

Seventh Edition

CHEMISTRY

McMurry • Fay • Robinson



Chemistry

SEVENTH EDITION

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Brief Contents

Preface	xii
For Instructors	xiv
1 Chemical Tools: Experimentation and Measurement	1
2 Atoms, Molecules, and Ions	33
3 Mass Relationships in Chemical Reactions	77
4 Reactions in Aqueous Solution	111
5 Periodicity and the Electronic Structure of Atoms	154
6 Ionic Compounds: Periodic Trends and Bonding Theory	195
7 Covalent Bonding and Electron-Dot Structures	222
8 Covalent Compounds: Bonding Theories and Molecular Structure	261
9 Thermochemistry: Chemical Energy	311
10 Gases: Their Properties and Behavior	358
11 Liquids, Solids, and Phase Changes	410
12 Solutions and Their Properties	447
13 Chemical Kinetics	491
14 Chemical Equilibrium	553
15 Aqueous Equilibria: Acids and Bases	603
16 Applications of Aqueous Equilibria	656
17 Thermodynamics: Entropy, Free Energy, and Equilibrium	715
18 Electrochemistry	756
19 Nuclear Chemistry	808
20 Transition Elements and Coordination Chemistry	840
21 Metals and Solid-State Materials	892
22 The Main-Group Elements	927
23 Organic and Biological Chemistry	978

Contents

Preface xii
For Instructors xiv

1 Chemical Tools: Experimentation and Measurement 1

- 1.1 The Scientific Method in a Chemical Context: Improved Pharmaceutical Insulin 2
- 1.2 Experimentation and Measurement 6
- 1.3 Mass and Its Measurement 8
- 1.4 Length and Its Measurement 8
- 1.5 Temperature and Its Measurement 9
- 1.6 Derived Units: Volume and Its Measurement 11
- 1.7 Derived Units: Density and Its Measurement 12
- 1.8 Derived Units: Energy and Its Measurement 14
- 1.9 Accuracy, Precision, and Significant Figures in Measurement 16
- 1.10 Rounding Numbers 18
- 1.11 Calculations: Converting from One Unit to Another 20

INQUIRY >>> What are the unique properties of nanoscale materials? 23

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems

2 Atoms, Molecules, and Ions 33

- 2.1 Chemistry and the Elements 34
- 2.2 Elements and the Periodic Table 35
- 2.3 Some Common Groups of Elements and Their Properties 38
- 2.4 Observations Supporting Atomic Theory: The Conservation of Mass and the Law of Definite Proportions 41
- 2.5 The Law of Multiple Proportions and Dalton's Atomic Theory 43
- 2.6 Atomic Structure: Electrons 45
- 2.7 Atomic Structure: Protons and Neutrons 47
- 2.8 Atomic Numbers 49
- 2.9 Atomic Weights and the Mole 51
- 2.10 Mixtures and Chemical Compounds; Molecules and Covalent Bonds 54
- 2.11 Ions and Ionic Bonds 58
- 2.12 Naming Chemical Compounds 60

INQUIRY >>> How is the principle of atom economy used to minimize waste in a chemical synthesis? 66

Study Guide • Key Terms • Conceptual Problems • Section Problems • Chapter Problems

3 Mass Relationships in Chemical Reactions 77

- 3.1 Representing Chemistry on Different Levels 78
- 3.2 Balancing Chemical Equations 79
- 3.3 Chemical Arithmetic: Stoichiometry 82
- 3.4 Yields of Chemical Reactions 86
- 3.5 Reactions with Limiting Amounts of Reactants 88
- 3.6 Percent Composition and Empirical Formulas 91
- 3.7 Determining Empirical Formulas: Elemental Analysis 94
- 3.8 Determining Molecular Weights: Mass Spectrometry 97

INQUIRY >>> Can alternative fuels decrease CO₂ emissions? 101

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems

4 Reactions in Aqueous Solution 111

- 4.1 Solution Concentration: Molarity 112
- 4.2 Diluting Concentrated Solutions 114
- 4.3 Electrolytes in Aqueous Solution 116
- 4.4 Types of Chemical Reactions in Aqueous Solution 118
- 4.5 Aqueous Reactions and Net Ionic Equations 119
- 4.6 Precipitation Reactions and Solubility Guidelines 120
- 4.7 Acids, Bases, and Neutralization Reactions 123
- 4.8 Solution Stoichiometry 127
- 4.9 Measuring the Concentration of a Solution: Titration 128
- 4.10 Oxidation–Reduction (Redox) Reactions 130
- 4.11 Identifying Redox Reactions 133
- 4.12 The Activity Series of the Elements 135
- 4.13 Redox Titrations 138
- 4.14 Some Applications of Redox Reactions 141

INQUIRY >>> How do sports drinks replenish the chemicals lost in sweat? 142

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

5 Periodicity and the Electronic Structure of Atoms 154

- 5.1 The Nature of Radiant Energy and the Electromagnetic Spectrum 155
- 5.2 Particlelike Properties of Radiant Energy: The Photoelectric Effect and Planck's Postulate 158
- 5.3 The Interaction of Radiant Energy with Atoms: Line Spectra 160
- 5.4 The Bohr Model of the Atom: Quantized Energy 163
- 5.5 Wavelike Properties of Matter: de Broglie's Hypothesis 165
- 5.6 The Quantum Mechanical Model of the Atom: Heisenberg's Uncertainty Principle 167
- 5.7 The Quantum Mechanical Model of the Atom: Orbitals and Quantum Numbers 168
- 5.8 The Shapes of Orbitals 170
- 5.9 Electron Spin and the Pauli Exclusion Principle 174
- 5.10 Orbital Energy Levels in Multielectron Atoms 175
- 5.11 Electron Configurations of Multielectron Atoms 176
- 5.12 Anomalous Electron Configurations 178
- 5.13 Electron Configurations and the Periodic Table 178
- 5.14 Electron Configurations and Periodic Properties: Atomic Radii 181

INQUIRY >>> How does knowledge of atomic emission spectra help us build more efficient light bulbs? 184

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

6 Ionic Compounds: Periodic Trends and Bonding Theory 195

- 6.1 Electron Configurations of Ions 196
- 6.2 Ionic Radii 198
- 6.3 Ionization Energy 200
- 6.4 Higher Ionization Energies 202
- 6.5 Electron Affinity 204
- 6.6 The Octet Rule 206
- 6.7 Ionic Bonds and the Formation of Ionic Solids 208
- 6.8 Lattice Energies in Ionic Solids 211

INQUIRY >>> How has an understanding of ionic compounds led to the production of safer solvents? 214

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

7 Covalent Bonding and Electron-Dot Structures 222

- 7.1 Covalent Bonding in Molecules 223
- 7.2 Strengths of Covalent Bonds 225
- 7.3 Polar Covalent Bonds: Electronegativity 226
- 7.4 A Comparison of Ionic and Covalent Compounds 229
- 7.5 Electron-Dot Structures: The Octet Rule 231
- 7.6 Procedure for Drawing Electron-Dot Structures 234
- 7.7 Drawing Electron-Dot Structures for Radicals 238
- 7.8 Electron-Dot Structures of Compounds Containing Only Hydrogen and Second-Row Elements 240
- 7.9 Electron-Dot Structures and Resonance 242
- 7.10 Formal Charges 246

