

# CHEMICAL PRINCIPLES



THE QUEST FOR INSIGHT

Seventh  
Edition

PETER ATKINS

LORETTA JONES

LEROY LAVERMAN

# Periodic Table of the Elements

		Group 1		Group 2																		
						<div style="border: 1px solid black; padding: 5px; display: inline-block;"> <b>H</b> 1 hydrogen 1.0079 1s<sup>1</sup> </div>																
		Period 2		Period 3		Period 4																
		Group 1		Group 2		Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9										
		Li 3 lithium 6.94 2s <sup>1</sup>		Be 4 beryllium 9.01 2s <sup>2</sup>																		
		Na 11 sodium 22.99 3s <sup>1</sup>		Mg 12 magnesium 24.31 3s <sup>2</sup>																		
Period	4	K 19 potassium 39.10 4s <sup>1</sup>	Ca 20 calcium 40.08 4s <sup>2</sup>	Sc 21 scandium 44.96 3d <sup>1</sup> 4s <sup>2</sup>	Ti 22 titanium 47.87 3d <sup>2</sup> 4s <sup>2</sup>	V 23 vanadium 50.94 3d <sup>3</sup> 4s <sup>2</sup>	Cr 24 chromium 52.00 3d <sup>5</sup> 4s <sup>1</sup>	Mn 25 manganese 54.94 3d <sup>5</sup> 4s <sup>2</sup>	Fe 26 iron 55.84 3d <sup>6</sup> 4s <sup>2</sup>	Co 27 cobalt 58.93 3d <sup>7</sup> 4s <sup>2</sup>												
	5	Rb 37 rubidium 85.47 5s <sup>1</sup>	Sr 38 strontium 87.62 5s <sup>2</sup>	Y 39 yttrium 88.91 4d <sup>1</sup> 5s <sup>2</sup>	Zr 40 zirconium 91.22 4d <sup>2</sup> 5s <sup>2</sup>	Nb 41 niobium 92.91 4d <sup>4</sup> 5s <sup>1</sup>	Mo 42 molybdenum 95.94 4d <sup>5</sup> 5s <sup>1</sup>	Tc 43 technetium (98) 4d <sup>5</sup> 5s <sup>2</sup>	Ru 44 ruthenium 101.07 4d <sup>7</sup> 5s <sup>1</sup>	Rh 45 rhodium 102.90 4d <sup>8</sup> 5s <sup>1</sup>												
	6	Cs 55 cesium 132.91 6s <sup>1</sup>	Ba 56 barium 137.33 6s <sup>2</sup>	La 57 lanthanum 138.91 5d <sup>1</sup> 6s <sup>2</sup>	Hf 72 hafnium 178.49 5d <sup>2</sup> 6s <sup>2</sup>	Ta 73 tantalum 180.95 5d <sup>3</sup> 6s <sup>2</sup>	W 74 tungsten 183.84 5d <sup>4</sup> 6s <sup>2</sup>	Re 75 rhenium 186.21 5d <sup>5</sup> 6s <sup>2</sup>	Os 76 osmium 190.23 5d <sup>6</sup> 6s <sup>2</sup>	Ir 77 iridium 192.22 5d <sup>7</sup> 6s <sup>2</sup>												
	7	Fr 87 francium (223) 7s <sup>1</sup>	Ra 88 radium (226) 7s <sup>2</sup>	Ac 89 actinium (227) 6d <sup>1</sup> 7s <sup>2</sup>	Rf 104 rutherfordium (265) 6d <sup>2</sup> 7s <sup>2</sup>	Db 105 dubnium (268) 6d <sup>3</sup> 7s <sup>2</sup>	Sg 106 seaborgium (271) 6d <sup>4</sup> 7s <sup>2</sup>	Bh 107 bohrium (272) 6d <sup>5</sup> 7s <sup>2</sup>	Hs 108 hassium (270) 6d <sup>6</sup> 7s <sup>2</sup>	Mt 109 meitnerium (276) 6d <sup>7</sup> 7s <sup>2</sup>												
					Lanthanoids (lanthanides)	6	Ce 58 cerium 140.12 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	Pr 59 praseodymium 140.91 4f <sup>3</sup> 6s <sup>2</sup>	Nd 60 neodymium 144.24 4f <sup>4</sup> 6s <sup>2</sup>	Pm 61 promethium (145) 4f <sup>5</sup> 6s <sup>2</sup>	Sm 62 samarium 150.36 4f <sup>6</sup> 6s <sup>2</sup>											
				Actinoids (actinides)	7	Th 90 thorium 232.04 6d <sup>2</sup> 7s <sup>2</sup>	Pa 91 protactinium 231.04 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	U 92 uranium 238.03 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	Np 93 neptunium (237) 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	Pu 94 plutonium (244) 5f <sup>6</sup> 7s <sup>2</sup>												

Molar masses (atomic weights) quoted to the number of significant figures given here can be regarded as typical of most naturally occurring samples.

Elements 113, 115, 117, and 118 have been identified but not yet (in 2016) formally named.

										18						
										He 2 helium 4.00 1s <sup>2</sup>						
										13	14	15	16	17		
										<b>B</b> 5 boron 10.81 2s <sup>2</sup> 2p <sup>1</sup>	<b>C</b> 6 carbon 12.01 2s <sup>2</sup> 2p <sup>2</sup>	<b>N</b> 7 nitrogen 14.01 2s <sup>2</sup> 2p <sup>3</sup>	<b>O</b> 8 oxygen 16.00 2s <sup>2</sup> 2p <sup>4</sup>	<b>F</b> 9 fluorine 19.00 2s <sup>2</sup> 2p <sup>5</sup>	<b>Ne</b> 10 neon 20.18 2s <sup>2</sup> 2p <sup>6</sup>	
										<b>Al</b> 13 aluminum 26.98 3s <sup>2</sup> 3p <sup>1</sup>	<b>Si</b> 14 silicon 28.09 3s <sup>2</sup> 3p <sup>2</sup>	<b>P</b> 15 phosphorus 30.97 3s <sup>2</sup> 3p <sup>3</sup>	<b>S</b> 16 sulfur 32.06 3s <sup>2</sup> 3p <sup>4</sup>	<b>Cl</b> 17 chlorine 35.45 3s <sup>2</sup> 3p <sup>5</sup>	<b>Ar</b> 18 argon 39.95 3s <sup>2</sup> 3p <sup>6</sup>	
<b>10</b>	<b>11</b>	<b>12</b>														
<b>Ni</b> 28 nickel 58.69 3d <sup>8</sup> 4s <sup>2</sup>	<b>Cu</b> 29 copper 63.55 3d <sup>10</sup> 4s <sup>1</sup>	<b>Zn</b> 30 zinc 65.41 3d <sup>10</sup> 4s <sup>2</sup>	<b>Ga</b> 31 gallium 69.72 4s <sup>2</sup> 4p <sup>1</sup>	<b>Ge</b> 32 germanium 72.64 4s <sup>2</sup> 4p <sup>2</sup>	<b>As</b> 33 arsenic 74.92 4s <sup>2</sup> 4p <sup>3</sup>	<b>Se</b> 34 selenium 78.96 4s <sup>2</sup> 4p <sup>4</sup>	<b>Br</b> 35 bromine 79.90 4s <sup>2</sup> 4p <sup>5</sup>	<b>Kr</b> 36 krypton 83.80 4s <sup>2</sup> 4p <sup>6</sup>								
<b>Pd</b> 46 palladium 106.42 4d <sup>10</sup>	<b>Ag</b> 47 silver 107.87 4d <sup>10</sup> 5s <sup>1</sup>	<b>Cd</b> 48 cadmium 112.41 4d <sup>10</sup> 5s <sup>2</sup>	<b>In</b> 49 indium 114.82 5s <sup>2</sup> 5p <sup>1</sup>	<b>Sn</b> 50 tin 118.71 5s <sup>2</sup> 5p <sup>2</sup>	<b>Sb</b> 51 antimony 121.76 5s <sup>2</sup> 5p <sup>3</sup>	<b>Te</b> 52 tellurium 127.60 5s <sup>2</sup> 5p <sup>4</sup>	<b>I</b> 53 iodine 126.90 5s <sup>2</sup> 5p <sup>5</sup>	<b>Xe</b> 54 xenon 131.29 5s <sup>2</sup> 5p <sup>6</sup>								
<b>Pt</b> 78 platinum 195.08 5d <sup>9</sup> 6s <sup>1</sup>	<b>Au</b> 79 gold 196.97 5d <sup>10</sup> 6s <sup>1</sup>	<b>Hg</b> 80 mercury 200.59 5d <sup>10</sup> 6s <sup>2</sup>	<b>Tl</b> 81 thallium 204.38 6s <sup>2</sup> 6p <sup>1</sup>	<b>Pb</b> 82 lead 207.2 6s <sup>2</sup> 6p <sup>2</sup>	<b>Bi</b> 83 bismuth 208.98 6s <sup>2</sup> 6p <sup>3</sup>	<b>Po</b> 84 polonium (209) 6s <sup>2</sup> 6p <sup>4</sup>	<b>At</b> 85 astatine (210) 6s <sup>2</sup> 6p <sup>5</sup>	<b>Rn</b> 86 radon (222) 6s <sup>2</sup> 6p <sup>6</sup>								
<b>Ds</b> 110 darmstadtium (281) 6d <sup>8</sup> 7s <sup>2</sup>	<b>Rg</b> 111 roentgenium (280) 6d <sup>10</sup> 7s <sup>1</sup>	<b>Cn</b> 112 copernicium (285) 6d <sup>10</sup> 7s <sup>2</sup>	113	<b>Fl</b> 114 flerovium (289) 7s <sup>2</sup> 7p <sup>2</sup>	115	<b>Lv</b> 116 livermorium (293) 7s <sup>2</sup> 7p <sup>4</sup>	117	118								
<b>Eu</b> 63 europium 151.96 4f <sup>7</sup> 6s <sup>2</sup>	<b>Gd</b> 64 gadolinium 157.25 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	<b>Tb</b> 65 terbium 158.93 4f <sup>9</sup> 6s <sup>2</sup>	<b>Dy</b> 66 dysprosium 162.50 4f <sup>10</sup> 6s <sup>2</sup>	<b>Ho</b> 67 holmium 164.93 4f <sup>11</sup> 6s <sup>2</sup>	<b>Er</b> 68 erbium 167.26 4f <sup>12</sup> 6s <sup>2</sup>	<b>Tm</b> 69 thulium 168.93 4f <sup>13</sup> 6s <sup>2</sup>	<b>Yb</b> 70 ytterbium 173.04 4f <sup>14</sup> 6s <sup>2</sup>	<b>Lu</b> 71 lutetium 174.97 5d <sup>1</sup> 6s <sup>2</sup>								
<b>Am</b> 95 americium (243) 5f <sup>7</sup> 7s <sup>2</sup>	<b>Cm</b> 96 curium (247) 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<b>Bk</b> 97 berkelium (247) 5f <sup>9</sup> 7s <sup>2</sup>	<b>Cf</b> 98 californium (251) 5f <sup>10</sup> 7s <sup>2</sup>	<b>Es</b> 99 einsteinium (252) 5f <sup>11</sup> 7s <sup>2</sup>	<b>Fm</b> 100 fermium (257) 5f <sup>12</sup> 7s <sup>2</sup>	<b>Md</b> 101 mendelevium (258) 5f <sup>13</sup> 7s <sup>2</sup>	<b>No</b> 102 nobelium (259) 5f <sup>14</sup> 7s <sup>2</sup>	<b>Lr</b> 103 lawrencium (262) 6d <sup>1</sup> 7s <sup>2</sup>								

Metal  
 Metalloid  
 Nonmetal

## FREQUENTLY USED TABLES AND FIGURES

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		<b>Page</b>
<b>Atomic and molecular properties</b>		
Atomic radii	Fig. 1F.4	54
Ionic radii	Fig. 1F.6	55
First ionization energies	Fig. 1F.8	57
Electron affinity	Fig. 1F.12	59
Electronegativity	Fig. 2D.2	97
Average bond lengths	Table 2D.3	101
Ground-state electron configurations	Appendix 2C	A18
The elements (physical properties)	Appendix 2D	A19
<b>Thermodynamic properties</b>		
Standard enthalpies of physical change	Table 4C.1	268
Lattice enthalpies	Table 4E.1	291
Mean bond enthalpies	Table 4E.3	293
Vapor pressure of water	Table 5A.2	351
Thermodynamic data	Appendix 2A	A9
<b>Solutions</b>		
Acidity constants at 25 °C	Table 6C.1	461
Basicity constants at 25 °C	Table 6C.2	462
Acidity constants of polyprotic acids at 25 °C	Table 6E.1	483
Solubility products	Table 6I.1	524
<b>Electrochemistry</b>		
Standard potentials	Table 6M.1	557
	Appendix 2B	A16

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Oxford University

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University of Northern Colorado

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	<b>FUNDAMENTALS</b>	F1
<b>Focus 1</b>	<b>ATOMS</b>	1
<b>Focus 2</b>	<b>MOLECULES</b>	67
<b>Focus 3</b>	<b>STATES OF MATTER</b>	145
<b>INTERLUDE</b>	<b>Ceramics and Glasses</b>	239
<b>Focus 4</b>	<b>THERMODYNAMICS</b>	241
<b>INTERLUDE</b>	<b>Free Energy and Life</b>	346
<b>Focus 5</b>	<b>EQUILIBRIUM</b>	347
<b>INTERLUDE</b>	<b>Homeostasis</b>	442
<b>Focus 6</b>	<b>REACTIONS</b>	443
<b>INTERLUDE</b>	<b>Practical Cells</b>	584
<b>Focus 7</b>	<b>KINETICS</b>	587
<b>Focus 8</b>	<b>THE MAIN-GROUP ELEMENTS</b>	643
<b>Focus 9</b>	<b>THE d-BLOCK ELEMENTS</b>	705
<b>Focus 10</b>	<b>NUCLEAR CHEMISTRY</b>	747
<b>Focus 11</b>	<b>ORGANIC CHEMISTRY</b>	777
<b>INTERLUDE</b>	<b>Technology: Fuels</b>	829

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Preface xv

## FUNDAMENTALS / F1

Introduction and Orientation F1

**A Matter and Energy** F5

- A.1** Symbols and Units / F5
- A.2** Accuracy and Precision / F8
- A.3** Force / F9
- A.4** Energy / F10
- FUNDAMENTALS A** Exercises / F13

**B Elements and Atoms** F15

- B.1** Atoms / F15
- B.2** The Nuclear Model / F16
- B.3** Isotopes / F18
- B.4** The Organization of the Elements / F19
- FUNDAMENTALS B** Exercises / F21

**C Compounds** F22

- C.1** What Are Compounds? / F22
- C.2** Molecules and Molecular Compounds / F23
- C.3** Ions and Ionic Compounds / F24
- FUNDAMENTALS C** Exercises / F28

