it allows you to treat many books simultaneously in a dry chamber. However, the volatility of ammonia works against you after the treatment. The process

$$NH_4^+ \longrightarrow NH_3 \uparrow + H^+$$

allows the ammonia to escape after a few days. Thus this treatment is too temporary. Even though this effort failed, it was still useful because it provided an opportunity to understand what is required to solve this problem. You need a gaseous substance that *permanently* reacts with the paper and that also consumes H⁺.

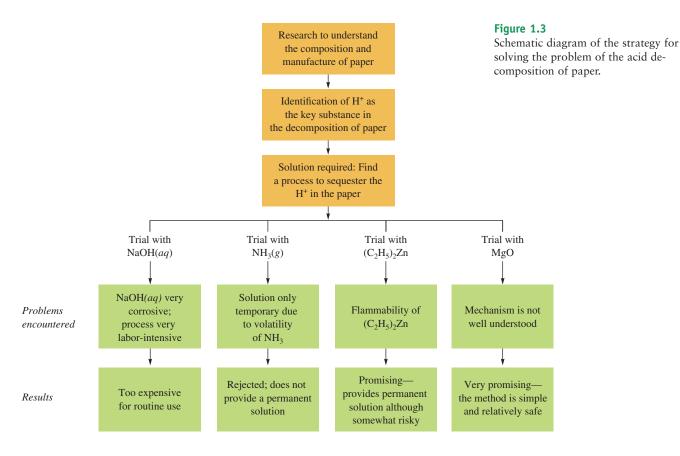
In discussing this problem over lunch, a colleague suggests the compound diethyl zinc $[(C_2H_5)_2Zn]$, which is quite volatile (boiling point = 117°C) and which reacts with water (moisture is present in paper) as follows:

$$(C_2H_5)_2Zn + H_2O \longrightarrow ZnO + 2C_2H_6$$

The C_2H_6 (ethane) is a gas that escapes, but the white solid, ZnO, becomes an integral part of the paper. The important part of ZnO is the oxide ion, O^{2-} , which reacts with H^+ to form water:

$$O^{2-} + 2H^+ \longrightarrow H_2O$$

Thus the ZnO is a nonvolatile base that can be placed in the paper by a gaseous substance. This process seems very promising. However, the major disadvantage of this process (there are always disadvantages) is that diethyl zinc is *very* flammable and great care must be exercised in its use. This leads to another question: Is the treatment effective enough to be worth the risks involved? As it turns out, the Library of Congress used diethyl zinc until 1994, but the process was discontinued because of its risks. Since then, a process known as Bookkeeper has been used. In this process, the book is immersed into a suspension of magnesium oxide (MgO). Small particles (submicron) of MgO are deposited in the pages, and these neutralize the acid and, like ZnO



formed from diethyl zinc, become an integral part of the paper. The advantages are the simplicity of the application and the safety of the method.

The type of problem solving illustrated by investigation of the acid decomposition of paper is quite typical of that which a practicing chemist confronts daily. The first step in successful problem solving is to identify the exact nature of the problem. Although this may seem trivial, it is often the most difficult and most important part of the process. Poor problem solving often results from a fuzzy definition of the problem. You cannot efficiently solve a problem if you do not understand the essence of the problem. Once the problem is well defined, then solutions can be advanced, usually by a process of intelligent trial and error. This process typically involves starting with the simplest potential solution and iterating to a final solution as the feedback from earlier attempts is used to refine the approach. Rarely, if ever, is the solution to a complex problem obvious immediately after the problem is defined. The best solution becomes apparent only as the results from various trial solutions are evaluated. A schematic summarizing the approach for dealing with the acid decomposition of paper is shown in Fig. 1.3 **A**.

1.3 The Scientific Method

Science is a framework for gaining and organizing knowledge. Science is not simply a set of facts but is also a plan of action—a *procedure* for processing and understanding certain types of information. Scientific thinking is useful in all aspects of life, but in this text we will use it to understand how the chemical world operates. The process that lies at the center of scientific inquiry is called the scientific method. There are actually many scientific methods depending on the nature of the specific problem under study and on the particular

See Appendix A1.6 for conventions regarding the use of significant figures in connection with measurements and the calculations involving measurements. Appendix 2 discusses methods for converting among various units. investigator involved. However, it is useful to consider the following general framework for a generic scientific method:

STEPS Steps in the Scientific Method

- 1 *Making observations*. Observations may be *qualitative* (the sky is blue; water is a liquid) or *quantitative* (water boils at 100°C; a certain chemistry book weighs 2 kilograms). A qualitative observation does not involve a number. A quantitative observation (called a **measurement**) involves both a number and a unit. ◄
- 2 Formulating hypotheses. A hypothesis is a possible explanation for the observation.
- **3** *Making predictions.* The hypothesis then is used to make a prediction that can be tested by performing an experiment.
- 4 *Performing experiments.* An experiment is carried out to test the hypothesis. This involves gathering new information that enables a scientist to decide whether the hypothesis is correct—that is, whether it is supported by the new information learned from the experiment. Experiments always produce new observations, and this brings the process back to the beginning again.