INQUIRY >>> How do we make organophosphate insecticides less toxic to humans? 250

Study Guide • Key Terms • Key Equations • Section Problems • Chapter Problems • Multiconcept Problems

8 Covalent Compounds: Bonding Theories and Molecular Structure 261

- 8.1 Molecular Shapes: The VSEPR Model 262
- 8.2 Valence Bond Theory 270
- 8.3 Hybridization and sp^3 Hybrid Orbitals 271
- 8.4 Other Kinds of Hybrid Orbitals 273
- 8.5 Polar Covalent Bonds and Dipole Moments 278
- 8.6 Intermolecular Forces 282
- 8.7 Molecular Orbital Theory: The Hydrogen Molecule 291
- 8.8 Molecular Orbital Theory: Other Diatomic Molecules 294
- 8.9 Combining Valence Bond Theory and Molecular Orbital Theory 297

INQUIRY >>> Why do different drugs have different physiological responses? 299

Study Guide • Key Terms • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

9 Thermochemistry: Chemical Energy 311

- 9.1 Energy and Its Conservation 312
- 9.2 Internal Energy and State Functions 314
- 9.3 Expansion Work 316
- 9.4 Energy and Enthalpy 318
- 9.5 Thermochemical Equations and the Thermodynamic Standard State 321
- 9.6 Enthalpies of Chemical and Physical Changes 323
- 9.7 Calorimetry and Heat Capacity 325
- 9.8 Hess's Law 329
- 9.9 Standard Heats of Formation 331
- 9.10 Bond Dissociation Energies 334
- 9.11 Fossil Fuels, Fuel Efficiency, and Heats of Combustion 335
- 9.12 An Introduction to Entropy 337
- 9.13 An Introduction to Free Energy 340

INQUIRY >>> How is the energy content of new fuels determined? 344

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

10 Gases: Their Properties and Behavior 358

- 10.1 Gases and Gas Pressure 359
- 10.2 The Gas Laws 364
- 10.3 The Ideal Gas Law 369
- 10.4 Stoichiometric Relationships with Gases 372
- 10.5 Mixtures of Gases: Partial Pressure and Dalton's Law 375
- 10.6 The Kinetic-Molecular Theory of Gases 378
- 10.7 Gas Diffusion and Effusion: Graham's Law 380
- 10.8 The Behavior of Real Gases 383
- 10.9 The Earth's Atmosphere and Air Pollution 384
- 10.10 The Greenhouse Effect 389
- 10.11 Climate Change 394

INQUIRY >>> Which gases are greenhouse gases? 392

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

11 Liquids, Solids, and Phase Changes 410

- 11.1 Properties of Liquids 411
- 11.2 Phase Changes between Solids, Liquids, and Gases 412

- 11.3 Evaporation, Vapor Pressure, and Boiling Point 417
- 11.4 Kinds of Solids 420
- 11.5 Probing the Structure of Solids: X-Ray Crystallography 422
- 11.6 The Packing of Spheres in Crystalline Solids: Unit Cells 425
- 11.7 Structures of Some Ionic Solids 430
- 11.8 Structures of Some Covalent Network Solids 432
- 11.9 Phase Diagrams 435

INQUIRY >>> How is caffeine removed from coffee? 437

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

12 Solutions and Their Properties 447

- 12.1 Solutions 448
- 12.2 Energy Changes and the Solution Process 449
- 12.3 Concentration Units for Solutions 454
- 12.4 Some Factors That Affect Solubility 458
- 12.5 Physical Behavior of Solutions: Colligative Properties 462
- 12.6 Vapor-Pressure Lowering of Solutions: Raoult's Law 462
- 12.7 Boiling-Point Elevation and Freezing-Point Depression of Solutions 469
- 12.8 Osmosis and Osmotic Pressure 473
- 12.9 Fractional Distillation of Liquid Mixtures 477

INQUIRY >>> How does hemodialysis cleanse the blood of patients with kidney failure? 479

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

13 Chemical Kinetics 491

- 13.1 Reaction Rates 492
- 13.2 Rate Laws and Reaction Order 497
- 13.3 Method of Initial Rates: Experimental Determination of a Rate Law 500
- 13.4 Integrated Rate Law: Zeroth-Order Reactions 503
- 13.5 Integrated Rate Law: First-Order Reactions 505
- 13.6 Integrated Rate Law: Second-Order Reactions 510
- 13.7 Reaction Rates and Temperature: The Arrhenius Equation 514
- 13.8 Using the Arrhenius Equation 518
- 13.9 Reaction Mechanisms 520
- 13.10 Rate Laws for Elementary Reactions 524
- 13.11 Rate Laws for Overall Reactions 526

- 13.12** Catalysis 530
13.13 Homogeneous and Heterogeneous Catalysts 533
13.14 Enzyme Catalysis 536

INQUIRY >>> What causes the ozone hole? 537

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

14 Chemical Equilibrium 553

- 14.1** The Equilibrium State 554
14.2 The Equilibrium Constant K_c 556
14.3 The Equilibrium Constant K_p 561
14.4 Heterogeneous Equilibria 564
14.5 Using the Equilibrium Constant 565
14.6 Factors that Alter the Composition of an Equilibrium Mixture: Le Châtelier's Principle 574
14.7 Altering an Equilibrium Mixture: Changes in Concentration 575
14.8 Altering an Equilibrium Mixture: Changes in Pressure and Volume 579
14.9 Altering an Equilibrium Mixture: Changes in Temperature 581
14.10 The Link between Chemical Equilibrium and Chemical Kinetics 584

INQUIRY >>> How does equilibrium affect oxygen transport in the bloodstream? 588

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

15 Aqueous Equilibria: Acids and Bases 603

- 15.1** Acid–Base Concepts: The Brønsted–Lowry Theory 604
15.2 Acid Strength and Base Strength 608
15.3 Factors That Affect Acid Strength 610
15.4 Dissociation of Water 613
15.5 The pH Scale 616
15.6 Measuring pH 618
15.7 The pH in Solutions of Strong Acids and Strong Bases 619
15.8 Equilibria in Solutions of Weak Acids 621
15.9 Calculating Equilibrium Concentrations in Solutions of Weak Acids 623
15.10 Percent Dissociation in Solutions of Weak Acids 627
15.11 Polyprotic Acids 628
15.12 Equilibria in Solutions of Weak Bases 632
15.13 Relation between K_a and K_b 634

- 15.14** Acid–Base Properties of Salts 636
15.15 Lewis Acids and Bases 640

INQUIRY >>> What is acid rain and what are its effects? 643

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

16 Applications of Aqueous Equilibria 656

- 16.1** Neutralization Reactions 657
16.2 The Common-Ion Effect 660
16.3 Buffer Solutions 664
16.4 The Henderson–Hasselbalch Equation 669
16.5 pH Titration Curves 672
16.6 Strong Acid–Strong Base Titrations 673
16.7 Weak Acid–Strong Base Titrations 676
16.8 Weak Base–Strong Acid Titrations 681
16.9 Polyprotic Acid–Strong Base Titrations 682
16.10 Solubility Equilibria for Ionic Compounds 686
16.11 Measuring K_{sp} and Calculating Solubility from K_{sp} 688
16.12 Factors That Affect Solubility 690
16.13 Precipitation of Ionic Compounds 698
16.14 Separation of Ions by Selective Precipitation 700
16.15 Qualitative Analysis 700