**D Nomenclature** F29

- D.1** Names of Cations / F29
- D.2** Names of Anions / F29
- D.3** Names of Ionic Compounds / F31
- TOOLBOX D.1** How to Name Ionic Compounds / F31
- D.4** Names of Inorganic Molecular Compounds / F32
- TOOLBOX D.2** How to Name Simple Inorganic Molecular Compounds / F33
- D.5** The Nomenclature of Some Common Organic Compounds / F35
- FUNDAMENTALS D** Exercises / F37

**E Moles and Molar Masses** F38

- E.1** The Mole / F38
- E.2** Molar Mass / F40
- FUNDAMENTALS E** Exercises / F44

**F The Determination of Composition** F46

- F.1** Mass Percentage Composition / F46
- F.2** Determining Empirical Formulas / F48
- F.3** Determining Molecular Formulas / F49
- FUNDAMENTALS F** Exercises / F50

**G Mixtures and Solutions** F51

- G.1** Classifying Mixtures / F51
- G.2** Separation Techniques / F53
- G.3** Concentration / F54
- G.4** Dilution / F56
- TOOLBOX G.1** How to Calculate the Volume of Stock Solution Required for a Given Dilution / F57
- FUNDAMENTALS G** Exercises / F58

**H Chemical Equations** F60

- H.1** Representing Chemical Reactions / F60
- H.2** Balanced Chemical Equations / F62
- FUNDAMENTALS H** Exercises / F64

**I Precipitation Reactions** F66

- I.1** Electrolytes / F66
- I.2** Precipitates / F67
- I.3** Ionic and Net Ionic Equations / F68
- I.4** Putting Precipitation to Work / F69
- FUNDAMENTALS I** Exercises / F71

**J Acids and Bases** F72

- J.1** Acids and Bases in Aqueous Solution / F73
- J.2** Strong and Weak Acids and Bases / F74
- J.3** Neutralization / F76
- FUNDAMENTALS J** Exercises / F77

**K Redox Reactions** F78

- K.1** Oxidation and Reduction / F78
- K.2** Oxidation Numbers / F80
- TOOLBOX K.1** How to Assign Oxidation Numbers / F80
- K.3** Oxidizing and Reducing Agents / F82
- K.4** Balancing Simple Redox Equations / F84
- FUNDAMENTALS K** Exercises / F85

**L Reaction Stoichiometry** F87

- L.1** Mole-to-Mole Predictions / F87
- L.2** Mass-to-Mass Predictions / F88

	<b>TOOLBOX L.1</b> How to Carry Out Mass-to-Mass Calculations / F88	
<b>L.3</b>	Volumetric Analysis / F90	
	<b>TOOLBOX L.2</b> How to Interpret a Titration / F91	
	<b>FUNDAMENTALS L</b> Exercises / F94	
<b>M</b>	<b>Limiting Reactants</b>	F96
<b>M.1</b>	Reaction Yield / F96	
<b>M.2</b>	The Limits of Reaction / F98	
	<b>TOOLBOX M.1</b> How to Identify the Limiting Reactant / F98	
<b>M.3</b>	Combustion Analysis / F101	
	<b>FUNDAMENTALS M</b> Exercises / F104	
<b>FOCUS 1</b>		
<b>ATOMS / 1</b>		
<b>Topic 1A</b>	<b>Investigating Atoms</b>	2
<b>1A.1</b>	The Nuclear Model of the Atom / 2	
<b>1A.2</b>	Electromagnetic Radiation / 4	
<b>1A.3</b>	Atomic Spectra / 6	
	<b>TOPIC 1A</b> Exercises / 9	
<b>Topic 1B</b>	<b>Quantum Theory</b>	11
<b>1B.1</b>	Radiation, Quanta, and Photons / 11	
<b>1B.2</b>	The Wave–Particle Duality of Matter / 17	
<b>1B.3</b>	The Uncertainty Principle / 19	
	<b>TOPIC 1B</b> Exercises / 21	
<b>Topic 1C</b>	<b>Wavefunctions and Energy Levels</b>	23
<b>1C.1</b>	The Wavefunction and Its Interpretation / 23	
<b>1C.2</b>	The Quantization of Energy / 24	
	<b>BOX 1C.1</b> Nanocrystals / 26	
	<b>TOPIC 1C</b> Exercises / 28	
<b>Topic 1D</b>	<b>The Hydrogen Atom</b>	30
<b>1D.1</b>	Energy Levels / 30	
<b>1D.2</b>	Atomic Orbitals / 31	
<b>1D.3</b>	Quantum Numbers, Shells, and Subshells / 33	
<b>1D.4</b>	The Shapes of Orbitals / 35	
<b>1D.5</b>	Electron Spin / 38	
	<b>BOX 1D.1</b> How Do We Know . . . That an Electron Has Spin? / 39	
	<b>1D.6</b> The Electronic Structure of Hydrogen / 39	
	<b>TOPIC 1D</b> Exercises / 40	
<b>Topic 1E</b>	<b>Many-Electron Atoms</b>	42
<b>1E.1</b>	Orbital Energies / 42	
<b>1E.2</b>	The Building-Up Principle / 44	
	<b>TOOLBOX 1E.1</b> How to Predict the Ground-State Electron Configuration of an Atom / 47	
	<b>TOPIC 1E</b> Exercises / 49	
<b>Topic 1F</b>	<b>Periodicity</b>	51
<b>1F.1</b>	The General Structure of the Periodic Table / 51	
<b>1F.2</b>	Atomic Radius / 53	
<b>1F.3</b>	Ionic Radius / 54	
<b>1F.4</b>	Ionization Energy / 56	
<b>1F.5</b>	Electron Affinity / 58	
<b>1F.6</b>	The Inert-Pair Effect / 60	
<b>1F.7</b>	Diagonal Relationships / 60	
<b>1F.8</b>	The General Properties of the Elements / 60	
	<b>TOPIC 1F</b> Exercises / 63	
<b>FOCUS 1</b>	Online Cumulative Example / 64	
<b>FOCUS 1</b>	Exercises / 64	
<b>FOCUS 2</b>		
<b>MOLECULES / 67</b>		
<b>Topic 2A</b>	<b>Ionic Bonding</b>	68
<b>2A.1</b>	The Ions That Elements Form / 68	
<b>2A.2</b>	Lewis Symbols / 70	
<b>2A.3</b>	The Energetics of Ionic Bond Formation / 71	
<b>2A.4</b>	Interactions Between Ions / 72	
	<b>TOPIC 2A</b> Exercises / 75	
<b>Topic 2B</b>	<b>Covalent Bonding</b>	77
<b>2B.1</b>	Lewis Structures / 77	
	<b>TOOLBOX 2B.1</b> How to Write the Lewis Structure of a Polyatomic Species / 79	
<b>2B.2</b>	Resonance / 81	
<b>2B.3</b>	Formal Charge / 84	
	<b>TOOLBOX 2B.2</b> How to Use Formal Charge to Identify the Most Likely Lewis Structure / 85	
	<b>TOPIC 2B</b> Exercises / 86	

<b>Topic 2C</b>	<b>Beyond the Octet Rule</b>	88
<b>2C.1</b>	Radicals and Biradicals / 88	
	<b>BOX 2C.1</b> What Has This to Do With . . . Staying Alive? Chemical Self-Preservation / 89	
<b>2C.2</b>	Expanded Valence Shells / 89	
<b>2C.3</b>	Incomplete Octets / 92	
	<b>TOPIC 2C</b> Exercises / 93	
<b>Topic 2D</b>	<b>The Properties of Bonds</b>	95
<b>2D.1</b>	Correcting the Covalent Model: Electronegativity / 95	
<b>2D.2</b>	Correcting the Ionic Model: Polarizability / 97	
<b>2D.3</b>	Bond Strengths / 98	
<b>2D.4</b>	Bond Lengths / 100	
	<b>TOPIC 2D</b> Exercises / 102	
<b>Topic 2E</b>	<b>The VSEPR Model</b>	103
<b>2E.1</b>	The Basic VSEPR Model / 103	
	<b>BOX 2E.1</b> Frontiers of Chemistry: Drugs by Design and Discovery / 104	
<b>2E.2</b>	Molecules with Lone Pairs on the Central Atom / 107	
	<b>TOOLBOX 2E.1</b> How to Use the VSEPR Model / 110	
<b>2E.3</b>	Polar Molecules / 112	
	<b>TOPIC 2E</b> Exercises / 115	
<b>Topic 2F</b>	<b>Valence-Bond Theory</b>	117
<b>2F.1</b>	Sigma and Pi Bonds / 117	
<b>2F.2</b>	Electron Promotion and the Hybridization of Orbitals / 119	
<b>2F.3</b>	Other Common Types of Hybridization / 120	
<b>2F.4</b>	Characteristics of Multiple Bonds / 123	
	<b>TOPIC 2F</b> Exercises / 126	
<b>Topic 2G</b>	<b>Molecular Orbital Theory</b>	127
<b>2G.1</b>	Molecular Orbitals / 127	
<b>2G.2</b>	Electron Configurations of Diatomic Molecules / 128	
	<b>BOX 2G.1</b> How Do We Know . . . The Energies of Molecular Orbitals? / 130	
	<b>TOOLBOX 2G.1</b> How to Determine the Electron Configuration and Bond Order of a Homonuclear Diatomic Species / 131	

**BOX 2G.2** How Do We Know . . . That Electrons Are Not Paired? / 133

**2G.3** Bonding in Heteronuclear Diatomic Molecules / 134

**2G.4** Orbitals in Polyatomic Molecules / 135

**TOPIC 2G** Exercises / 137

**FOCUS 2** Online Cumulative Example / 139

**FOCUS 2** Exercises / 139

## FOCUS 3

### STATES OF MATTER / 145

**Topic 3A** **The Nature of Gases** 147

**3A.1** Observing Gases / 147

**3A.2** Pressure / 148

**3A.3** Alternative Units of Pressure / 150

**TOPIC 3A** Exercises / 151

**Topic 3B** **The Gas Laws** 153

**3B.1** The Experimental Observations / 153

**3B.2** Applications of the Ideal Gas Law / 156

**3B.3** Molar Volume and Gas Density / 159

**TOPIC 3B** Exercises / 161

**Topic 3C** **Gases in Mixtures and Reactions** 163

**3C.1** Mixtures of Gases / 163

**3C.2** The Stoichiometry of Reacting Gases / 166

**TOPIC 3C** Exercises / 168

**Topic 3D** **Molecular Motion** 170

**3D.1** Diffusion and Effusion / 170

**3D.2** The Kinetic Model of Gases / 171

**3D.3** The Maxwell Distribution of Speeds / 175

**BOX 3D.1** How Do We Know . . . The Distribution of Molecular Speeds? / 176

**TOPIC 3D** Exercises / 177

**Topic 3E** **Real Gases** 179

**3E.1** Deviations from Ideality / 179

**3E.2** Equations of State of Real Gases / 180

**3E.3** The Liquefaction of Gases / 182

**TOPIC 3E** Exercises / 183

**Topic 3F** **Intermolecular Forces** 185

**3F.1** The Origin of Intermolecular Forces / 185

<b>3F.2</b>	Ion–Dipole Forces / 186	
<b>3F.3</b>	Dipole–Dipole Forces / 187	
<b>3F.4</b>	London Forces / 189	
<b>3F.5</b>	Hydrogen Bonding / 191	
<b>3F.6</b>	Repulsions / 192	
	<b>TOPIC 3F Exercises</b> / 193	
<b>Topic 3G</b>	<b>Liquids</b>	195
<b>3G.1</b>	Order in Liquids / 195	
<b>3G.2</b>	Viscosity and Surface Tension / 195	
<b>3G.3</b>	Liquid Crystals / 197	
<b>3G.4</b>	Ionic Liquids / 198	
	<b>TOPIC 3G Exercises</b> / 199	
<b>Topic 3H</b>	<b>Solids</b>	201
<b>3H.1</b>	Classification of Solids / 201	
	<b>BOX 3H.1</b> How Do We Know . . . What a Surface Looks Like? / 202	
<b>3H.2</b>	Molecular Solids / 204	
<b>3H.3</b>	Network Solids / 204	
<b>3H.4</b>	Metallic Solids / 206	
<b>3H.5</b>	Unit Cells / 209	
<b>3H.6</b>	Ionic Solids / 212	
	<b>TOPIC 3H Exercises</b> / 215	
<b>Topic 3I</b>	<b>Inorganic Materials</b>	218
<b>3I.1</b>	Alloys / 218	
<b>3I.2</b>	Silicates / 220	
<b>3I.3</b>	Calcium Carbonate / 221	
<b>3I.4</b>	Cement and Concrete / 222	
	<b>TOPIC 3I Exercises</b> / 223	
<b>Topic 3J</b>	<b>Materials for New Technologies</b>	224
<b>3J.1</b>	Electrical Conduction in Solids / 224	
<b>3J.2</b>	Semiconductors / 225	
<b>3J.3</b>	Superconductors / 227	
<b>3J.4</b>	Luminescent Materials / 228	
<b>3J.5</b>	Magnetic Materials / 229	
<b>3J.6</b>	Nanomaterials / 229	
<b>3J.7</b>	Nanotubes / 230	
	<b>TOPIC 3J Exercises</b> / 231	
<b>FOCUS 3</b>	Online Cumulative Example / 233	
<b>FOCUS 3</b>	Exercises / 233	
<b>INTERLUDE</b>	<b>Ceramics and Glasses</b> / 239	

## THERMODYNAMICS / 241

<b>Topic 4A</b>	<b>Work and Heat</b>	243
<b>4A.1</b>	Systems and Surroundings / 243	
<b>4A.2</b>	Work / 244	
<b>4A.3</b>	Expansion Work / 245	
<b>4A.4</b>	Heat / 250	
<b>4A.5</b>	The Measurement of Heat / 250	
	<b>TOPIC 4A Exercises</b> / 255	
<b>Topic 4B</b>	<b>Internal Energy</b>	256
<b>4B.1</b>	The First Law / 256	
<b>4B.2</b>	State Functions / 257	
<b>4B.3</b>	A Molecular Interlude / 260	
	<b>TOPIC 4B Exercises</b> / 262	
<b>Topic 4C</b>	<b>Enthalpy</b>	263
<b>4C.1</b>	Heat Transfers at Constant Pressure / 263	
<b>4C.2</b>	Heat Capacities at Constant Volume and Constant Pressure / 264	
<b>4C.3</b>	The Molecular Origin of the Heat Capacities of Gases / 265	
<b>4C.4</b>	The Enthalpy of Physical Change / 267	
<b>4C.5</b>	Heating Curves / 269	
	<b>BOX 4C.1</b> How Do We Know . . . The Shape of a Heating Curve? / 270	
	<b>TOPIC 4C Exercises</b> / 272	
<b>Topic 4D</b>	<b>Thermochemistry</b>	273
<b>4D.1</b>	Reaction Enthalpy / 273	
<b>4D.2</b>	The Relation Between $\Delta H$ and $\Delta U$ / 274	
<b>4D.3</b>	Standard Reaction Enthalpies / 276	
	<b>BOX 4D.1</b> What Has This to Do With . . . The Environment? Alternative Fuels / 277	
<b>4D.4</b>	Combining Reaction Enthalpies: Hess's Law / 280	
	<b>TOOLBOX 4D.1</b> How to Use Hess's Law / 280	
<b>4D.5</b>	Standard Enthalpies of Formation / 282	
<b>4D.6</b>	The Variation of Reaction Enthalpy with Temperature / 285	
	<b>TOPIC 4D Exercises</b> / 287	
<b>Topic 4E</b>	<b>Contributions to Enthalpy</b>	290
<b>4E.1</b>	Ion Formation / 290	
<b>4E.2</b>	The Born–Haber Cycle / 290	