Critical Thinking

What if everyone in the government used the scientific method to analyze and solve society's problems, and politics were never involved in the solutions? How would this be different from the present situation, and would it be better or worse?

To understand a given phenomenon, these steps are repeated many times, gradually accumulating the knowledge necessary to provide a possible explanation of the phenomenon.

As scientists observe nature, they often see that the same observation applies to many different systems. For example, innumerable chemical changes have shown that the total observed mass of the materials involved is the same before and after the change. Such generally observed behavior is formulated into a statement called a **natural law.** For example, the observation that the total mass of materials is not affected by a chemical change in those materials is called the law of conservation of mass. This law tells us *what* happens, but it does not tell us *why*. To try to explain why, we continue to make observations, formulate hypotheses, and test these against observations.

Once a set of hypotheses that agree with the various observations is obtained, the hypotheses are assembled into a theory. A **theory**, which is often called a *model*, is a set of tested hypotheses that gives an overall explanation of some natural phenomenon.

It is very important to distinguish between observations and theories. An observation is something that is witnessed and can be recorded. A theory is an *interpretation*—a possible explanation of *why* nature behaves in a particular way. For example, in Chapter 2 we will read about Dalton's atomic theory, in which John Dalton proposed that a chemical reaction is a reorganization of atoms in reacting substances to produce new substances. As we discussed, we know that mass is conserved (it is a natural law), and we can explain it by claiming that all matter is made of nonchanging atoms (the theory).

Theories inevitably change as more information becomes available. For example, we will also see in Chapter 2 that with further experimentation and observations, the atomic theory came to include subatomic particles—electrons,

This portrayal of the classical scientific method probably overemphasizes the importance of observations in current scientific practice. Now that we know a great deal about the nature of matter, scientists often start with a hypothesis that they try to refute as they push forward the frontiers of science. See the writings of Karl Popper for more information on this view.

CHEMICAL INSIGHTS

Critical Units!

How important are conversions from one unit to another? If you ask the National Aeronautics and Space Administration (NASA), very important! In 1999 NASA lost a \$125 million Mars Climate Orbiter because of a failure to convert from English to metric units.

The problem arose because two teams working on the Mars mission were using different sets of units. NASA's scientists at the Jet Propulsion Laboratory in Pasadena, California, assumed that the thrust data for the rockets on the orbiter they received from Lockheed Martin Astronautics in Denver, which built the spacecraft, were in metric units. In reality, the units were English. As a result the orbiter dipped 100 kilometers lower into the Mars atmosphere than planned, and the friction from the atmosphere caused the craft to burn up.

NASA's mistake refueled the controversy over whether Congress should require the United States to switch to the metric system. About 95% of the world now uses the metric system, and the United States is slowly switching from English to metric. For example, the automobile industry has adopted metric fasteners, and we buy our soda in 2-liter bottles.

Artist's conception of the lost Mars Climate Orbiter.

Units can be very important. In fact, they can mean the difference between life and death on some occasions. In 1983, for example, a Canadian jetliner almost ran out of fuel when someone pumped 22,300 pounds of fuel into the aircraft instead of 22,300 kilograms. Remember to watch your units!

protons, and neutrons. The "indivisible" atom of Dalton is not indivisible after all. We see the idea of changing theories in all realms of science. For example, the motions of the sun and stars have remained virtually the same over the thousands of years during which humans have been observing them, but our explanations—our theories—for these motions have changed greatly since ancient times.

The point is that scientists do not stop asking questions just because a given theory seems to account satisfactorily for some aspect of natural behavior. They continue doing experiments to refine or replace the existing theories. This is generally done by using the currently accepted theory to make a prediction and then performing an experiment (making a new observation) to see whether the results bear out this prediction.

Always remember that theories (models) are human inventions. They represent attempts to explain observed natural behavior in terms of human experiences. A theory is actually an educated guess. We must continue to do experiments and to refine our theories (making them consistent with new knowledge) if we hope to approach a more nearly complete understanding of nature.

In this section we have described the scientific method as it might ideally be applied (\triangleright Fig. 1.4). However, it is important to remember that science does not always progress smoothly and efficiently. For one thing, hypotheses and observations are not totally independent of each other, as we have assumed in the description of the idealized scientific method. The coupling of

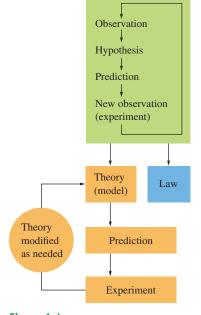


Figure 1.4 The various parts of the scientific method.