INQUIRY >>> What is causing a decrease in the pH of the oceans? 703

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

17 Thermodynamics: Entropy, Free Energy, and Equilibrium 715

- 17.1** Spontaneous Processes 716
17.2 Enthalpy, Entropy, and Spontaneous Processes: A Brief Review 717
17.3 Entropy and Probability 720
17.4 Entropy and Temperature 724
17.5 Standard Molar Entropies and Standard Entropies of Reaction 726
17.6 Entropy and the Second Law of Thermodynamics 728
17.7 Free Energy and the Spontaneity of Chemical Reactions 730
17.8 Standard Free-Energy Changes for Reactions 733
17.9 Standard Free Energies of Formation 736

17.10 Free-Energy Changes for Reactions under Nonstandard-State Conditions 738

17.11 Free Energy and Chemical Equilibrium 740

INQUIRY >>> Does entropy prevent the evolution of biological complexity? 744

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

18 Electrochemistry 756

18.1 Balancing Redox Reactions by the Half-Reaction Method 757

18.2 Galvanic Cells 761

18.3 Shorthand Notation for Galvanic Cells 766

18.4 Cell Potentials and Free-Energy Changes for Cell Reactions 767

18.5 Standard Reduction Potentials 769

18.6 Using Standard Reduction Potentials 773

18.7 Cell Potentials under Nonstandard-State Conditions: The Nernst Equation 775

18.8 Electrochemical Determination of pH 777

18.9 Standard Cell Potentials and Equilibrium Constants 779

18.10 Batteries 782

18.11 Corrosion 785

18.12 Electrolysis and Electrolytic Cells 787

18.13 Commercial Applications of Electrolysis 790

18.14 Quantitative Aspects of Electrolysis 793

INQUIRY >>> How do hydrogen fuel cells work? 795

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

19 Nuclear Chemistry 808

19.1 Nuclear Reactions and Their Characteristics 809

19.2 Radioactivity 810

19.3 Nuclear Stability 813

19.4 Radioactive Decay Rates 816

19.5 Energy Changes during Nuclear Reactions 819

19.6 Nuclear Fission and Fusion 822

19.7 Nuclear Transmutation 827

19.8 Detecting and Measuring Radioactivity 828

19.9 Some Applications of Nuclear Chemistry 830

INQUIRY >>> Are there any naturally occurring nuclear reactors? 833

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

20 Transition Elements and Coordination Chemistry 840

20.1 Electron Configurations 842

20.2 Properties of Transition Elements 844

20.3 Oxidation States of Transition Elements 847

20.4 Chemistry of Selected Transition Elements 849

20.5 Coordination Compounds 854

20.6 Ligands 856

20.7 Naming Coordination Compounds 858

20.8 Isomers 862

20.9 Enantiomers and Molecular Handedness 867

20.10 Color of Transition Metal Complexes 869

20.11 Bonding in Complexes: Valence Bond Theory 870

20.12 Crystal Field Theory 874

INQUIRY >>> How does cisplatin kill cancer cells? 880

Study Guide • Key Terms • Key Equations • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

21 Metals and Solid-State Materials 892

21.1 Sources of the Metallic Elements 893

21.2 Metallurgy 894

21.3 Iron and Steel 897

21.4 Bonding in Metals 899

21.5 Semiconductors 902

21.6 Semiconductor Applications 905

21.7 Superconductors 909

21.8 Ceramics 912

21.9 Composites 915

INQUIRY >>> What are quantum dots and what controls their color? 916

Study Guide • Key Terms • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

22 The Main-Group Elements 927

22.1 A Review of General Properties and Periodic Trends 928

22.2 Distinctive Properties of the Second-Row Elements 930

22.3 Group 1A: Hydrogen 932

22.4 Group 1A: Alkali Metals 937

22.5 Group 2A: Alkaline-Earth Metals 939

- 22.6** Group 3A: Elements 940
- 22.7** Group 4A: Carbon 942
- 22.8** Group 4A: Silicon 946
- 22.9** Group 5A: Nitrogen 950
- 22.10** Group 5A: Phosphorus 954
- 22.11** Group 6A: Oxygen 957
- 22.12** Group 6A: Sulfur 961
- 22.13** Group 7A: The Halogens 964
- 22.14** Group 8A: Noble Gases 966

INQUIRY >>> What are the barriers to a hydrogen economy? 967

Study Guide • Key Terms • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

23 Organic and Biological Chemistry 978

- 23.1** Organic Molecules and Their Structures: Alkanes 979
- 23.2** Families of Organic Compounds: Functional Groups 983
- 23.3** Naming Organic Compounds 985
- 23.4** Carbohydrates: A Biological Example of Isomers 990
- 23.5** Valence Bond Theory and Orbital Overlap Pictures 993
- 23.6** Lipids: A Biological Example of Cis–Trans Isomerism 997

- 23.7** Formal Charge and Resonance in Organic Compounds 1001
- 23.8** Conjugated Systems 1006
- 23.9** Proteins: A Biological Example of Conjugation 1009
- 23.10** Aromatic Compounds and Molecular Orbital Theory 1014
- 23.11** Nucleic Acids: A Biological Example of Aromaticity 1017

INQUIRY >>> Which is better, natural or synthetic? 1021

Study Guide • Key Terms • Conceptual Problems • Section Problems • Chapter Problems • Multiconcept Problems

Appendix A: Mathematical Operations A-1

- A.1** Scientific Notation A-1
- A.2** Logarithms A-4
- A.3** Straight-Line Graphs and Linear Equations A-6
- A.4** Quadratic Equations A-7