4E.3	Bond Enthalpies / 292	
	TOPIC 4E Exercises / 295	
<b>Topic 4F</b>	<b>Entropy</b>	296
4F.1	Spontaneous Change / 296	
4F.2	Entropy and Disorder / 296	
4F.3	Entropy and Volume / 298	
4F.4	Entropy and Temperature / 300	
4F.5	Entropy and Physical State / 303	
	TOPIC 4F Exercises / 306	
<b>Topic 4G</b>	<b>The Molecular Interpretation of Entropy</b>	308
4G.1	The Boltzmann Formula / 308	
4G.2	The Equivalence of Statistical and Thermodynamic Entropies / 311	
	TOPIC 4G Exercises / 313	
<b>Topic 4H</b>	<b>Absolute Entropies</b>	314
4H.1	Standard Molar Entropies / 314	
	BOX 4H.1 Frontiers of Chemistry: The Quest for Absolute Zero / 315	
4H.2	Standard Reaction Entropies / 318	
	TOPIC 4H Exercises / 319	
<b>Topic 4I</b>	<b>Global Changes in Entropy</b>	321
4I.1	The Surroundings / 321	
4I.2	The Overall Change in Entropy / 323	
4I.3	Equilibrium / 326	
	TOPIC 4I Exercises / 328	
<b>Topic 4J</b>	<b>Gibbs Free Energy</b>	329
4J.1	Focusing on the System / 329	
4J.2	Gibbs Free Energy of Reaction / 332	
4J.3	The Gibbs Free Energy and Nonexpansion Work / 335	
4J.4	The Effect of Temperature / 337	
	TOPIC 4J Exercises / 339	
<b>FOCUS 4</b>	Online Cumulative Example / 341	
<b>FOCUS 4</b>	Exercises / 341	
<b>INTERLUDE</b>	<b>Free Energy and Life</b> / 346	
		<b>FOCUS 5</b>
	<b>EQUILIBRIUM / 347</b>	
<b>Topic 5A</b>	<b>Vapor Pressure</b>	349
5A.1	The Origin of Vapor Pressure / 349	
5A.2	Volatility and Intermolecular Forces / 350	
5A.3	The Variation of Vapor Pressure with Temperature / 351	
5A.4	Boiling / 354	
	TOPIC 5A Exercises / 355	
<b>Topic 5B</b>	<b>Phase Equilibria in One-Component Systems</b>	357
5B.1	One-Component Phase Diagrams / 357	
5B.2	Critical Properties / 360	
	TOPIC 5B Exercises / 362	
<b>Topic 5C</b>	<b>Phase Equilibria in Two-Component Systems</b>	364
5C.1	The Vapor Pressure of Mixtures / 364	
5C.2	Binary Liquid Mixtures / 366	
5C.3	Distillation / 369	
5C.4	Azeotropes / 369	
	TOPIC 5C Exercises / 371	
<b>Topic 5D</b>	<b>Solubility</b>	373
5D.1	The Limits of Solubility / 373	
5D.2	The Like-Dissolves-Like Rule / 374	
5D.3	Pressure and Gas Solubility / 376	
5D.4	Temperature and Solubility / 377	
5D.5	The Thermodynamics of Dissolving / 377	
5D.6	Colloids / 380	
	TOPIC 5D Exercises / 381	
<b>Topic 5E</b>	<b>Molality</b>	383
	TOOLBOX 5E.1 How to Use the Molality / 384	
	TOPIC 5E Exercises / 387	
<b>Topic 5F</b>	<b>Colligative Properties</b>	388
5F.1	Boiling-Point Elevation and Freezing-Point Depression / 388	
5F.2	Osmosis / 390	
	BOX 5F.1 Frontiers of Chemistry: Drug Delivery / 391	
	TOOLBOX 5F.1 How to Use Colligative Properties to Determine Molar Mass / 393	
	TOPIC 5F Exercises / 396	
<b>Topic 5G</b>	<b>Chemical Equilibrium</b>	397
5G.1	The Reversibility of Reactions / 397	
5G.2	Equilibrium and the Law of Mass Action / 399	

- 5G.3** The Origin of Equilibrium Constants / 402
- 5G.4** The Thermodynamic Description of Equilibrium / 403
- TOPIC 5G** Exercises / 407
- Topic 5H Alternative Forms of the Equilibrium Constant** 410
- 5H.1** Multiples of the Chemical Equation / 410
- 5H.2** Composite Equations / 411
- 5H.3** Molar Concentrations of Gases / 411
- TOPIC 5H** Exercises / 414
- Topic 5I Equilibrium Calculations** 415
- 5I.1** The Extent of Reaction / 415
- 5I.2** The Direction of Reaction / 416
- 5I.3** Calculations with Equilibrium Constants / 418
- TOOLBOX 5I.1** How to Set Up and Use an Equilibrium Table / 418
- TOPIC 5I** Exercises / 423
- Topic 5J The Response of Equilibria to Changes in Conditions** 426
- 5J.1** Adding and Removing Reagents / 426
- 5J.2** Compressing a Reaction Mixture / 429
- 5J.3** Temperature and Equilibrium / 431
- TOPIC 5J** Exercises / 434
- FOCUS 5** Online Cumulative Example / 436
- FOCUS 5** Exercises / 436
- INTERLUDE Homeostasis** / 442
- FOCUS 6**
- 
- REACTIONS / 443**
- 
- Topic 6A The Nature of Acids and Bases** 445
- 6A.1** Brønsted–Lowry Acids and Bases / 445
- 6A.2** Lewis Acids and Bases / 448
- 6A.3** Acidic, Basic, and Amphoteric Oxides / 449
- 6A.4** Proton Exchange Between Water Molecules / 450
- TOPIC 6A** Exercises / 453
- Topic 6B The pH Scale** 455
- 6B.1** The Interpretation of pH / 455
- 6B.2** The pOH of Solutions / 457
- TOPIC 6B** Exercises / 458
- Topic 6C Weak Acids and Bases** 460
- 6C.1** Acidity and Basicity Constants / 460
- 6C.2** The Conjugate Seesaw / 463
- 6C.3** Molecular Structure and Acid Strength / 465
- 6C.4** The Strengths of Oxoacids and Carboxylic Acids / 467
- TOPIC 6C** Exercises / 470
- Topic 6D The pH of Aqueous Solutions** 472
- 6D.1** Solutions of Weak Acids / 472
- TOOLBOX 6D.1** How to Calculate the pH of a Solution of a Weak Acid / 473
- 6D.2** Solutions of Weak Bases / 475
- TOOLBOX 6D.2** How to Calculate the pH of a Solution of a Weak Base / 475
- 6D.3** The pH of Salt Solutions / 477
- TOPIC 6D** Exercises / 482
- Topic 6E Polyprotic Acids and Bases** 483
- 6E.1** The pH of a Polyprotic Acid Solution / 483
- 6E.2** Solutions of Salts of Polyprotic Acids / 484
- 6E.3** The Concentrations of Solute Species / 486
- TOOLBOX 6E.1** How to Calculate the Concentrations of All Species in a Polyprotic Acid Solution / 486
- 6E.4** Composition and pH / 489
- BOX 6E.1** What Has This to Do With . . . The Environment? Acid Rain and the Gene Pool / 490
- TOPIC 6E** Exercises / 493
- Topic 6F Autoprotolysis and pH** 494
- 6F.1** Very Dilute Solutions of Strong Acids and Bases / 494
- 6F.2** Very Dilute Solutions of Weak Acids / 496
- TOPIC 6F** Exercises / 498
- Topic 6G Buffers** 499
- 6G.1** Buffer Action / 499
- 6G.2** Designing a Buffer / 500
- 6G.3** Buffer Capacity / 505
- BOX 6G.1** What Has This to Do With . . . Staying Alive? Physiological Buffers / 506
- TOPIC 6G** Exercises / 507

<b>Topic 6H</b>	<b>Acid–Base Titrations</b>	509
<b>6H.1</b>	Strong Acid–Strong Base Titrations / 509	
	<b>TOOLBOX 6H.1</b> How to Calculate the pH During a Strong Acid–Strong Base Titration / 510	
<b>6H.2</b>	Strong Acid–Weak Base and Weak Acid–Strong Base Titrations / 511	
	<b>TOOLBOX 6H.2</b> How to Calculate the pH During a Titration of a Weak Acid or a Weak Base / 514	
<b>6H.3</b>	Acid–Base Indicators / 516	
<b>6H.4</b>	Polyprotic Acid Titrations / 518	
	<b>TOPIC 6H</b> Exercises / 520	
<b>Topic 6I</b>	<b>Solubility Equilibria</b>	523
<b>6I.1</b>	The Solubility Product / 523	
<b>6I.2</b>	The Common-Ion Effect / 525	
<b>6I.3</b>	Complex Ion Formation / 527	
	<b>TOPIC 6I</b> Exercises / 528	
<b>Topic 6J</b>	<b>Precipitation</b>	530
<b>6J.1</b>	Predicting Precipitation / 530	
<b>6J.2</b>	Selective Precipitation / 531	
<b>6J.3</b>	Dissolving Precipitates / 533	
<b>6J.4</b>	Qualitative Analysis / 533	
	<b>TOPIC 6J</b> Exercises / 535	
<b>Topic 6K</b>	<b>Representing Redox Reactions</b>	537
<b>6K.1</b>	Half-Reactions / 537	
<b>6K.2</b>	Balancing Redox Equations / 538	
	<b>TOOLBOX 6K.1</b> How to Balance Complicated Redox Equations / 538	
	<b>TOPIC 6K</b> Exercises / 543	
<b>Topic 6L</b>	<b>Galvanic Cells</b>	545
<b>6L.1</b>	The Structure of Galvanic Cells / 545	
<b>6L.2</b>	Cell Potential and Reaction Gibbs Free Energy / 546	
<b>6L.3</b>	The Notation for Cells / 549	
	<b>TOOLBOX 6L.1</b> How to Write a Cell Reaction Corresponding to a Cell Diagram / 551	
	<b>TOPIC 6L</b> Exercises / 553	
<b>Topic 6M</b>	<b>Standard Potentials</b>	554
<b>6M.1</b>	The Definition of Standard Potential / 554	
<b>6M.2</b>	The Electrochemical Series / 559	
	<b>TOPIC 6M</b> Exercises / 560	
<b>Topic 6N</b>	<b>Applications of Standard Potentials</b>	561
<b>6N.1</b>	Standard Potentials and Equilibrium Constants / 561	
	<b>TOOLBOX 6N.1</b> How to Calculate Equilibrium Constants from Electrochemical Data / 562	
<b>6N.2</b>	The Nernst Equation / 563	
<b>6N.3</b>	Ion-Selective Electrodes / 566	
<b>6N.4</b>	Corrosion / 567	
	<b>TOPIC 6N</b> Exercises / 569	
<b>Topic 6O</b>	<b>Electrolysis</b>	571
<b>6O.1</b>	Electrolytic Cells / 571	
<b>6O.2</b>	The Products of Electrolysis / 573	
	<b>TOOLBOX 6O.1</b> How to Predict the Result of Electrolysis / 574	
<b>6O.3</b>	Applications of Electrolysis / 576	
	<b>TOPIC 6O</b> Exercises / 577	
<b>FOCUS 6</b>	Online Cumulative Example / 578	
<b>FOCUS 6</b>	Exercises / 578	
<b>INTERLUDE</b>	<b>Practical Cells</b> / 584	
	<b>FOCUS 7</b>	
	<b>KINETICS / 587</b>	
<b>Topic 7A</b>	<b>Reaction Rates</b>	588
<b>7A.1</b>	Concentration and Reaction Rate / 588	
	<b>BOX 7A.1</b> How Do We Know . . . What Happens to Atoms During a Reaction? / 591	
<b>7A.2</b>	The Instantaneous Rate of Reaction / 591	
<b>7A.3</b>	Rate Laws and Reaction Order / 592	
	<b>TOPIC 7A</b> Exercises / 598	
<b>Topic 7B</b>	<b>Integrated Rate Laws</b>	600
<b>7B.1</b>	First-Order Integrated Rate Laws / 600	
<b>7B.2</b>	Half-Lives for First-Order Reactions / 604	
<b>7B.3</b>	Second-Order Integrated Rate Laws / 606	
	<b>TOPIC 7B</b> Exercises / 609	
<b>Topic 7C</b>	<b>Reaction Mechanisms</b>	611
<b>7C.1</b>	Elementary Reactions / 611	
<b>7C.2</b>	The Rate Laws of Elementary Reactions / 612	
<b>7C.3</b>	Combining Elementary Rate Laws / 613	