Appendix B: Thermodynamic Properties at 25 °C A-8

Appendix C: Equilibrium Constants at 25 °C A-13

Appendix D: Standard Reduction Potentials at 25 °C A-17

Appendix E: Properties of Water A-19

Answers to Selected Problems A-21

Glossary G-1

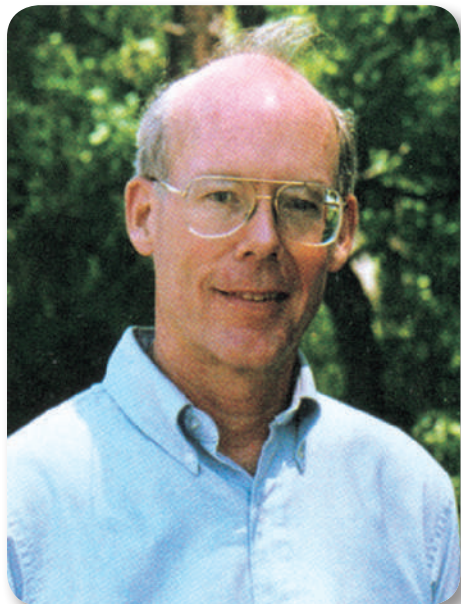
Index I-1

Photo/Text Credits C-1

List of Inquiries

- 1** Inquiry >>> What are the unique properties of nanoscale materials? 23
- 2** Inquiry >>> How is the principle of atom economy used to minimize waste in a chemical synthesis? 66
- 3** Inquiry >>> Can alternative fuels decrease CO₂ emissions? 101
- 4** Inquiry >>> How do sports drinks replenish the chemicals lost in sweat? 142
- 5** Inquiry >>> How does knowledge of atomic emission spectra help us build more efficient light bulbs? 184
- 6** Inquiry >>> How has an understanding of ionic compounds led to the production of safer solvents? 214
- 7** Inquiry >>> How do we make organophosphate insecticides less toxic to humans? 250
- 8** Inquiry >>> Why do different drugs have different physiological responses? 299
- 9** Inquiry >>> How is the energy content of new fuels determined? 344
- 10** Inquiry >>> Which gases are greenhouse gases? 392
- 11** Inquiry >>> How is caffeine removed from coffee? 437
- 12** Inquiry >>> How does hemodialysis cleanse the blood of patients with kidney failure? 479
- 13** Inquiry >>> What causes the ozone hole? 537
- 14** Inquiry >>> How does equilibrium affect oxygen transport in the bloodstream? 588
- 15** Inquiry >>> What is acid rain and what are its effects? 643
- 16** Inquiry >>> What is causing a decrease in the pH of the oceans? 703
- 17** Inquiry >>> Does entropy prevent the evolution of biological complexity? 744
- 18** Inquiry >>> How do hydrogen fuel cells work? 795
- 19** Inquiry >>> Are there any naturally occurring nuclear reactors? 833
- 20** Inquiry >>> How does cisplatin kill cancer cells? 880
- 21** Inquiry >>> What are quantum dots and what controls their color? 916
- 22** Inquiry >>> What are the barriers to a hydrogen economy? 967
- 23** Inquiry >>> Which is better, natural or synthetic? 1021

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FOR THE STUDENT

Francie came away from her first chemistry lecture in a glow. In one hour she found out that everything was made up of atoms which were in continual motion. She grasped the idea that nothing was ever lost or destroyed. Even if something was burned up or rotted away, it did not disappear from the face of the earth; it changed into something else—gases, liquids, and powders. Everything, decided Francie after that first lecture, was vibrant with life and there was no death in chemistry. She was puzzled as to why learned people didn't adopt chemistry as a religion.

—Betty Smith, *A Tree Grows in Brooklyn*

OK, not everyone has such a breathless response to their chemistry lectures, and few would mistake chemistry as a religion, yet chemistry *is* a subject with great logical beauty. We love chemistry because it explains the “why” behind many observations of the world around us and we use it every day to help us make informed choices about our health, lifestyle, and politics. Moreover, chemistry is the fundamental, enabling science that underlies many of the great advances of the last century that have so lengthened and enriched our lives. Chemistry provides a strong understanding of the physical world and will give you the foundation you need to go on and make important contributions to science and humanity.

HOW TO USE THIS BOOK

You no doubt have experience using textbooks and know they are not meant to read like a novel. We have written this book to provide you with a clear, cohesive introduction to chemistry in a way that will help you, as a new student of chemistry, understand and relate to the subject. While you *could* curl up with this book, you will greatly benefit from continually formulating questions and checking your understanding as you *work* through each section. The way this book is designed and written will help you keep your mind active, thus allowing you to digest big ideas as you learn some of the many principles of chemistry. Features of this book and how you should use them to maximize your learning are described below.

- 1. Narrative:** As you read through the text, always challenge yourself to understand the “why” behind the concept. For example, you will learn that carbon forms four bonds, and the narrative will give the reason why. By gaining a conceptual understanding, you will *not need to memorize* a large collection of facts, making learning and retaining important principles much easier!
- 2. Figures:** Figures are not optional! Most are carefully designed to summarize and convey important points. *Figure It Out* questions are included to draw your attention to a key principle. Answer the question by examining the figure and perhaps rereading the related narrative. Answers to *Figure It Out* questions are provided near the figure.
- 3. Worked Examples:** Numerous worked examples are given throughout the text to show the approach for solving a certain type of problem. A stepwise procedure is used within each worked example.

Identify—The first step in problem solving is to identify key information and classify it as a known or unknown quantity. This step also involves translating between words and chemical symbols. Listing knowns on one side and unknowns on the other organizes the information and makes the process of identifying the correct strategy more visual. The *Identify* step will be used in numerical problems.

Strategy—The strategy describes how to solve the problem without actually solving it. Failing to articulate the needed strategy is a common pitfall; too often students

start manipulating numbers and variables without first identifying key equations or making a plan. Articulating a strategy will develop conceptual understanding and is highly preferable to simply memorizing the steps involved in solving a certain type of problem.

Solution—Once the plan is outlined, the key information can be used and the answer obtained.

Check—A problem is not completed until you have thought about whether the answer makes sense. Use both your practical knowledge of the world and knowledge of chemistry to evaluate your answer. For example, if heat is added to a sample of liquid water and you are asked to calculate the final temperature, you should critically consider your answer: Is the final temperature lower than the original? Shouldn't adding heat raise the temperature? Is the new temperature above 100 °C, the boiling point of water? The **Check** step will be used in problems when the magnitude and sign of a number can be estimated or the physical meaning of the answer verified based on familiar observations.

To test your mastery of the concept explored in worked examples, two problems will follow. **PRACTICE** problems are similar in style and complexity to the worked example and will test your basic understanding. Once you have correctly completed this problem, tackle the **APPLY** problem, in which the concept is used in new situation. Video tutorials explaining some of the **APPLY** problems illustrate the process of expert thinking and point out how the same principle can be used in multiple ways.

- 4. Conceptual Problems:** Conceptual understanding is a primary focus of this book. Conceptual problems are intended to help you with the critical skill of visualizing the structure and interactions of atoms and molecules while probing your understanding of key principles rather than your ability to correctly use numbers in an equation. The time you spend mastering these problems will provide high long-term returns by solidifying main ideas.
- 5. Inquiries:** Inquiry sections connect chemistry to the world around you by highlighting useful links in the future careers of many science students. Typical themes are materials, medicine, and the environment. The goal of these sections is to deepen your understanding and aid in retention by tying concepts to memorable applications. These sections can be considered as a capstone for each chapter because *Inquiry* problems review several main concepts and calculations. These sections will also help you prepare for professional exams because they were written in the same style as new versions of these exams. For example, starting in 2015 the MCAT will provide a reading passage about a medical situation and you will be required to apply physical and chemical principles to interpret the system.
- 6. End-of-Chapter Study Guide and Problem Sets:** The end-of-chapter study guide can be used either during active study of the chapter or to prepare for an exam. The concept summary provides the central idea for each section, and learning objectives specify key skills needed to solve a variety of problems. Learning objectives are linked to end-of-chapter problems so that you can assess your mastery of that skill.

Working problems is essential for success in chemistry! The number and variety of problems at the end of chapter will give you the practice needed to gain mastery of specific concept. Answers to every other problem are given in the “Answers” section at the back of the book so that you can assess your understanding.

NEW TO THIS EDITION

One of the biggest challenges for general chemistry students is that they are often overwhelmed by the number of topics and massive amount information in the course. Frequently, they do not see connections between new material and previous content, thus creating barriers to learning. *Therefore, the table of contents was revised to create more uniform themes* within chapters and a coherent progression of concepts that build on one another.