<b>7C.4</b>	Rates and Equilibrium / 617	
<b>7C.5</b>	Chain Reactions / 618	
	<b>TOPIC 7C</b> Exercises / 619	
<b>Topic 7D</b>	<b>Models of Reactions</b>	621
<b>7D.1</b>	The Effect of Temperature / 621	
<b>7D.2</b>	Collision Theory / 624	
	<b>BOX 7D.1</b> How Do You Know . . . What Happens During a Molecular Collision? / 627	
<b>7D.3</b>	Transition State Theory / 628	
	<b>TOPIC 7D</b> Exercises / 630	
<b>Topic 7E</b>	<b>Catalysis</b>	631
<b>7E.1</b>	How Catalysts Work / 631	
	<b>BOX 7E.1</b> What Has This to Do With . . . The Environment? Protecting the Ozone Layer / 632	
<b>7E.2</b>	Industrial Catalysts / 635	
<b>7E.3</b>	Living Catalysts: Enzymes / 635	
	<b>TOPIC 7E</b> Exercises / 637	
<b>FOCUS 7</b>	Online Cumulative Example / 639	
<b>FOCUS 7</b>	Exercises / 639	
<b>FOCUS 8</b>		
<b>THE MAIN-GROUP ELEMENTS / 643</b>		
<b>Topic 8A</b>	<b>Periodic Trends</b>	644
<b>8A.1</b>	Atomic Properties / 644	
<b>8A.2</b>	Bonding Trends / 645	
<b>8A.3</b>	Trends Exhibited by Hydrides and Oxides / 646	
	<b>TOPIC 8A</b> Exercises / 648	
<b>Topic 8B</b>	<b>Hydrogen</b>	649
<b>8B.1</b>	The Element / 649	
	<b>BOX 8B.1</b> What Has This to Do With . . . The Environment? The Greenhouse Effect / 650	
<b>8B.2</b>	Compounds of Hydrogen / 652	
	<b>TOPIC 8B</b> Exercises / 653	
<b>Topic 8C</b>	<b>Group 1: The Alkali Metals</b>	654
<b>8C.1</b>	The Group 1 Elements / 654	
<b>8C.2</b>	Compounds of Lithium, Sodium, and Potassium / 656	
	<b>TOPIC 8C</b> Exercises / 658	
<b>Topic 8D</b>	<b>Group 2: The Alkaline Earth Metals</b>	659
<b>8D.1</b>	The Group 2 Elements / 659	
<b>8D.2</b>	Compounds of Beryllium, Magnesium, and Calcium / 661	
	<b>TOPIC 8D</b> Exercises / 663	
<b>Topic 8E</b>	<b>Group 13: The Boron Family</b>	664
<b>8E.1</b>	The Group 13 Elements / 664	
<b>8E.2</b>	Group 13 Oxides, Halides, and Nitrides / 666	
<b>8E.3</b>	Boranes, Borohydrides, and Borides / 668	
	<b>TOPIC 8E</b> Exercises / 669	
<b>Topic 8F</b>	<b>Group 14: The Carbon Family</b>	670
<b>8F.1</b>	The Group 14 Elements / 670	
	<b>BOX 8F.1</b> Frontiers of Chemistry: Self-Assembling Materials / 673	
<b>8F.2</b>	Oxides of Carbon and Silicon / 674	
<b>8F.3</b>	Other Important Group 14 Compounds / 675	
	<b>TOPIC 8F</b> Exercises / 676	
<b>Topic 8G</b>	<b>Group 15: The Nitrogen Family</b>	677
<b>8G.1</b>	The Group 15 Elements / 677	
<b>8G.2</b>	Compounds with Hydrogen and the Halogens / 679	
<b>8G.3</b>	Nitrogen Oxides and Oxoacids / 681	
<b>8G.4</b>	Phosphorus Oxides and Oxoacids / 682	
	<b>TOPIC 8G</b> Exercises / 684	
<b>Topic 8H</b>	<b>Group 16: The Oxygen Family</b>	685
<b>8H.1</b>	The Group 16 Elements / 685	
<b>8H.2</b>	Compounds with Hydrogen / 688	
<b>8H.3</b>	Sulfur Oxides and Oxoacids / 690	
	<b>TOPIC 8H</b> Exercises / 692	
<b>Topic 8I</b>	<b>Group 17: The Halogens</b>	693
<b>8I.1</b>	The Group 17 Elements / 693	
<b>8I.2</b>	Compounds of the Halogens / 695	
	<b>TOPIC 8I</b> Exercises / 697	
<b>Topic 8J</b>	<b>Group 18: The Noble Gases</b>	699
<b>8J.1</b>	The Group 18 Elements / 699	
<b>8J.2</b>	Compounds of the Noble Gases / 700	
	<b>TOPIC 8J</b> Exercises / 701	
<b>FOCUS 8</b>	Online Cumulative Example / 702	
<b>FOCUS 8</b>	Exercises / 702	

## FOCUS 9

## THE d-BLOCK ELEMENTS / 705

**Topic 9A** Periodic Trends of the d-Block Elements 706

- 9A.1** Trends in Physical Properties / 706  
**9A.2** Trends in Chemical Properties / 708  
**TOPIC 9A** Exercises / 710

**Topic 9B** Selected d-Block Elements: A Survey 711

- 9B.1** Scandium Through Nickel / 711  
**9B.2** Groups 11 and 12 / 716  
**TOPIC 9B** Exercises / 718

**Topic 9C** Coordination Compounds 720

- 9C.1** Coordination Complexes / 720  
**BOX 9C.1** What Has This to Do With ... Staying Alive? Why We Need to Eat d-Metals / 721  
**TOOLBOX 9C.1** How to Name d-Metal Complexes and Coordination Compounds / 723  
**9C.2** The Shapes of Complexes / 725  
**9C.3** Isomers / 726  
**BOX 9C.2** How Do We Know...That a Substance Is Optically Active? / 729  
**TOPIC 9C** Exercises / 731

**Topic 9D** The Electronic Structure of d-Metal Complexes 733

- 9D.1** Crystal Field Theory / 733  
**9D.2** The Spectrochemical Series / 735  
**9D.3** The Colors of Complexes / 737  
**9D.4** Magnetic Properties of Complexes / 739  
**9D.5** Ligand Field Theory / 741  
**TOPIC 9D** Exercises / 742

**FOCUS 9** Online Cumulative Example / 744**FOCUS 9** Exercises / 744

## FOCUS 10

## NUCLEAR CHEMISTRY / 747

**Topic 10A** Nuclear Decay 748

- 10A.1** The Evidence for Spontaneous Nuclear Decay / 748  
**10A.2** Nuclear Reactions / 750

**10A.3** The Pattern of Nuclear Stability / 753**10A.4** Predicting the Type of Nuclear Decay / 754**10A.5** Nucleosynthesis / 755**BOX 10A.1** What Has This to Do With...Staying Alive? Nuclear Medicine / 756**TOPIC 10A** Exercises / 758**Topic 10B** Radioactivity 760**10B.1** The Biological Effects of Radiation / 760**10B.2** Measuring the Rate of Nuclear Decay / 761**BOX 10B.1** How Do We Know... How Radioactive a Material Is? / 762**10B.3** Uses of Radioisotopes / 765**TOPIC 10B** Exercises / 766**Topic 10C** Nuclear Energy 768**10C.1** Mass–Energy Conversion / 768**10C.2** The Extraction of Nuclear Energy / 770**10C.3** The Chemistry of Nuclear Power / 772**TOPIC 10C** Exercises / 773**FOCUS 10** Online Cumulative Example / 775**FOCUS 10** Exercises / 775

## FOCUS 11

## ORGANIC CHEMISTRY / 777

**Topic 11A** Structures of Aliphatic Hydrocarbons 778**11A.1** Types of Aliphatic Hydrocarbons / 778**TOOLBOX 11A.1** How to Name Aliphatic Hydrocarbons / 780**11A.2** Isomers / 783**11A.3** Physical Properties of Alkanes and Alkenes / 786**TOPIC 11A** Exercises / 787**Topic 11B** Reactions of Aliphatic Hydrocarbons 789**11B.1** Alkane Substitution Reactions / 789**11B.2** Synthesis of Alkenes and Alkynes / 789**11B.3** Electrophilic Addition / 790**TOPIC 11B** Exercises / 792

<b>Topic 11C</b>	<b>Aromatic Compounds</b>	793
11C.1	Nomenclature / 793	
11C.2	Electrophilic Substitution / 794	
	<b>TOPIC 11C Exercises / 797</b>	
<b>Topic 11D</b>	<b>Common Functional Groups</b>	798
11D.1	Haloalkanes / 798	
11D.2	Alcohols / 799	
11D.3	Ethers / 800	
11D.4	Phenols / 800	
11D.5	Aldehydes and Ketones / 801	
11D.6	Carboxylic Acids / 802	
11D.7	Esters / 802	
11D.8	Amines, Amino Acids, and Amides / 803	
	<b>TOOLBOX 11D.1</b> How to Name Simple Compounds with Functional Groups / 805	
	<b>TOPIC 11D Exercises / 806</b>	
<b>Topic 11E</b>	<b>Polymers and Biological Macromolecules</b>	808
11E.1	Addition Polymerization / 808	
11E.2	Condensation Polymerization / 810	
11E.3	Copolymers and Composite Materials / 812	
11E.4	Physical Properties of Polymers / 813	
	<b>BOX 11E.1</b> Frontiers of Chemistry: Conducting Polymers / 815	
11E.5	Proteins / 817	
11E.6	Carbohydrates / 819	
11E.7	Nucleic Acids / 820	
	<b>TOPIC 11E Exercises / 822</b>	
<b>FOCUS 11</b>	Online Cumulative Example / 824	
<b>FOCUS 11</b>	Exercises / 824	
<b>INTERLUDE</b>	<b>Technology: Fuels</b> / 829	

## MAJOR TECHNIQUES (ONLINE ONLY)

- 1 Infrared and Microwave Spectroscopy
- 2 Ultraviolet and Visible Spectroscopy

- 3 X-ray Diffraction
- 4 Chromatography
- 5 Mass Spectrometry
- 6 Nuclear Magnetic Resonance
- 7 Computation

## APPENDICES

<b>APPENDIX 1</b>	<b>Symbols, Units, and Mathematical Techniques</b>	A1
1A	Symbols / A1	
1B	Units and Unit Conversions / A3	
1C	Scientific Notation / A5	
1D	Exponents and Logarithms / A6	
1E	Equations and Graphs / A7	
1F	Calculus / A8	
<b>APPENDIX 2</b>	<b>Experimental Data</b>	A9
2A	Thermodynamic Data at 25 °C / A9	
2B	Standard Potentials at 25 °C / A16	
2C	Ground-State Electron Configurations / A18	
2D	The Elements / A19	
<b>APPENDIX 3</b>	<b>Nomenclature</b>	A25
3A	The Nomenclature of Polyatomic Ions / A25	
3B	Common Names of Chemicals / A26	
3C	Traditional Names of Some Common Cations With Variable Charge Numbers / A26	

**GLOSSARY** B1

**ANSWERS** C1

Self-Tests B C1

Odd-Numbered Exercises C12

**INDEX** D1

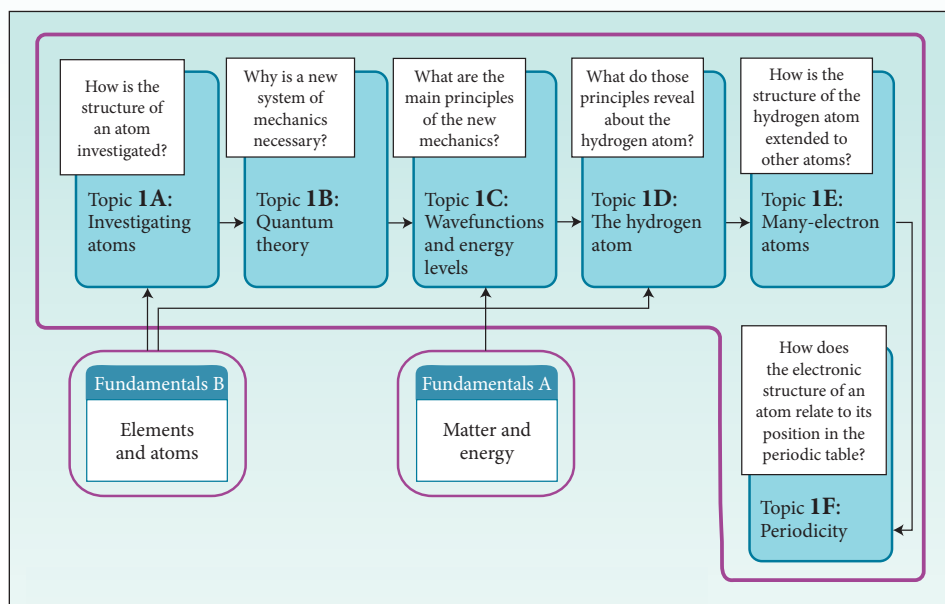
## Chemical Principles

The central theme of this text is to challenge students to think and question, while providing a sound foundation in the principles of chemistry. Students of all levels also benefit from assistance in learning how to think, pose questions, and approach problems. We show students how to build models, refine them systematically in the light of experimental input, and express them quantitatively. To that end, *Chemical Principles: The Quest for Insight*, Seventh Edition, aims to build understanding and offer students a wide array of pedagogical support.

## New Overall Organization

In this seventh edition, we have implemented a new organization. The content is presented as a series of 85 short *Topics* arranged into 11 thematic groups called *Focuses*. Our aim is twofold: to present reader and instructor with maximum flexibility and digestibility. We had a particular structure in mind when writing this edition, but instructors might have different ideas. Although the content is arranged along the lines of an atoms first approach, the division of Topics allows the instructor not only to tailor the text within the time constraints of the course, as it will be much easier to omit selected Topics, but also to take a path through the text that matches individual teaching and learning objectives. We have carefully avoided language that suggests the Topics should be read in the order they appear in the book. The student should also find the Topics easy to absorb and review, as each Topic is organized into smaller, more manageable sections. As such, since the Focuses are of very different lengths, instructors should target Topics, and not necessarily entire Focuses, when assigning content in their syllabi.

Each Focus begins with a brief discussion of how its Topics share a theme and how that theme links to others in the book. This contextual relationship is also captured visually by the “Road Map” that prefaces each Focus. We wanted to convey the intellectual structure of the subject, while leaving open the order of presentation.



Our core motivation is to help students to master the course content. Thus, each Topic opens with two questions a student typically faces: “Why do you need to know this material?”, and “What do you need to know already?” The answers to the second question point to other Topics that we consider appropriate to have studied in advance of the Topic at hand. We listened to the thoughtful advice of our reviewers and have

**Why Do You Need to Know This Material?** Ionic bonding is one of the principal forms of bonding between atoms. Understanding how bonds form between ions allows you to predict the formulas of ionic compounds and to estimate how strongly the ions are held together.

**What Do You Need to Know Already?** You need to know about electron configurations of many-electron atoms (Topic 1E), the concept of potential energy, and the nature of the Coulomb interaction between charges (*Fundamentals A*). You need to be familiar with ionic radii and the ionization energy and electron affinity of elements (Topic 1F).

ensured that this new organization guides and supports instructors and students through the individual paths they choose, to provide an improved classroom experience. Even the Road Map is designed to be an encouragement to learn, because we show how each Topic is inspired by a conceptual question.

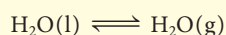
New to this edition, and specifically to Focus 5, is a new two-column approach for presenting derivations from both a kinetic and a thermodynamic viewpoint. This innovation aims to accommodate instructors who approach equilibrium from differing viewpoints and allows the instructors to take either path or to include both perspectives in their instruction.

Finally, we have collected all the Major Techniques in one group. These technique sections have been placed online for convenient access from laboratories or classroom, on our textbook catalog page: <http://macmillanhighered.com/chemicalprinciples7e>.

### How Is That Explained...

#### ...using kinetics?

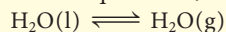
The *kinetic interpretation* of equilibrium is based on a comparison of competing rates, in this instance, the rates of evaporation and condensation. Vapor forms as molecules leave the surface of the liquid through evaporation. However, as the number of molecules in the vapor increases, more of them are available to condense, that is, to strike the surface of the liquid, stick to it, and become part of the liquid again. Eventually, the rate of molecules returning to the liquid matches the rate escaping (FIG. 5A.2). The vapor is now condensing as fast as the liquid is vaporizing, and so the equilibrium is *dynamic* in the sense that both the forward and reverse processes are still occurring but now their rates are equal. The **dynamic equilibrium** between liquid water and its vapor is denoted



Wherever the symbol  $\rightleftharpoons$  appears, it means that the species on both sides of it are in dynamic equilibrium with each other. With this picture in mind, the **vapor pressure** of a liquid (or a solid) can be defined as the pressure exerted by its vapor when the vapor and the liquid (or the solid) are in dynamic equilibrium with each other.

#### ...using thermodynamics?

In the *thermodynamic interpretation* of equilibrium, the condensed and vapor phases of a substance are in equilibrium, denoted



when there is no change in Gibbs free energy,  $\Delta G = 0$  for the phase change process. In short, neither the forward nor the reverse process is spontaneous at equilibrium. The **vapor pressure** of a liquid (or a solid) is the pressure exerted by its vapor when the vapor and the liquid (or the solid) are in equilibrium with each other.