- The focus of Chapter 1 has been changed to experimentation and measurements. In this 7th edition, the periodic table and element properties are covered in Chapter 2 (Chemistry Fundamentals: Elements, Molecules, and Ions).
- Coverage of nuclear reactions, radioactivity, and nuclear stability has been consolidated in this edition. Copy on nuclear reactions formerly found in Chapter 2 has been moved to Chapter 19 to keep all nuclear chemistry within one chapter.
- Solution stoichiometry and titrations were moved from Chapter 3 (Mass Relationships in Chemical Reactions) to Chapter 4 (Reactions in Aqueous Solutions).
- At the suggestion of instructors who used the last edition, coverage of redox stoichiometry now appears in the electrochemistry chapter where it is most needed. This change simplifies Chapter 4, which now serves as an introduction to aqueous reactions.
- The new edition features a chapter dedicated to main group chemistry. Main group chemistry sections formerly appearing in Chapter 6: Ionic Compounds: Periodic Trends and Bonding Theory are now incorporated into Chapter 22: The Main Group Elements.
- Covalent bonding and molecular structure are now covered in two chapters (7 and 8) to avoid having to cover an overwhelming amount of material in one chapter. The topic of intermolecular forces was added to Chapter 8 to reinforce its connection to polarity.
- Nuclear chemistry has been moved forward in the table of contents because of its relevance in energy production, medicine, and the environment.
- The chapter on hydrogen and oxygen has been omitted, but key chemical properties and reactions of hydrogen and oxygen are now covered in Chapter 22: The Main Group Elements.
- Chapter 10 dealing with gases now includes content on air pollution and climate change.
- Chapter 23 has been heavily revised to review important general chemistry principles of bonding and structure as they apply to organic and biological molecules. This chapter may be covered as a standalone chapter or sections may be incorporated into earlier chapters if an instructor prefers to cover organic and biological chemistry throughout the year.

NEW! All Worked Examples have been carefully revisited in the context of newly articulated Learning Outcomes.

Worked examples are now tied to Learning Outcomes listed at chapter end and to representative EOC problems so that students can test their own mastery of each skill.

Select worked examples now contain a section called **Identify**, which lays out the known and unknown variables for students. Listing knowns on one side and unknowns on the other organizes the information and makes the process of identifying the correct strategy more visual. The *Identify* step will be used in numerical problems with equations.

Worked examples in the 7th edition now conclude with two problems, one called **Practice** and the other called **Apply**, to help students see how the same principle can be used in different types of problems with different levels of complexity.

To discourage a plug-and-chug approach to problem solving, related Worked Examples from the previous edition have been consolidated, giving students a sense of how different approaches are related.

The number of in-chapter problems has increased by 20% to encourage the students to work problems actively immediately after reading.

NEW! Inquiry Sections have been updated and integrated conceptually into each chapter.

Inquiry sections highlight the importance of chemistry, promote student interest, and deepen the students understanding of the content. The new Inquiry sections include problems that revisit several chapter concepts and can be covered in class, recitation sections, or assigned as homework in MasteringChemistry.

NEW! Chapter Study Guide offers a modern and innovative way for students to review each chapter.

Prepared in a grid format, the main lessons of each chapter are reiterated and linked to learning objectives, associated worked examples, and representative end-of-chapter problems.

NEW! Figure It Out questions promote active learning.

Selected figures are tagged with questions designed to prompt students to look at each illustration more carefully, and interpret graphs and recognize key ideas.

NEW! Looking Forward Notes are now included.

Looking Forward Notes, in addition to Remember Notes, are included to underscore and reiterate connections between topics in different chapters.

NEW! Over 600 new problems have been written for the 7th edition.

New problems ensure there is a way to assess each learning objective in the Study Guide, all of which are suitable for use in MasteringChemistry.

The seventh edition was extensively revised. Here is a list of some of the key changes made in each chapter:

Chapter 1 Chemical Tools: Experimentation and Measurement

- Chapter 1 focuses on experimentation, the scientific method, and measurement and offers a new, robust Inquiry on nanotechnology.
- The scientific method is described in the context of a case study for the development of an insulin drug.

Chapter 2 Atoms, Molecules, and Ions

- Material on the elements and periodic table previously found in Chapter 1 has been relocated here, and nuclear chemistry has been moved to the nuclear chemistry chapter.
- Coverage of the naming of binary molecular compounds was moved to a later point in the chapter to consolidate coverage of the naming of ionic compounds.
- A new Inquiry on green chemistry, focusing on the concept of atom economy, revisits the Law of Conservation of Mass.

Chapter 3 Mass Relationships in Chemical Reactions

- Section 3.2 includes a revised Worked Example on balancing chemical reactions to give students a chance to use the method in simple and complex problems.
- New coverage of mass spectrometry in Section 3.8 explains how molecular weights are measured and mass spectral data

is utilized in problems. The topic of mass spectrometry is connected to crime scene analysis and offers a good example of how the new edition presents chemistry in a modern way.

- A new Inquiry explores CO₂ emissions from various alternative fuels using concepts of stoichiometry.

Chapter 4 Reactions in Aqueous Solution

- Section order and coverage were revised to keep the focus on solution chemistry.
- Problems and worked examples are rearranged so that conceptual worked examples lead off the discussion rather than wrap it up.
- The new Inquiry on sports drinks applies the concepts of electrolytes, solution concentration, and solution stoichiometry.

Chapter 5 Periodicity and Electronic Structure of Atoms

- Section 5.3 on line spectra has been revised to better show how spectral lines of the elements are produced.
- Sections 5.7–5.10 offer a more continuous description of how orbitals can be described using quantum numbers.
- The Inquiry on fluorescent lights was revised to include problems that require students to write electron configurations and interpret line spectra.

Chapter 6 Ionic Compounds: Periodic Trends and Bonding Theory

- As this is the first of three chapters on bonding, it now includes some introduction to topic sequence in Chapters 6–8.
- Every chapter problem is now preceded by a Worked Example and followed by Practice and Apply problems.
- New figures in Section 6.2 help visualize why creating an ion changes the size of an atom.
- Updated Inquiry on ionic liquids includes problems on writing ion electron configurations and relating ion size to properties of the ionic compound.
- Main group chemistry now appears in Chapter 22 (Main Group Chemistry).

Chapter 7 Covalent Bonding and Electron-Dot Structures

- Chapter 7 is now dedicated to covalent bonding using the Lewis electron-dot model. Valence shell electron pair repulsion theory, molecular shape, and molecular orbital theory now appear in Chapter 8.
- Section 7.6 summarizes a general procedure for drawing electron-dot structures and applies the procedure in new Worked Examples.
- The coverage of resonance includes an introduction to the use of curved arrows to denote rearrangement of electrons, a practice that is commonly used in organic chemistry courses.
- The new Inquiry, “How do we make organophosphate insecticides less toxic to humans?,” builds on several concepts introduced in this chapter, including polar covalent bonds, electron-dot structures, and resonance.
- The chapter includes many new figures. Much of the new art appears in revised Worked Examples, replacing and/or embellishing Worked Examples appearing in the prior edition.

Chapter 8 Covalent Compounds: Bonding Theories and Molecular Structure

- The focus of Chapter 7 is covalent bonds and electron-dot structures, whereas the focus of Chapter 8 is quantum mechanical theories of covalent bonding, molecular shape, polarity, and intermolecular forces. Polarity and intermolecular forces are a direct extension of molecular shape and have been moved from Chapter 10 to Chapter 8.
- Section 8.1 on the VSEPR model explains use of solid wedges and dashed lines to draw the 3-D structure of molecules.
- Many Worked Examples in this chapter were substantively revised to reflect the chapter’s new emphasis. New figures for Worked Examples 8.3 and 8.4 illustrate orbital overlap involved in each type of bond.
- Section 8.5 includes new Figure 8.8: A flowchart to show the strategy for determining molecular polarity. Worked Example 8.6 was revised to follow this flowchart.
- A New Conceptual Worked Example on drawing hydrogen bonds and new end of chapter problems were developed.
- The Inquiry for this chapter was expanded to include intermolecular forces in biomolecular binding. Two new figures were

added to illustrate how the mirror image has a different geometric arrangement of atoms and how this can lead to discrimination between these two molecules by a receptor site. New cumulative problems were added that include all topics in the chapter thus far: geometry, hybridization, polarity, intermolecular forces, and mirror images.

Chapter 9 Thermochemistry: Chemical Energy

- Section 9.2, Internal Energy and State Function, includes a new figure to illustrate ΔE in an example of the caloric content of food.
- Section 9.4, Energy and Enthalpy, has a new figure illustrating energy transfer as heat and work in a car’s engine to help students grasp the meaning of internal energy.
- Section 9.5, entitled “Thermochemical Equations and the Thermodynamic Standard State,” covers all aspects of writing and manipulating thermochemical equations (standard state, stoichiometry, reversibility, and importance of specifying phases).
- Section 9.6 on Enthalpy of Chemical and Physical Change offers improved definitions of endothermic and exothermic phenomena, including new Worked Examples and problems on classifying reactions and identifying direction of heat transfer.

Chapter 10 Gases: Their Properties and Behavior

- Chapter 10 is revised to include three new sections on atmospheric chemistry (air pollution, the greenhouse effect, and climate change) and a new Inquiry on greenhouse gases.
- There are thirty new end-of-chapter problems that require students to describe atmospheric chemistry and utilize many chemistry skills covered thus far in the book.

Chapter 11 Liquids, Solids, and Phase Changes

- Worked Example 11.2 is new and describes how to calculate the energy change associated with heating and phase changes.
- New Section 11.5 now includes two new images to enhance discussion of X-ray diffraction experiments.
- The Inquiry on decaffeination is new and builds on the topics of phase diagrams and energy of phase changes.

Chapter 12 Solutions and Their Properties

- Section 12.2 on Energy Changes and the Solution Process includes a new figure illustrating the hydrogen bonding interactions between solute and solvent (added emphasis on chemical structure and visual explanation of solubility).
- Section 12.3 on Concentration Units for Solutions has refined coverage of concentration units and a new Worked Example on ppm and ppb.
- Section 12.6 on Vapor-Pressure Lowering includes new Worked Examples on the van’t Hoff factor and on vapor pressure lowering with a volatile solute.
- The Inquiry on dialysis was expanded and improved through the addition of an illustration of dialysis and follow-up problems dealing with solution concentration and colligative properties.

Chapter 13 Chemical Kinetics

- The first section includes a generic introduction to the concept of a reaction rate, which is now used in problems throughout the chapter instead of reaction rates specific to a reactant or product.
- A new section on Enzyme Catalysis (Section 13.14) has been added, along with new end-of-chapter problems on this topic.
- Coverage of radioactive decay formerly included in this chapter has been moved to the nuclear chemistry chapter.
- The new Inquiry on ozone depletion builds on various kinetics concepts including activation energy determination, calculation of rate, reaction mechanisms, catalysis.

Chapter 14 Chemical Equilibrium

- Section 14.2 on The Equilibrium Constant K_c has an expanded discussion and new Worked Examples dealing with manipulating equations and calculating new values of K_c .
- Section 14.4 on Heterogeneous Equilibria has been revised to clarify when concentrations of pure solids and liquids present in a chemical equation are not included in the equilibrium constant.
- Section 14.5 on Using the Equilibrium Constant has been enhanced by the addition of a new worked example on Judging the Extent of a Reaction.
- Figure 14.6, entitled Steps in Calculating Equilibrium Concentrations, was modified to include the important first step of determining reaction direction.
- The Inquiry on equilibrium and oxygen transport now includes several follow-up problems that give students practice with various equilibrium concepts.

Chapter 15 Aqueous Equilibria: Acids and Bases

- Section 15.3, Factors that Affect Acid Strength, now appears earlier in the chapter to explain *why* chemical structure affects acid strength, and is bolstered by new Worked Example 15.4 entitled 'Evaluating Acid Strength Based Upon Molecular Structure' as well as new end-of-chapter problems.
- Section 15.5 on the pH scale includes new problems exploring environmental issues.
- The Inquiry on acid rain has been updated to include new statistics and a new figure illustrating changes in acid rainfall over time.

Chapter 16 Applications of Aqueous Equilibria

- Coverage of the Henderson-Hasselbalch Equation has been reworked so that students progress from simpler problems to more complex ones.
- Reaction tables are now routinely included in titration problems to help students see what species remain at the end of the neutralization reaction. New Worked Examples are included.
- Section 16.12 on Factors that Affect Solubility has been enhanced with relevant new examples (e.g., tooth decay).
- The new and highly pertinent Inquiry for Chapter 16 on ocean acidification revisits key concepts such as acid-base reactions, buffers, and solubility equilibria in a meaningful environmental context.

Chapter 17 Thermodynamics: Entropy, Free Energy, and Equilibrium

- Section 17.3 on Entropy and Probability is enhanced with a new Worked Example and follow-up problems on the expansion of an ideal gas.
- Different signs of enthalpy and entropy in are broken down on a case-by-case basis in Section 17.7.
- The Inquiry on biological complexity was heavily revised to describe why some biological reactions are spontaneous. The Inquiry now includes concrete examples of the thermodynamics of living systems and four relevant follow-up problems.

Chapter 18 Electrochemistry

- Section on balancing redox reactions using the half-reaction method was taken out of Chapter 4 and placed in Chapter 18 based on reviewer feedback.
- Coverage of fuel cells has been streamlined and incorporated into the Inquiry. New Inquiry problems revisit core thermodynamic and electrochemical concepts.

Chapter 19 Nuclear Chemistry

- All the nuclear chemistry content is now contained in Chapter 19.
- Coverage on balancing a nuclear reaction was revised to more clearly show that mass number and atomic number are equal on both sides of the equation.
- Figure 19.3 was added to illustrate the concept of a radioactive decay series.
- Several improvements were made in Section 19.6 on Fission and Fusion: the difference between nuclear fuel rods used in a reactor and weapons-grade nuclear fuel has been clarified; Figure 19.8 has been updated to include 2013 figures for nuclear energy output.
- New end-of-chapter problems dealing with aspects of nuclear power and nuclear weapons have been added.

Chapter 20 Transition Elements and Coordination Chemistry

- Worked Example 20.5, Identifying Diastereomers, has been revised and moved earlier so that students begin with a conceptual problem.
- Worked Example 20.6, Drawing Diastereomers for Square Planar and Octahedral Complexes, was rewritten to promote conceptual understanding and discourage rote memorization.
- A new Inquiry on the mechanism of action of the antitumor drug cisplatin reinforces several concepts covered in the chapter, including nomenclature, chirality, the formation of coordination compounds, and crystal field theory.