## Reviewing the Basics

The *Fundamentals* sections are identified by green-edged pages. These sections provide a streamlined overview of the basics of chemistry. This material can be used either to provide a useful, succinct review of elementary material to which students can refer for extra help as they progress through the course, or as a concise survey of material before starting on the main text.

To support the *Fundamentals* sections pedagogically, we continue to provide the *Fundamentals Diagnostic Test*. This test allows instructors to determine what their students understand and where they need additional support. Instructors can then make appropriate assignments from the *Fundamentals*. The test includes 5 to 10 problems for each *Fundamentals* section. The diagnostic test was created by Cynthia LaBrake at the University of Texas, Austin. More information about the Fundamentals Diagnostic test can be found on our catalog page: <http://macmillanhighered.com/chemicalprinciples7e>.

## Innovative Math Coverage

- **What Does This Equation Tell You?** helps students to interpret an equation in physical and chemical terms. We aim to show that math is a language that reveals aspects of reality.

The result of the calculation is that the work done when a system expands by  $\Delta V$  against a constant external pressure  $P_{\text{ex}}$  is

$$w = -P_{\text{ex}}\Delta V \quad (3)$$

This expression applies to all systems. A gas is easiest to visualize, but the expression also applies to an expanding liquid or solid. However, Eq. 3 applies *only when the external pressure is constant* during the expansion.

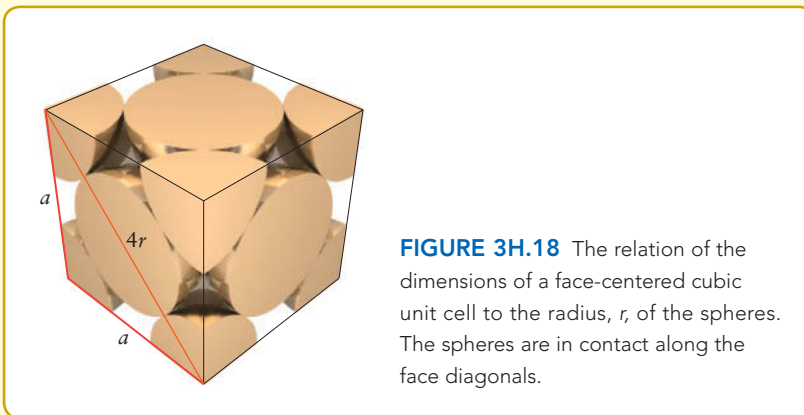
**What Does This Equation Tell You?** When the system expands,  $\Delta V$  is positive. Therefore the minus sign in Eq. 3 tells you that the internal energy of the system decreases when the system expands. The factor  $P_{\text{ex}}$  tells you that more work is done for a given change in volume when the external pressure is high. The factor  $\Delta V$  tells you that, for a given external pressure, more work is done the greater the change in volume.

- How Is That Done?** The text is designed so that mathematical derivations are set apart from the body of the text, making it easy for instructors to avoid or assign this material. This feature, which is structured in a way that encourages students to appreciate the power of math (by showing that vital progress depends on it), sets off derivations of key equations from the rest of the text. Virtually all the calculus in the text is confined to this feature, so it can be avoided if appropriate. For instructors who judge that their students can cope with this material and who want their students to realize the power that math puts into their hands, these derivations provide that encouragement. A selection of end-of-Focus exercises that make use of calculus is provided and marked with an icon:  $\int dx$ . Some derivations that we consider to be beyond this level but are useful as a resource, are located on the website.

### How Is That Done?

To calculate the fraction of occupied space in a close-packed structure, consider a ccp structure. First, look at how the cube is built from the spheres representing the atoms. **FIGURE 3H.18** shows that eight spheres lie at the corners of the cubes. Only  $\frac{1}{8}$  of each of these spheres projects into the cube, so the eight corner spheres collectively contribute  $8 \times \frac{1}{8} = 1$  sphere to the cube. Half a sphere on each of the six faces projects into the cube, so the spheres on each face contribute  $6 \times \frac{1}{2} = 3$  spheres, giving four spheres in all within the cube. The length of the diagonal of the face of the cube shown in Fig. 3H.18 is  $4r$ , where  $r$  is the radius of the sphere. Each of the two corner spheres contributes  $r$  and the sphere at the center of the face contributes  $2r$ . According to the Pythagorean theorem, the length of the side of the face,  $a$ , is related to the diagonal by  $a^2 + a^2 = (4r)^2$ , or  $2a^2 = 16r^2$ , and so  $a = 8^{1/2}r$ . The volume of the cube is therefore  $a^3 = 8^{3/2}r^3$ . The volume of each sphere is  $\frac{4}{3}\pi r^3$ , so the total volume of the spheres inside the cube is  $4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$ . The ratio of this occupied volume to the total volume of the cube is therefore

$$\frac{\text{Total volume of spheres}}{\text{Total volume of cube}} = \frac{(16/3)\pi r^3}{8^{3/2}r^3} = \frac{16\pi}{3 \times 8^{3/2}} = 0.74\dots$$



**FIGURE 3H.18** The relation of the dimensions of a face-centered cubic unit cell to the radius,  $r$ , of the spheres. The spheres are in contact along the face diagonals.

- Annotated equations** help students interpret an equation and see the connection between symbols and numerical values. We consider the correct use of units an important part of a student's vocabulary, not only because it is a part of the international language of chemistry but also because it encourages a systematic approach to calculations; in more complicated or unfamiliar contexts, we also use annotations to explain the manipulation of units.

$$w = -\overbrace{(0.100 \text{ mol})}^n \times \overbrace{(8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})}^R \times \overbrace{(298 \text{ K})}^T \times \ln \frac{V_2/V_1}{1.00 \text{ L}} = -172 \text{ J}$$

## Emphasis on Problem Solving

- **Notes on Good Practice** encourage conformity to the language of science by setting out the language and procedures adopted by the International Union of Pure and Applied Chemistry (IUPAC). In many cases, they identify common mistakes and explain how to avoid them.

**A Note on Good Practice:** A property  $y$  is said to “vary linearly with  $x$ ” if the relation between  $y$  and  $x$  can be written  $y = b + mx$ , where  $b$  and  $m$  are constants. A property  $y$  is said to be “proportional to  $x$ ” if  $y = mx$  (that is,  $b = 0$ ).

- **Anticipate/Plan/Solve/Evaluate Strategy.** This problem-solving approach encourages students to anticipate or predict what a problem’s answer should be qualitatively and to map out the solution before trying to solve the problem quantitatively. Following the solution, the original anticipation is evaluated. Students are often

### EXAMPLE 6B.1 Calculating a pH from a concentration

You are working in a medical laboratory monitoring the recovery of patients in intensive care. The pH of their blood must be carefully monitored and controlled because even small deviations from normal levels can be fatal. What is the pH of (a) human blood, in which the concentration of  $\text{H}_3\text{O}^+$  ions is  $4.0 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$ ; (b)  $0.020 \text{ M HCl(aq)}$ ; (c)  $0.040 \text{ M KOH(aq)}$ ?

**ANTICIPATE** The concentration of  $\text{H}_3\text{O}^+$  ions in blood is lower than in pure water, so you should expect  $\text{pH} > 7$ ; in  $\text{HCl(aq)}$ , an acid, you should expect  $\text{pH} < 7$ , and in  $\text{KOH(aq)}$ , a base,  $\text{pH} > 7$ .

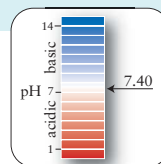
**PLAN** The pH is calculated from Eq. 1b. For strong acids, the molar concentration of  $\text{H}_3\text{O}^+$  is equal to the molar concentration of the acid. For strong bases, first find the concentration of  $\text{OH}^-$ , then convert that concentration into  $[\text{H}_3\text{O}^+]$  by using  $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$  in the form  $[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-]$ .

**What should you assume?** Assume that any strong acid (HCl here) is fully deprotonated in solution and any ionic compound (KOH here) is fully dissociated in solution.

#### SOLVE

(a) From  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ ,

$$\text{pH} = -\log(4.0 \times 10^{-8}) = 7.40$$

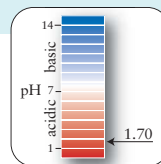


(b) HCl is a strong acid, so it is treated as completely deprotonated in water.

$$[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.020 \text{ mol}\cdot\text{L}^{-1}$$

From  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ ,

$$\text{pH} = -\log 0.020 = 1.70$$



(c) Because KOH is assumed to dissociate completely in solution each formula unit provides one  $\text{OH}^-$  ion,

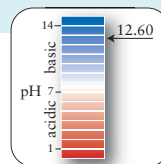
$$[\text{OH}^-] = [\text{KOH}] = 0.040 \text{ mol}\cdot\text{L}^{-1}$$

Find  $[\text{H}_3\text{O}^+]$  from  $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$  in the form  $[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-]$ .

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.040} = 2.5 \dots \times 10^{-13}$$

From  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ ,

$$\text{pH} = -\log(2.5 \dots \times 10^{-13}) = 12.60$$



**EVALUATE** The calculated pH values are in line with what was anticipated.

**Self-test 6B.1A** Calculate the pH of (a) household ammonia, in which the  $\text{OH}^-$  concentration is about  $3 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ; (b)  $6.0 \times 10^{-5} \text{ M HClO}_4(\text{aq})$ .

[Answer: (a) 11.5; (b) 4.22]

**Self-test 6B.1B** Calculate the pH of  $0.077 \text{ M NaOH(aq)}$ .

**Related Exercises:** 6B.3, 6B.4

puzzled about what they should assume in a calculation; many worked examples now include an explicit statement about what should be assumed. Because students process information in different ways, many steps in the worked examples are broken down into three components: a *qualitative* statement about what is being done, a *quantitative* explanation with the mathematics worked out, and a *visual* representation to aid with interpreting each step.

- **Real-world contexts for Worked Examples.** We want to motivate students and encourage them to see that the calculations are relevant to all kinds of careers and applications. With that aim in mind, we pose the problem in a context in which such calculations might occur.
- **Self-Tests** are provided as pairs throughout the book. They enable students to test their understanding of the material covered in the preceding section or worked example. The answer to the first self-test is provided immediately, and the answer to the second can be found at the back of the book.
- **Thinking Points** encourage students to speculate about the implications of what they are learning and to transfer their knowledge to new situations. This edition now provides instructors with suggested answers to the Thinking Points online on the textbook's catalog page: <http://macmillanhighered.com/chemicalprinciples7e>.

#### THINKING POINT

By what factor does the unique average reaction rate change if the coefficients in a chemical equation are doubled?

- **Toolboxes** show students how to tackle major types of calculations and demonstrate how to connect concepts to problem solving. The Toolboxes are designed as learning aids and handy summaries of key material. Each summarizes the conceptual basis of the following steps, because we are concerned that students understand what they are doing as well as be able to do it. Each Toolbox is followed immediately by one or more related Examples; these Examples apply the problem-solving strategy outlined in the Toolbox and illustrate each step of the procedure explicitly.

### Toolbox 6H.2 HOW TO CALCULATE THE pH DURING A TITRATION OF A WEAK ACID OR A WEAK BASE

#### CONCEPTUAL BASIS

The pH is governed by the major solute species present in solution. As strong base is added to a solution of a weak acid, a salt of the conjugate base of the weak acid is formed. This salt affects the pH and needs to be taken into account. **TABLE 6H.1** outlines the regions encountered during a titration and the primary equilibrium to consider in each region.

#### PROCEDURE

The procedure is like that in Toolbox 6H.1, except that an additional step is required to calculate the pH from the proton transfer equilibrium. First use reaction stoichiometry to find the amount of excess acid or base. Begin by writing the chemical equation for the reaction, then:

**Step 1** Calculate the amount of weak acid or base in the original analyte solution. Use  $n_j = V_{\text{analyte}}[J]$ .

**Step 2** Calculate the amount of  $\text{OH}^-$  ions (or  $\text{H}_3\text{O}^+$  ions if the titrant is an acid) in the volume of titrant added. Use  $n_j = V_{\text{titrant}}[J]$ .

**Step 3** Use reaction stoichiometry to calculate the following amounts:

- Weak acid–strong base titration: the amount of conjugate base formed in the neutralization reaction, and the amount of weak acid remaining.

- Weak base–strong acid titration: the amount of conjugate acid formed in the neutralization reaction, and the amount of weak base remaining.

Calculate the concentrations.

**Step 4** Find the “initial” molar concentrations of the conjugate acid and base in solution after neutralization, but before any proton transfer equilibrium with water is taken into account. Use  $[J] = n_j/V$ , where  $V$  is the total volume of the solution,  $V = V_{\text{analyte}} + V_{\text{titrant}}$ .

Calculate the pH.

**Step 5** Use the expression for  $K_a$  or  $K_b$  to find the  $\text{H}_3\text{O}^+$  concentration in a weak acid or the  $\text{OH}^-$  concentration in a weak base. Alternatively, if the concentrations of conjugate acid and base calculated in step 4 are both large relative to the concentration of hydronium ions, use them in the Henderson–Hasselbalch equation, Eq. 2 of Topic 6G,  $\text{pH} \approx \text{p}K_a + \log([\text{base}]_{\text{initial}}/[\text{acid}]_{\text{initial}})$ , to determine the pH. In each case, if the pH is less than 6 or greater than 8, assume that the autoprotolysis of water does not significantly affect the pH. If necessary, convert between  $K_a$  and  $K_b$  by using  $K_a \times K_b = K_w$ .

*This procedure is illustrated in Example 6H.3.*



- “**The skills you have mastered are the ability to:**” are checklists of key concepts provided at the end of each Topic. These checklists not only are a reminder of the subjects with which students should feel comfortable by the end of the topic but also offer a satisfying opportunity to check off the items that they consider they have grasped.

**The skills you have mastered are the ability to:**

- 1.** Determine the activation energy from the experimental temperature dependence of reaction rate constants (Example 7D.1).
- 2.** Predict the rate constant for a reaction at a new temperature if the activation energy and rate constant at one temperature are known (Example 7D.2).
- 3.** Discuss the Arrhenius parameters,  $A$  and  $E_a$ , in terms of models of reactions (Sections 7D.2 and 7D.3).

- **Margin Notes** are brief asides, placed in the margin right next to the relevant text, that provide an extra note of help to clarify concepts or usage or to make a historical point.

The VSEPR model was first proposed by the British chemists Nevil Sidgwick and Herbert Powell and has been developed by the Canadian chemist Ronald Gillespie.

Lewis structures (Topics 2B and 2C) show only how the atoms are connected and how the electrons are arranged around them. The **valence-shell electron-pair repulsion model** (VSEPR model) extends Lewis's theory of bonding by adding rules that account for bond angles and molecular shapes:

- **NEW! Interludes** describe a number of contemporary applications of chemistry by showing how chemistry is being used in a variety of modern contexts. New for this edition, there are five interludes, placed between various Focuses.
- **NEW! Topic- and Focus-Specific Exercises** give students the opportunity to practice solving problems that draw upon one Topic (these appear at the end of every Topic) and exercises that include and combine concepts from the entire Focus (these appear at the end of each Focus).

## Topic 3I Exercises

**3I.1** Estimate the relative density (compared to pure aluminum) of magnalium, a magnesium–aluminum alloy in which 30.0% of the aluminum atoms have been replaced by magnesium atoms without distortion of the crystal structure.

**3I.2** Estimate the relative density (compared to pure copper) of aluminium bronze, an alloy that is 8.0% by mass aluminium. Assume no distortion of the crystal structure.



**3I.9** A unit cell for the calcite structure can be found at <http://webmineral.com>. From this structure, identify (a) the crystal system and (b) the number of formula units present in the unit cell.



**3I.10** Consult <http://webmineral.com> and examine the unit cells of calcite and dolomite. (a) In what respects are these two structures the same? (b) In what respect are they different? (c) Where are the magnesium and calcium ions located in dolomite?

The following Example and Exercises draw on material from throughout Focus 3.

### FOCUS 3 Online Cumulative Example

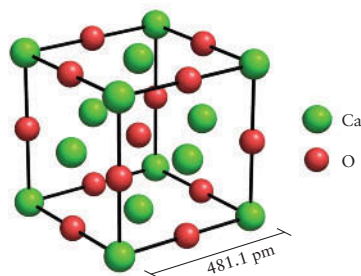
Some of the earliest mortars were *nonhydraulic cements*, which harden by reaction with  $\text{CO}_2$  rather than with water. These cements are prepared by heating calcite,  $\text{CaCO}_3(\text{s})$ , strongly to drive off  $\text{CO}_2$  gas and form quicklime,  $\text{CaO}(\text{s})$ . The resulting solid is mixed with water to give a paste of slaked lime,  $\text{Ca}(\text{OH})_2$ , to which sand or volcanic ash is added to form lime mortar. The Roman Colosseum and Pantheon were constructed with this type of mortar and have endured the ages. You are investigating ancient building methods and want to understand the chemistry of these materials.

(a) Write the balanced chemical equations for (i) the conversion of calcite to quicklime, (ii) the reaction of quicklime with water to form slaked lime, and (iii) the reaction of slaked lime with  $\text{CO}_2$  to form calcium carbonate.

(b) Preparing quicklime releases the greenhouse gas carbon dioxide. If 1.000 t ( $1 \text{ t} = 10^3 \text{ kg}$ ) of  $\text{CaCO}_3$  is placed in a kiln and heated to  $850^\circ\text{C}$ , what volume of  $\text{CO}_2(\text{g})$  is formed at  $850^\circ\text{C}$  and 1 atm?

(c) If the  $\text{CO}_2(\text{g})$  from part (b) is cooled to room temperature of  $22^\circ\text{C}$  what volume would it occupy?

(d) Calcium oxide has the cubic structure shown in (1). The length of each edge is 481.1 pm. All the atoms are on an edge, face, or corner of the cube with one O atom in the center of the cube. Use this information and the density of  $\text{CaCO}_3(\text{s})$ ,  $2.711 \text{ g}\cdot\text{cm}^{-3}$ , to calculate the change in volume of the solid as  $\text{CO}_2$  is driven off from 1.0 t of  $\text{CaCO}_3$ .



1 Calcium oxide,  $\text{CaO}$

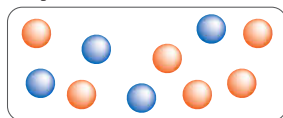
(e) From the results in part (d), suggest a reason why buildings constructed of bricks held together with lime mortar might collapse during a fire.



The online Cumulative Example solution can be found at <http://macmillanhighered.com/chemicalprinciples7e>

### FOCUS 3 Exercises

3.1 The drawing below shows a tiny section of a flask containing two gases. The orange spheres represent neon atoms and the blue spheres represent argon atoms. (a) If the partial pressure of neon in this mixture is 420. Torr, what is (a) the partial pressure of argon; (b) the total pressure?

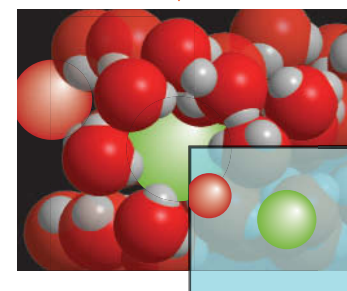
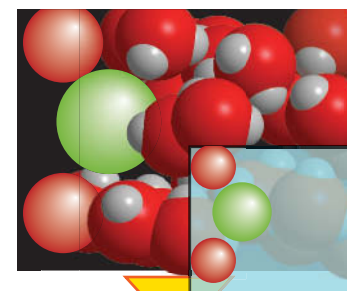
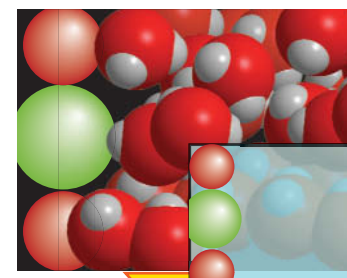


3.2 The four flasks below were prepared with the same volume

of gas. The partial pressure of carbon dioxide in the first flask is 0.26 Torr and that the temperature of the gas is  $20^\circ\text{C}$ . What is the volume of air at 1.0 atm needed to produce the same amount of  $\text{CO}_2$  as in the first flask?

3.4 Roommates fill ten balloons for a party and five with helium. After the party the hydrogen balloons have lost one-fifth of their hydrogen due to effusion. What fraction of helium balloons have lost at that same time?

3.5 Suppose that 200. mL of hydrogen chloride gas at  $20^\circ\text{C}$  and 1.0 atm is dissolved in 100. mL of water. The solution is then titrated to the stoichiometric point with 15.7 mL of




**FIGURE 5D.1** The events that take place at the interface of a solid ionic solute and a solvent (water). Only the surface layer of ions is shown. When the ions at the surface of the solid become hydrated, they move off into the solution. The insets at the right show the ions alone.

- **NEW! Online worked examples.** Each Focus ends with a Cumulative Example that challenges students to combine their understanding of concepts from several parts of the Focus. Full solutions presented in the same format as the worked examples in the text are available to students on the book's online catalog page: <http://macmillanhighered.com/chemicalprinciples7e>.

## Improved Illustration Program

- **NEW!** All the line art has been redrawn or refreshed for this edition using a new and more vibrant color palette.
- We have replaced many of the photographs with more revealing and often more relevant images.

# Contemporary Chemistry for All Students

Chemistry has an extraordinary range of applications, and we have sought to be inclusive and extensive in our discussion and use of examples. The brief contextual remarks in the worked examples help to illustrate this range. So too do some of the end-of-Focus exercises and the boxes that illustrate modern applications that occur throughout the text. We have kept in mind that engineers need a knowledge of chemistry, that biologists need a knowledge of chemistry, and that anyone anticipating a career in which materials are involved needs chemistry. Specific points relevant to the study of green chemistry are noted with an icon: . An important aspect of chemistry is that it provides transferable skills that can be deployed in a wide variety of careers; we have kept that in mind throughout, by showing readers how to think systematically, to build models based on observation, to be aware of magnitudes, to express qualitative ideas, concepts, and models quantitatively, and to interpret mathematical expressions physically.

## Media and Supplements

### For Students

We believe a student needs to interact with a concept several times in a variety of scenarios in order to obtain a thorough understanding. With that in mind, Macmillan Learning has developed a comprehensive package of student learning resources.

### Printed Resources

**Student Study Guide**, by John Krenos, Rutgers University  
ISBN: 1-319-01755-X


*The Student Study Guide* helps students to improve their problem-solving skills, avoid common mistakes, and understand key concepts. After a brief review of each Topic's critical ideas, students are taken through worked-out examples, try-it-yourself examples, and quizzes, all structured to reinforce the text's objectives and build problem-solving techniques.

**Student Solutions Manual**, by Laurence Lavelle, University of California, Los Angeles; Yinfa Ma, Missouri University of Science and Technology; and Christina Johnson, University of California, San Diego  
ISBN: 1-319-01756-8

*The Student Solutions Manual* follows the problem-solving structure set out in the main text and includes detailed solutions to all odd-numbered exercises in the text.

### Media Resources

The *Chemical Principles* student resources at <http://macmillanhigared.com/chemical-principles7e> provide a range of tools for problem solving and chemical explorations.

- **Solutions to Cumulative Examples.** Each Focus ends with a Cumulative Example that combines concepts from several parts of the Focus. Full solutions, presented in the same format as the worked examples in the text, are available to students on the catalog page.
- **Major Techniques** have been placed online for convenient access.
-  **Media Tools:**
  - **Living Graphs** allow the user to control the parameters.
  - **Animations** from the Vischem group are once again available to students and instructors.
  - **Lab Videos** are connected to figures in the text and demonstrate a laboratory experiment.

- **Molecule Database** links to *ChemSpider*, a free database of chemical structures, providing students access to information on over 35 million structures from hundreds of data sources. ChemSpider ID numbers have been provided in selected exercises to help students find the correct structures.
- **ChemCasts** replicate the face-to-face experience of watching an instructor work a problem. Using a virtual whiteboard, these video tutors show students the steps involved in solving key worked examples, while explaining the concepts along the way. They are easy to view on a computer screen or to download to a tablet or other media player.
- **Key Equations**, a compilation of key equations from the text
- **Interactive Periodic Table of Elements** links to [www.Ptable.com](http://www.Ptable.com), a dynamic periodic table with extensive information about each of the elements.

## For Instructors

Whether you are teaching the course for the first time or the hundredth time, the Instructor Resources to accompany *Chemical Principles* provide the resources you need to make teaching preparation efficient.

### Media Resources

Instructors can access valuable teaching tools through the *Chemical Principles* catalog page, <http://macmillanhighered.com/chemicalprinciples7e>. These resources are designed to aid the instructor throughout the teaching experience. They include:

- **Instructor's Solutions Manual**, by Laurence Lavelle, University of California, Los Angeles; Yinfu Ma, Missouri University of Science and Technology; and Christina Johnson, University of California, San Diego, which contains full, worked-out solutions to all even-numbered exercises in the text.
- **Updated Illustrations from the textbook** are offered as high-resolution .jpeg files and in PowerPoint format.
- **Newly Updated Lecture PowerPoints with Integrated Clicker Questions** have been developed to minimize preparation time for new users of the book. These files offer suggested lectures, including key illustrations, summaries, and clicker questions that instructors can adapt to their teaching styles.
- **Test Bank**, by Robert Balahura, University of Guelph, and Mark Benvenuto, University of Detroit, Mercy, which offers over 1400 multiple-choice, fill-in-the-blank, and essay questions and is available exclusively on the book's catalog page.

### Online Learning Environment

#### Sapling Learning

[www.saplinglearning.com](http://www.saplinglearning.com)

Developed by educators with both online expertise and extensive classroom experience, Sapling Learning provides highly effective interactive homework and instruction that improve student learning outcomes for the problem-solving disciplines. Sapling Learning offers an enjoyable teaching and effective learning experience that is distinctive in three important ways:

- **Ease of Use:** Sapling Learning's easy-to-use interface keeps students engaged in problem solving, not struggling with software.
- **Targeted Instructional Content:** Sapling Learning increases student engagement and comprehension by delivering immediate feedback and targeted instructional content.
- **Unsurpassed Service and Support:** Sapling Learning makes teaching more enjoyable by providing a dedicated Masters- or Ph.D.-level colleague to serve instructors' unique needs throughout the course, including help with content customization.

We offer bundled packages that include Sapling Learning Online Homework with all versions of our text.

### Lab Resources

Available stand-alone or bundled with the text for a nominal charge.  
ACS Molecular Structure Model Set, by Maruzen Company, Ltd.  
ISBN: 0-7167-4822-3

Molecular modeling helps students understand physical and chemical properties by providing a way to visualize the three-dimensional arrangement of atoms. This model set uses polyhedra to represent atoms and plastic connectors to represent bonds (scaled to correct bond length). Plastic plates representing orbital lobes are included for indicating lone pairs of electrons, radicals, and multiple bonds—a feature unique to this set.

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Welcome to chemistry! You are about to embark on a remarkable journey that will take you to the center of science. Looking in one direction, toward physics, you will see how the principles of chemistry are based on the behavior of atoms and molecules. Looking in another direction, toward biology, you will see how chemists contribute to an understanding of that most awesome property of matter, life. Eventually, you will be able to look at an everyday object, see in your mind's eye its composition in terms of atoms, and understand how that composition determines its properties.

## Introduction and Orientation

**Chemistry** is the science of matter and the changes it can undergo. The world of chemistry therefore embraces everything material around us—the stones you stand on, the food you eat, the flesh you are made of, and the silicon in your computers. There is nothing material beyond the reach of chemistry, be it living or dead, vegetable or mineral, on Earth or in a distant star.

### Chemistry and Society

In the earliest days of civilization, when the Stone Age gave way to the Bronze Age and then to the Iron Age, people did not realize that they were doing chemistry when they changed the material they found as stones—they would now be called *minerals*—into metals (FIG. 1). The possession of metals gave them a new power over their environment, and treacherous nature became less brutal. Civilization emerged as skills in transforming materials grew: glass, jewels, coins, ceramics, and, inevitably, weapons became more varied and effective. Art, agriculture, and warfare became more sophisticated. None of this would have happened without chemistry.

The development of steel accelerated the profound impact of chemistry on society. Better steel led to the Industrial Revolution, when muscles gave way to steam and giant enterprises could be contemplated. With improved transport and greater output from



**FIGURE 1** Copper is easily extracted from its ores and was one of the first metals worked. The Bronze Age followed the discovery that adding some tin to copper made the metal harder and stronger. These four bronze swords date from 1250 to 850 BCE, the Late Bronze Age, and are from a collection in the Naturhistorisches Museum, Vienna, Austria. From bottom to top, they are a short sword, an antenna-type sword, a tongue-shaped sword, and a Liptau-type sword. (Erich Lessing/Art Resource, NY.)





**FIGURE 2** Cold weather triggers chemical processes that reduce the amount of the green chlorophyll in leaves, allowing the colors of various other pigments to show. (David Q. Cavagnaro/Photolibary/Getty Images.)



**FIGURE 3** When magnesium burns in air, it gives off a lot of heat and light. The gray-white powdery product looks like smoke. (©1991 Richard Megna—Fundamental Photographs.)

 **LAB VIDEO FIGURE 3**

factories came more extensive trade, and the world became simultaneously a smaller but busier place. None of this would have happened without chemistry.

With the twentieth century, and now the twenty-first, came enormous progress in the development of the chemical industry. Chemistry transformed agriculture. Synthetic fertilizers provided the means of feeding the enormous, growing population of the world. Chemistry transformed communication and transportation. Today chemistry provides advanced materials, such as polymers for fabrics, ultrapure silicon for computers, and glass for optical fibers. It is producing more efficient renewable fuels and the tough, light alloys that are needed for modern aircraft and space travel. Chemistry has transformed medicine, substantially extended life expectancy, and provided the foundations of genetic engineering. The deep understanding of life that we are developing through molecular biology is currently one of the most vibrant areas of science. None of this progress would have been achieved without chemistry.