Chapter 21 Metals and Solid-State Materials

- Band theory in metals has been clarified by
 - describing the formation of band from MOs in more detail in the text
 - revising Figure 21.6 to show that bands contain many closely spaced MOs
 - the addition of Figure It Out questions that require extension of band theory to different systems.
- New Figure 21.10 on doping of semiconductors correlates molecular picture with energy level diagrams.

- The connection between LED color and periodic trends is described in Section 21.6. New problems are included.
- The Inquiry on quantum dots was heavily revised to more clearly connect with chapter content on band theory and semiconductors.

Chapter 22 The Main-Group Elements

- Main group chemistry is consolidated into one chapter. The content has been trimmed and key concepts related to periodic trends, bonding, structure, and reactivity are reviewed in the context of main group chemistry.
- The Inquiry Section dealing with barriers to a hydrogen economy describes hydrogen production and storage methods including recent development in photocatalysts.

Chapter 23 Organic and Biological Chemistry

- This chapter was revised so that the focus is on important concepts of structure and bonding that organic chemistry instructors would like students to master in general chemistry.
- Over 50 end-of-chapter problems are completely new.
- Section 23.1 offers an introduction to skeletal structures (line drawings) commonly used as a shorthand method for drawing organic structures.
- Coverage of the alkanes is consolidated in Section 23.1 (the cycloalkanes were formerly covered in Section 23.5 in 6e.).
- Coverage of the naming of organic compounds was shortened in 7e Section 23.3 because the primary focus of the new chapter is on bonding and structure.
- Section 23.4, entitled “Carbohydrates: A Biological Example of Isomers” offers a good example of how the applied chapters at the end of the book explore key concepts (isomerism) in a relevant context (carbohydrates).

- Section 23.4 also offers a good example of how key concepts from other chapters are revisited in the applied chapters at book end. Here chirality is revisited, a subject first presented in the Chapter 8 Inquiry.
- Section 23.5 considers cis-trans isomerism in the context of valence bond theory. Two new Worked Examples are included that describe orbital overlap in organic molecules.
- The theme of cis-trans isomerism is revisited in Section 23.6 with the introduction of the lipids. New Figure 23.6, for example, shows the difference in packing of saturated and unsaturated fats and the role played by intermolecular forces.
- Section 23.5 revisits the concepts of formal charge and resonance first introduced in Ch 7. Problems in this section give students additional practice in the drawing of electron-dot structures and electron “pushing.” Common patterns of resonance in organic molecules are introduced as well.
- Section 23.8 is new to the 7th edition, covering conjugated systems in the context of resonance and orbital diagrams. New worked examples tie the section together, offering problems on drawing conjugated π systems, and exploring how to recognize localized vs delocalized electrons.
- Section 23.9, entitled “Proteins: A Biological Example of Conjugation” follows logically from Section 23.8 to look at conjugation in the peptide bond and proteins.
- Section 23.10, new to the 7th edition, considers aromatic compounds in the context of molecular orbital theory. Building on students’ understanding of conjugation, molecular orbital theory is invoked to describe the stability of benzene.
- Section 23.11 on the nucleic acids expands on the discussion of aromaticity in describing how aromaticity makes base stacking in the interior of the DNA molecule possible.

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Showing Students the Connections in Chemistry and Why They Matter

McMurry/Fay/Robinson's Chemistry, Seventh Edition provides a streamlined presentation that blends the quantitative and visual aspects of chemistry, organizes content to highlight connections between topics and emphasizes the application of chemistry to students lives and careers. New content provides a better bridge between organic and biochemistry and general chemistry content, and new and improved pedagogical features make the text a true teaching tool and not just a reference book.

New MasteringChemistry features include conceptual worked examples and integrated Inquiry sections that help make critical connections clear and visible and increase students' understanding of chemistry. The Seventh Edition fully integrates the text with new MasteringChemistry content and functionality to support the learning process before, during, and after class.

INQUIRY >>> HOW IS CAFFEINE REMOVED FROM COFFEE?

437



Organic compounds with carbon-hydrogen bonds are nonpolar. Caffeine has high solubility in the nonpolar solvent benzene because a significant portion of the molecule is nonpolar.

CN1C=NC2=C1C(=O)N(C(=O)N2C)C
Caffeine

C1=CC=CC=C1
Benzene

A much safer method uses supercritical CO₂ to extract caffeine from coffee beans. CO₂ is nontoxic, nonflammable, easily separated from a food sample, and recyclable. It is a nonpolar molecule and dissolves nonpolar solutes such as caffeine. However, at room temperature and pressure (25 °C and 1 atm), CO₂ is a gas and cannot be used as a solvent. Raising the temperature and pressure produces the supercritical phase of CO₂, which has unique properties between those of gases and liquids. Supercritical CO₂ has solvent properties like the liquid phase, but the extraction can be performed faster than with a conventional organic solvent because it diffuses rapidly and flows easily like a gas. Supercritical CO₂ also has low surface tension allowing it to permeate into tiny pores in the coffee beans and dissolve caffeine on the inside.

The phase diagram of CO₂ shown in **FIGURE 11.23** shows that the supercritical phase of CO₂ can be reached at a relatively

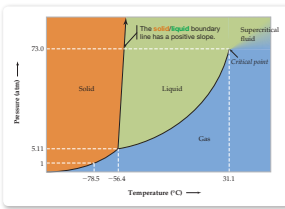


FIGURE 11.23
A phase diagram for CO₂. The pressure and temperature axes are not to scale.

moderate temperature and pressure (31.1 °C and 73.0 atm). The easily attainable critical point for CO₂ makes it the most widely used supercritical fluid. Industrial and research applications use supercritical CO₂ as a solvent in environmentally friendly dry cleaning, analytical separations, and polymerization reactions. The phase diagram for CO₂ has many of the same features as that of water (Figure 11.21) but differs in several interesting respects. First, the triple point is at $P_3 = 5.11$ atm, meaning that CO₂ can't be a liquid below this pressure, no matter what the temperature. At 1 atm pressure, CO₂ is a solid below -78.5 °C but a gas above this temperature. This means that carbon dioxide never exists in the liquid form at standard pressure. Second, the slope of the solid/liquid boundary is positive, meaning that the solid phase is favored as the pressure rises and that the melting point of solid CO₂ therefore increases with pressure.

The transition between a liquid and a supercritical fluid can be observed using a high pressure cell (**FIGURE 11.24**). Initially, CO₂ is present in the cell in the liquid phase and there is clear distinction between the gas and liquid phase. In the high pressure cell at 75 atm, increasing the temperature causes the liquid to become less dense, so that the separation between the liquid and gas phases becomes less distinct. Upon reaching the critical temperature, the density of the gas and liquid phase are identical and the boundary between them no longer exists.

PROBLEM 11.17 A fire extinguisher containing carbon dioxide has a pressure of 70 atm at 75 °C. What phase of CO₂ is present in the tank?

PROBLEM 11.18 Look at the phase diagram of CO₂ in Figure 11.23, and describe what happens to a CO₂ sample when the following changes are made:

(a) The temperature is increased from -100 °C to 0 °C at a constant pressure of 2 atm.

(b) The pressure is reduced from 72 atm to 5.0 atm at a constant temperature of 30 °C.

(c) The pressure is first increased from 3.5 atm to 76 atm at -10 °C, and the temperature is then increased from -10 °C to 45 °C.

PROBLEM 11.19 Liquid carbon dioxide is also used as nontoxic solvent in dry cleaning. Refer to the phase diagram for CO₂ (Figure 11.23) to answer the following questions.