However, the price of all these benefits has been high. The rapid growth of industry and agriculture, for instance, has stressed the Earth and damaged our inheritance. There is now widespread concern about the preservation of our extraordinary planet. It will be up to you and your contemporaries to draw on chemistry—in whatever career you choose—to build on what has already been achieved. Perhaps you will help to start a new phase of civilization based on new materials, just as semiconductors transformed society in the twentieth century. Perhaps you will help to reduce the harshness of the impact of progress on our environment. To do that, you will need chemistry.

### Chemistry: A Science at Three Levels

Chemistry can be understood at three levels. At one level, chemistry is about matter and its transformations. This is the level at which you can see the changes, as when a leaf changes color in the fall (FIG. 2) or magnesium burns brightly in air (FIG. 3). This level is the **macroscopic level**, the level dealing with the properties of large, visible objects. However, there is an underworld of change, a world that you cannot see directly. At this deeper, **microscopic level**, chemistry interprets these phenomena in terms of the rearrangements of atoms (FIG. 4). The third level is the **symbolic level**, the expression of chemical phenomena in terms of chemical symbols and mathematical equations. A chemist thinks at the microscopic level, conducts experiments at the macroscopic level, and represents both symbolically. These three aspects of chemistry can be mapped as a triangle (FIG. 5). As you read further in this text, you will find that sometimes the topics and explanations are close to one vertex of the triangle, sometimes to another. Because it is helpful in understanding chemistry to make connections among these levels, in the worked examples in this book you will find drawings of the molecular level as well as graphical interpretations of equations. As your understanding of chemistry grows, so will your ability to travel easily within the triangle as you connect, for example, a laboratory observation to the symbols on a page and to mental images of atoms and molecules.

### How Science Is Done

Scientists pursue ideas in an ill-defined but effective way called the **scientific method**. There is no strict rule of procedure that will lead you from a good idea to a Nobel Prize or even to a publishable discovery. Some scientists are meticulously careful; others are highly creative. The best scientists are probably both careful and creative. Although there are various scientific methods in use, a typical approach consists of a series of steps (FIG. 6). The first step is often to collect **data**, the record of observations and measurements. These measurements are usually made on small **samples** of matter, representative pieces of the material being studied.

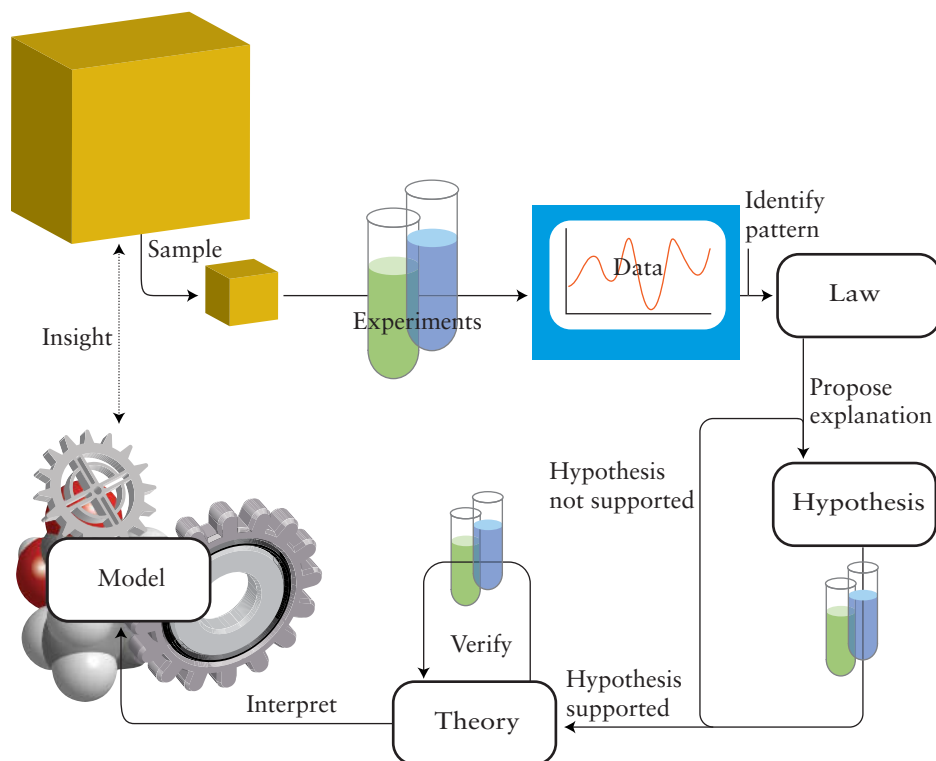
Scientists are always on the lookout for patterns. When a pattern is observed in the data, it can be stated as a scientific **law**, a succinct summary of a wide range of observations. For example, water was found to have eight times the mass of oxygen as it has of

hydrogen, regardless of the source of the water or the size of the sample. One of the earliest laws of chemistry summarized those types of observations as the **law of constant composition**, which states that a compound has the same composition regardless of the source of the sample.

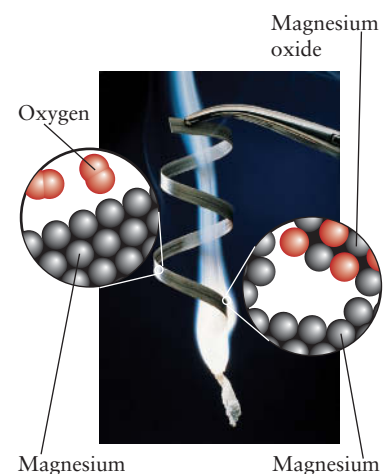
Formulating a law is just one way, not the only way, of summarizing data. There are many properties of matter (such as superconductivity, the ability of a few cold solids to conduct electricity without any resistance) that are currently at the forefront of research but are not described by grand “laws” that embrace hundreds of different compounds. A major current puzzle, which might be resolved in the future either by finding the appropriate law or by detailed individual computation, is what determines the shapes of protein molecules such as those that govern almost every aspect of life, including serious diseases such as Alzheimer’s, Parkinson’s, and cancer.

Once they have detected patterns, scientists may develop **hypotheses**, possible explanations of the laws—or the observations—in terms of more fundamental concepts. Observation requires careful attention to detail, but the development of a hypothesis requires insight, imagination, and creativity. In 1807, John Dalton interpreted experimental results to propose his **atomic hypothesis**, that matter consists of atoms. Although Dalton could not see individual atoms, he was able to imagine them and formulate his hypothesis. Dalton’s hypothesis was a monumental insight that helped others to understand the world in a new way. The process of scientific discovery never stops. With luck and application, you may acquire that kind of insight as you read through this text, and one day you may make your own extraordinary and significant hypotheses.

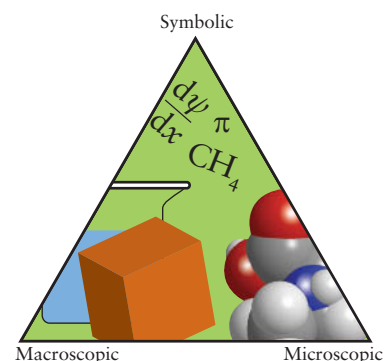
After formulating a hypothesis, scientists design further **experiments**—carefully controlled tests—to verify it. Designing and conducting good experiments often requires ingenuity and sometimes good luck. If the results of repeated experiments—often in other laboratories and sometimes by skeptical coworkers—support the hypothesis, scientists may go on to formulate a **theory**, a formal explanation of a law. Quite often the theory is expressed mathematically. A theory originally envisioned as a **qualitative** concept—a concept expressed in words or pictures—is converted into a



**FIGURE 6** A summary of the principal activities in a common version of the scientific method. The ideas proposed must be tested and possibly revised at each stage.



**FIGURE 4** When a chemical reaction takes place, atoms exchange partners, as in Fig. 3, where magnesium and oxygen atoms form magnesium oxide. As a result, two forms of matter (left inset) are changed into another form of matter (right inset). Atoms are neither created nor destroyed in chemical reactions. (Photo: ©1991 Richard Megna—Fundamental Photographs.)



**FIGURE 5** This triangle illustrates the three modes of scientific inquiry used in chemistry: macroscopic, microscopic, and symbolic. Sometimes chemists work more at one corner than at the others, but it is important to be able to move from one approach to another inside the triangle.



**FIGURE 7** Scientific research today often requires sophisticated equipment and computers. These scientists are using a portable gamma spectrometer to measure gamma radiation levels near Quezon City in the Philippines. (Bullit Marquez/AP Photo.)

**quantitative** form—the same concept expressed in terms of mathematics. After a concept has been expressed quantitatively, it can be used to make numerical predictions and is subjected to rigorous experimental confirmation. You will have plenty of practice with the quantitative aspects of chemistry while working through this text.

Scientists commonly interpret a theory in terms of a **model**, a simplified version of the object of study that they can use to make predictions. Like hypotheses, theories and models must be subjected to experiment and revised if experimental results do not support them. For example, the current model of the atom has gone through many formulations and progressive revisions, starting from Dalton's vision of an atom as an uncuttable solid sphere to the current, much more detailed model, which is described in Focus 1. One of the goals of this text is to show you how chemists build models, turn them into a testable form, and then refine them in the light of additional evidence.

## The Branches of Chemistry

Chemistry is more than test tubes and beakers. New technologies have transformed chemistry dramatically in the past 50 years, and new areas of research have emerged (FIG. 7). Traditionally, the field of chemistry has been organized into three main branches: **organic chemistry**, the study of compounds of carbon; **inorganic chemistry**, the study of all the other elements and their compounds; and **physical chemistry**, the study of the principles of chemistry.

New areas of study have developed as information has been acquired in specialized areas or as a result of the use of particular techniques. They include biochemistry, analytical chemistry, theoretical chemistry, computational chemistry, chemical engineering, medicinal chemistry, and biological chemistry. Various interdisciplinary branches of knowledge with roots in chemistry have also arisen, including **molecular biology**, the study of the chemical and physical basis of biological function and diversity; **materials science**, the study of the chemical structure and composition of materials; and **nanotechnology**, the study of matter on the scale of nanometers, at which structures consisting of a small number of atoms can be manipulated.



A newly emerging concern of chemistry is **sustainable development**, the economical utilization and renewal of resources coupled with hazardous waste reduction and concern for the environment. This sensitive approach to the environment and our planetary inheritance is known colloquially as **green chemistry**.

When it is appropriate to draw your attention to this important development, we display the small icon shown here.

All sciences, medicine, and many fields of commercial activity draw on chemistry. You can be confident that whatever career you choose in a scientific or technical field, it will make use of the concepts discussed in this text. Chemistry is truly central to science.

## Mastering Chemistry

You might already have a strong background in chemistry. These introductory pages with colored edges will provide you with a summary of a number of basic concepts and techniques. Your instructor will advise you how to use these sections to prepare yourself for the Topics in the text itself.

If you have little experience of chemistry, these pages are for you, too. They contain a brief but systematic summary of the basic concepts and calculations of chemistry that you should know before studying the Topics in the text. You can return to them as needed. If you need to review the mathematics required for chemistry, especially algebra and logarithms, Appendix 1 has a brief review of the important procedures.

## A Matter and Energy

Whenever you touch, pour, or weigh something, you are working with matter. Chemistry is concerned with the properties of matter and particularly the conversion of one form of matter into another kind. But what is matter? Matter is in fact difficult to define precisely without drawing on advanced ideas from elementary particle physics, but a straightforward working definition is that **matter** is anything that has mass and takes up space. Thus, gold, water, and flesh are forms of matter; electromagnetic radiation (which includes light) and justice are not.

One characteristic of science is that it uses common words from everyday language but gives them a precise meaning. In everyday language, a “substance” is just another name for matter. However, in chemistry, a **substance** is a *single, pure form of matter*. Thus, gold and water are distinct substances. Flesh is a mixture of many different substances, and, in the technical sense used in chemistry, it is not a “substance.” Air is matter, but, because it is a mixture of several gases, it is not a substance in the technical sense.

Substances, and matter in general, can take different forms, called **states of matter**. The three most common states of matter are solid, liquid, and gas.

A **solid** is a form of matter that retains its shape and does not flow.

A **liquid** is a fluid form of matter that has a well-defined surface; it takes the shape of the part of the container it occupies.

A **gas** is a fluid form of matter that fills any vessel containing it.

The term **vapor** denotes the gaseous form of a substance that is normally a solid or liquid. For example, water exists as solid (ice), liquid, and vapor (steam).

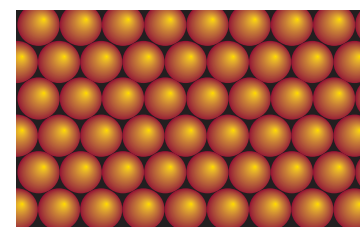
**FIGURE A.1** shows the different arrangements and mobilities of atoms and molecules in these three states of matter. In a solid, such as copper metal, the atoms are packed together closely; the solid is rigid because the atoms cannot move past one another. However, the atoms in a solid are not motionless: they oscillate around their average locations, and the oscillation becomes more vigorous as the temperature is raised. The atoms (and molecules) of a liquid are packed together about as closely as they are in a solid, but they have enough energy to move past one another readily. As a result, a liquid, such as water or molten copper, flows in response to a force, such as gravity. In a gas, such as air (which is mostly nitrogen and oxygen) and water vapor, the molecules have achieved almost complete freedom from one another: they fly through empty space at close to the speed of sound, colliding when they meet and immediately flying off in another direction.

### A.1 Symbols and Units

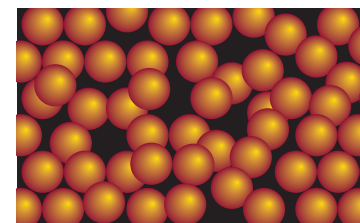
Chemistry is concerned with the **properties** of matter, its distinguishing characteristics. A **physical property** of a substance is a characteristic that can be observed or measured without changing the identity of the substance. For example, two physical properties of a sample of water are its mass and its temperature. Physical properties include characteristics such as melting point (the temperature at which a solid turns into a liquid), hardness, color, state of matter (solid, liquid, or gas), and density. When a substance undergoes a **physical change**, the identity of the substance does not change; only its physical properties are different. For example, when water freezes, the solid ice is still water. A **chemical property** refers to the ability of a substance to be changed into another substance. For example, a chemical property of the gas hydrogen is that it reacts with (burns in) oxygen to produce water; a chemical property of the metal zinc is that it reacts with acids to produce hydrogen gas. When a substance undergoes a **chemical change**, it is transformed into a different substance, such as hydrogen changing to water.

A measurable physical property is represented by an italic or sloping letter (thus, *m* for mass, not m). The result of the measurement, the “value” of a physical property, is reported as a multiple of a **unit**, such as reporting a mass as 15 kilograms, which is understood to be 15 times the unit “1 kilogram.” Scientists have reached international agreement on the units to use when reporting measurements, so their results can be used with

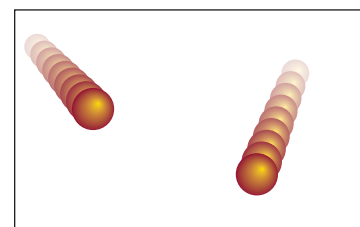
- A.1** Symbols and Units
- A.2** Accuracy and Precision
- A.3** Force
- A.4** Energy



(a)



(b)



(c)

**FIGURE A.1** Molecular representations of the three states of matter. In each case, the spheres represent particles that may be atoms, molecules, or ions. (a) In a solid, the particles are packed tightly together and held in place, but they continue to oscillate. (b) In a liquid, the particles are in contact, but they have enough energy to move past one another. (c) In a gas, the particles are far apart, move almost completely freely, and are in ceaseless random motion.

confidence and checked by people anywhere in the world. You will find most of the symbols used in this textbook together with their units in Appendix 1.

**A Note on Good Practice:** All units are denoted by Roman letters, such as *m* for meter and *s* for second, which distinguishes them from the physical quantity to which they refer (such as *l* for length and *t* for time).

The **Système International** (SI) is the internationally accepted form and elaboration of the metric system. It defines seven **base units** in terms of which all measurable physical properties can be expressed. At this stage all you need are

1 meter, 1 m	1 <b>meter</b> , the unit of length
1 kilogram, 1 kg	1 <b>kilogram</b> , the unit of mass
1 second, 1 s	1 <b>second</b> , the unit of time

All the units are defined in Appendix 1B. Each unit may be modified by a prefix that represents a multiple of 10 (and typically  $10^3$  or  $1/10^3$ ). The full set is given in Appendix 1B; some common examples are

Prefix	Symbol	Factor	Example
kilo-	k	$10^3$ (1000)	1 km = $10^3$ m (1 kilometer)
centi-	c	$10^{-2}$ (1/100, 0.01)	1 cm = $10^{-2}$ m (1 centimeter)
milli-	m	$10^{-3}$ (1/1000, 0.001)	1 ms = $10^{-3}$ s (1 millisecond)
micro-	$\mu$	$10^{-6}$ (1/1 000 000, 0.000 001)	1 $\mu$ g = $10^{-6}$ g (1 microgram)
nano-	n	$10^{-9}$ (1/1 000 000 000, 0.000 000 001)	1 nm = $10^{-9}$ m (1 nanometer)

Units may be combined into **derived units** to express a property that is more complicated than mass, length, or time. For example, **volume**, *V*, the amount of space occupied by a substance, is the product of three lengths; therefore, the derived unit of volume is (meter)<sup>3</sup>, denoted m<sup>3</sup>. Similarly, **density**, the mass of a sample divided by its volume, is expressed in terms of the base unit for mass divided by the derived unit for volume—namely, kilogram/(meter)<sup>3</sup>, denoted kg/m<sup>3</sup> or, equivalently, kg·m<sup>-3</sup>.

**A Note on Good Practice:** The SI convention is that a power, such as the 3 in cm<sup>3</sup>, refers to the base unit and its prefix. That is, cm<sup>3</sup> should be interpreted as (cm)<sup>3</sup> or  $10^{-6}$  m<sup>3</sup>, *not* as c(m<sup>3</sup>) or  $10^{-2}$  m<sup>3</sup>.

It is often necessary to convert measurements from another set of units into SI units. For example, when converting a length measured in inches (in.) into centimeters (cm), it is necessary to use the relation 1 in. = 2.54 cm. Relations between common units can be found in Table 5 of Appendix 1B. They are used to construct a **conversion factor** of the form

$$\text{Conversion factor} = \frac{\text{units required}}{\text{units given}}$$

which is then used as follows:

$$\text{Information required} = \text{information given} \times \text{conversion factor}$$

When using a conversion factor, treat the units just like algebraic quantities: they can be multiplied or canceled in the normal way.

### EXAMPLE A.1 Converting units

Suppose you are in a store—perhaps in Canada or Europe—where paint is sold in liters. You know you need 1.7 qt of a particular paint. What is that volume in liters?

**ANTICIPATE** A glance at Table 5 in Appendix 1B shows that 1 L is slightly more than 1 qt, so you should expect a volume of slightly less than 1.7 L.

**PLAN** Identify the relation between the two units from Table 5 of Appendix 1B:

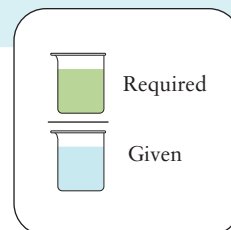
$$1 \text{ qt} = 0.946\,3525 \text{ L}$$

Then set up the conversion factor from the units given (qt) to the units required (L).

**SOLVE**

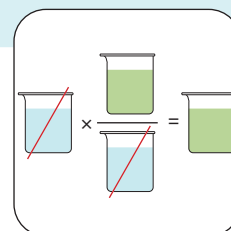
Form the conversion factor as (units required)/(units given).

$$\text{Conversion factor} = \frac{0.946\,3525 \text{ L}}{1 \text{ qt}}$$



Convert the measurement into the required units.

$$\text{Volume (L)} = (1.7 \text{ qt}) \times \frac{0.946\,3525 \text{ L}}{1 \text{ qt}} = 1.6 \text{ L}$$



**EVALUATE** As expected, you need slightly less than 1.7 L. The answer has been rounded to two digits, as explained in Appendix 1.

**Self-test A.1A** Express the height of a person 6.00 ft tall in centimeters.

[Answer: 183 cm]

**Self-test A.1B** Express the mass in ounces of a 250.-g package of breakfast cereal.

**Related Exercises** A.13, A.14, A.31, A.32

It is often necessary to convert a unit that has been raised to a power (including negative powers). In such cases, the conversion factor is raised to the same power. For example, to convert a density,  $d$ , of  $11\,700 \text{ kg}\cdot\text{m}^{-3}$  into grams per centimeter cubed ( $\text{g}\cdot\text{cm}^{-3}$ ), use the two relations

$$1 \text{ kg} = 10^3 \text{ g} \text{ and } 1 \text{ cm} = 10^{-2} \text{ m}$$

as follows:

$$\begin{aligned} d &= (11\,700 \text{ kg}\cdot\text{m}^{-3}) \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \left(\frac{1 \text{ cm}}{10^{-2} \text{ m}}\right)^{-3} \\ &= (11\,700 \text{ kg}\cdot\text{m}^{-3}) \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{10^{-6} \text{ m}^3}{1 \text{ cm}^3} \\ &= 11.7 \frac{\text{g}}{\text{cm}^3} = 11.7 \text{ g}\cdot\text{cm}^{-3} \end{aligned}$$

**Self-test A.2A** Express a density of  $6.5 \text{ g}\cdot\text{mm}^{-3}$  in micrograms per nanometer cubed ( $\mu\text{g}\cdot\text{nm}^{-3}$ ).

[Answer:  $6.5 \times 10^{-12} \mu\text{g}\cdot\text{nm}^{-3}$ ]

**Self-test A.2B** Express an acceleration of  $9.81 \text{ m}\cdot\text{s}^{-2}$  in kilometers per hour squared.

As remarked above, units are treated like algebraic quantities and are multiplied and canceled just like numbers. One consequence is that a quantity like  $m = 5 \text{ kg}$  could also

Answers to all B self-tests are in the back of this book.



**FIGURE A.2** Mass is an extensive property, but temperature is intensive. These two samples of iron(II) sulfate solution were taken from the same well-mixed supply; they have different masses but the same temperature. (W.H. Freeman photo by Ken Karp.)

Units for physical properties and temperature scales are discussed in Appendix 1B.

be reported as  $m/\text{kg} = 5$  by dividing both sides by kg. Likewise, the answer in the density conversion could have been reported as  $d/(\text{g}\cdot\text{cm}^{-3}) = 11.7$ .

Properties can be classified according to their dependence on the size of a sample:

An **extensive property** is a property that depends on the size (“extent”) of the sample.

An **intensive property** is independent of the size of the sample.

More precisely, if a system is divided into parts and it is found that the property of the complete system has a value that is the sum of the values of the property of all the parts, then that property is extensive. If that is not the case, then the property is intensive. Volume is an extensive property: 2 kg of water occupies twice the volume of 1 kg of water. Temperature is an intensive property, because whatever the size of the sample taken from a uniform bath of water, it has the same temperature (FIG. A.2). The importance of the distinction is that different substances can be identified by their intensive properties. Thus, a sample can be recognized as water by noting its color, density ( $1.00\text{ g}\cdot\text{cm}^{-3}$ ), melting point ( $0\text{ }^\circ\text{C}$ ), boiling point ( $100\text{ }^\circ\text{C}$ ), and the fact that it is a liquid.

Some intensive properties are ratios of two extensive properties. For example, density is a ratio of the mass,  $m$ , of a sample divided by its volume,  $V$ :

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \quad \text{or} \quad d = \frac{m}{V} \quad (1)$$

The density of a substance is independent of the size of the sample because doubling the volume also doubles the mass, so the ratio of mass to volume remains the same. Density is therefore an intensive property and can be used to identify a substance. Most properties of a substance depend on its state of matter and conditions, such as the temperature and pressure. For example, the density of water at  $0\text{ }^\circ\text{C}$  is  $1.000\text{ g}\cdot\text{cm}^{-3}$ , but at  $100\text{ }^\circ\text{C}$  it is  $0.958\text{ g}\cdot\text{cm}^{-3}$ . The density of ice at  $0\text{ }^\circ\text{C}$  is  $0.917\text{ g}\cdot\text{cm}^{-3}$ , but the density of water vapor at  $100\text{ }^\circ\text{C}$  and atmospheric pressure is nearly 2000 times less, at  $0.597\text{ g}\cdot\text{L}^{-1}$ .

#### THINKING POINT

When you heat a gas at constant pressure, it expands. Does the density of a gas increase, decrease, or stay the same as it expands?

**Self-test A.3A** The density of selenium is  $4.79\text{ g}\cdot\text{cm}^{-3}$ . What is the mass of  $6.5\text{ cm}^3$  of selenium?

[Answer: 31 g]

**Self-test A.3B** The density of helium gas at  $0\text{ }^\circ\text{C}$  and  $1.00\text{ atm}$  is  $0.17685\text{ g}\cdot\text{L}^{-1}$ . What is the volume of a balloon containing  $10.0\text{ g}$  of helium under the same conditions?

*Chemical properties involve changing the identity of a substance; physical properties do not. Extensive properties depend on the size of the sample; intensive properties do not.*

## A.2 Accuracy and Precision

All measured quantities have some uncertainty associated with them; in science it is important to convey the degree to which you are confident about not only the values you report but also the results of calculations using those values. Notice that in Example A.1 the result of multiplying 1.7 by 0.946 3525 is written as 1.6, not 1.608 799 25. The number of digits reported in the result of a calculation must reflect the number of digits known from the data, not the entire set of digits the calculator might provide.

The number of **significant figures** in a numerical value is the number of digits that can be justified by the data:

When reporting the results of multiplication and division, identify the number of digits in the least precise value and retain that number of digits in the answer.

Thus, the measurement 1.7 qt has two significant figures (2 sf) and 0.946 3525 has seven (7 sf), so in Example A.1 the result is limited to 2 sf.

When reporting the results of addition or subtraction, identify the quantity with the least number of digits following the decimal point and retain that number of digits in the answer.

For instance, two very precise measurements of length might give 55.845 mm and 15.99 mm, and the total length would be reported as

$$55.845 \text{ mm} + 15.99 \text{ mm} = 71.83 \text{ mm}$$

with the precision of the answer governed by the number of digits in the data (shown here in red). The full set of rules for counting the number of significant figures and determining the number of significant figures in the result of a calculation is given in Appendix 1C, together with the rules for rounding numerical values.

An ambiguity may arise when dealing with a whole number ending in a zero, because the number of significant figures in the number may be less than the number of digits. For example, does 400 mean  $4 \times 10^2$  (1 sf),  $4.0 \times 10^2$  (2 sf), or  $4.00 \times 10^2$  (3 sf)? To avoid ambiguity, in this book, when all the digits in a number ending in zero are significant, the number is followed by a decimal point. Thus, the number 400. has 3 sf. In the “real world,” this helpful convention only rarely is adopted.

To make sure of their data, scientists usually repeat their measurements several times, report the average value, and assess the precision and accuracy of their measurements:

The **precision** of a measurement is an indication of how close repeated measurements are to one another.

The **accuracy** of a series of measurements is the closeness of their average value to the true value.

The illustration in **FIG. A.3** distinguishes precision from accuracy. As the illustration suggests, even precise measurements can give inaccurate values.

More often than not, measurements are accompanied by two kinds of error. A **systematic error** is an error that is present in every one of a series of repeated measurements. Systematic errors in a series of measurements always have the same sign and magnitude. For instance, a laboratory balance might not be calibrated correctly and all recorded masses will be reported as either too high or too low. If you are using that balance to measure the mass of a sample of silver, then even though you might be justified in reporting your measurements to a precision of five significant figures (such as 5.0450 g), the reported mass of the sample will be inaccurate. In principle, systematic errors can be discovered and corrected, but they often go unnoticed and in practice may be hard to identify. A **random error** is an error that varies in both sign and magnitude and can average to zero over a series of observations. An example is the effect of drafts of air from an open window moving a balance pan either up or down a little, decreasing or increasing the mass measurements randomly. Scientists attempt to minimize random error by making many observations and taking the average of the results.

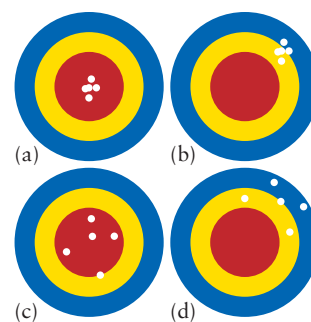
#### THINKING POINT

What are some means that scientists can use to identify and eliminate systematic errors?

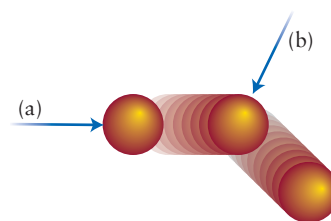
*The precision of a measurement is an indication of how close together repeated measurements are; the accuracy of a measurement is its closeness to the true value.*

### A.3 Force

**Speed**,  $v$ , is the rate of change of a body's position and is reported (in SI units) in meters per second ( $\text{m}\cdot\text{s}^{-1}$ ). **Velocity** is closely related to speed but takes into account the direction of motion as well as its rate. Thus, a particle moving in a circle at a constant speed has a constantly changing velocity. **Acceleration**,  $a$ , is the rate of change of velocity: a particle moving in a straight line at a constant speed is not accelerating (its speed and direction of travel is unchanging), but a particle moving at a constant speed in a curved path accelerates because although its speed is constant its velocity is changing (**FIG. A.4**). In SI units, acceleration is reported in meters per second squared ( $\text{m}\cdot\text{s}^{-2}$ ).



**FIGURE A.3** The holes in these targets represent measurements that are (a) precise and accurate, (b) precise but inaccurate, (c) imprecise but accurate on average, and (d) both imprecise and inaccurate.



**FIGURE A.4** (a) When a force acts along the direction of travel, the speed (the magnitude of the velocity) changes, but the direction of motion does not. (b) The direction of travel can be changed without affecting the speed if the force is applied in an appropriate direction. Both changes in velocity correspond to acceleration.