(a) What is the minimum pressure at which liquid CO₂ can exist?

(b) What is the minimum temperature at which liquid CO₂ can exist?

(c) What is the maximum temperature at which liquid CO₂ can exist?

PROBLEM 11.20

(a) For the phase transition CO₂(s) → CO₂(g), predict the sign of ΔS .

(b) At what temperature does CO₂(s) spontaneously sublime at 1 atm? Use the phase diagram for CO₂ (Figure 11.23) to answer this question.

(c) If ΔH for the sublimation of 1 mol of CO₂(s) is 26.1 kJ, calculate ΔS in (J/K·mol) for this phase transition. (Hint: Use the temperature found in part b to calculate the answer.)

PROBLEM 11.21 A sample of supercritical carbon dioxide was prepared by heating 100.0 g of CO₂(s) at -78.5 °C to CO₂(g) at 35 °C. Then the pressure was increased to 75.0 atm. How much heat was required to sublime the sample of CO₂(s) and subsequently heat CO₂(g)? ($\Delta H_{\text{sub}} = 26.1$ kJ/mol; C_p for CO₂(g) = 35.0 J/mol·°C)

Inquiry Updated inquiry sections now include worked examples and practice problems so that students can apply concepts and skills to scenarios that have relevance to their daily lives. These sections not only highlight the importance of chemistry and promote interest but also deepen students understanding of the content.

CHAPTER
16

Applications of Aqueous Equilibria

CONTENTS

- 16.1 ▶ Neutralization Reactions
- 16.2 ▶ The Common-Ion Effect
- 16.3 ▶ Buffer Solutions
- 16.4 ▶ The Henderson-Hasselbalch Equation
- 16.5 ▶ pH Titration Curves
- 16.6 ▶ Strong Acid-Strong Base Titrations
- 16.7 ▶ Weak Acid-Strong Base Titrations
- 16.8 ▶ Weak Base-Strong Acid Titrations
- 16.9 ▶ Polyprotic Acid-Strong Base Titrations
- 16.10 ▶ Solubility Equilibria for Ionic Compounds
- 16.11 ▶ Measuring K_{sp} and Calculating Solubility from K_{sp}
- 16.12 ▶ Factors That Affect Solubility
- 16.13 ▶ Precipitation of Ionic Compounds
- 16.14 ▶ Separation of Ions by Selective Precipitation
- 16.15 ▶ Qualitative Analysis

The limestone (CaCO_3) framework of a coral reef is in equilibrium with Ca^{2+} and CO_3^{2-} ions in the ocean.

? What is causing a decrease in the pH of the oceans?

The answer to this question can be found in the **INQUIRY** ▶▶ on page 703.

STUDY GUIDE

Chapter Openers introduce a topic and question, related to the content in the chapter that will be further discussed in the Inquiry section. The goal is to provide students with a central topic to serve as a waypoint for why the content matters to them beyond what they need to pass the next exam.

CHAPTER
1

Chemical Tools: Experimentation and Measurement

CONTENTS

- 1.1 ▶ The Scientific Method in a Chemical Context: Improved Pharmaceutical Insulin
- 1.2 ▶ Experimentation and Measurement
- 1.3 ▶ Mass and Its Measurement
- 1.4 ▶ Length and Its Measurement
- 1.5 ▶ Temperature and Its Measurement
- 1.6 ▶ Derived Units: Volume and Its Measurement
- 1.7 ▶ Derived Units: Density and Its Measurement
- 1.8 ▶ Derived Units: Energy and Its Measurement
- 1.9 ▶ Accuracy, Precision, and Significant Figures in Measurement
- 1.10 ▶ Rounding Numbers
- 1.11 ▶ Calculations: Converting from One Unit to Another

Instruments for scientific measurements have changed greatly over the centuries. Modern technology has enabled scientists to make images of extremely tiny particles, even individual atoms, using instruments like this atomic force microscope.

? What are the unique properties of nanoscale ($1 \text{ nm} = 10^{-9} \text{ m}$) materials?

The answer to this question can be found in the **INQUIRY** ▶▶ on page 23.

STUDY GUIDE

Study Guide The end-of-chapter material now includes a Study Guide to help students review each chapter. Prepared in a grid format, the main lessons of each chapter are laid out and linked to learning objectives, associated worked examples, and representative end-of-chapter problems that allow students to assess their comprehension of the material.

28 CHAPTER 1 Chemical Tools: Experimentation and Measurement		STUDY GUIDE	
Section	Concept Summary	Learning Objectives	Test Your Understanding
1.1 • The Scientific Method	The scientific method is an iterative process used to perform research. A driving question, often based upon observations, is the first step. Next a hypothesis is developed to explain the observation. Experiments are designed to test the hypothesis and the results are used to verify or modify the original hypothesis. Theories arise when numerous experiments validate a hypothesis and are used to make new predictions. Models are simplified representations of complex systems that help make theories more concrete.	1.1 Identify the steps in the scientific method. 1.2 Differentiate between a qualitative and quantitative measurement.	Problems 1.28–1.30 Problems 1.33–1.35
1.2 • Experimentation and Measurement	Accurate measurement is crucial to scientific experimentation. Scientists use units of measure established by the <i>Système International (SI units)</i> . There are seven fundamental SI units, together with other derived units. (Table 1.1)	1.3 Write numbers in scientific notation and use prefixes for multiples of SI units.	Worked Example 1.1; Problems 1.39, 1.49, 1.52, 1.58, and 1.59
1.3 • Mass and Its Measurement	Mass, the amount of matter in an object, is measured in the SI unit of kilograms (kg)	1.4 Describe the difference between mass and weight. 1.5 Convert between different prefixes used in mass measurements.	Problem 1.36 Problem 1.50
1.4 • Length and Its Measurement	Length is measured in the SI unit of meters (m)	1.6 Convert between different prefixes used in length measurements.	Problem 1.52 (a) and (b)
1.5 • Temperature and Its Measurement	Fahrenheit (°F) is the most common unit for measuring temperature in the United States, whereas Celsius (°C) is more common in other parts of the world. Kelvin (K) is the standard temperature unit in scientific work.	1.7 Convert between common units of temperature measurements.	Worked Example 1.2; Problems 1.74–1.77
1.6 • Derived Units: Volume and Its Measurement	Volume, the amount of space occupied by an object, is measured in SI units by the cubic meter (m^3)	1.8 Convert between SI and metric units of volume. 1.9 Convert between different prefixes used in volume measurements.	Problems 1.42 and 1.43; Problem 1.51
1.7 • Derived Units: Density and Its Measurement	Density is a property that relates mass to volume and is measured in the derived SI unit g/cm^3 or g/mL .	1.10 Calculate mass, volume, or density using the formula for density. 1.11 Predict whether a substance will float or sink in another substance based on density.	Worked Example 1.3; Problems 1.80–1.88, 1.96, 1.100, 1.101 Problem 1.27, 1.97, 1.107
1.8 • Derived Units: Energy and Its Measurement	Energy is the capacity to supply heat or do work and is measured in the derived SI unit ($\text{kg}\cdot\text{m}^2/\text{s}^2$), or joule (J). Energy is of two kinds, potential and kinetic. Kinetic energy (E_k) is the energy of motion, and potential energy (E_p) is stored energy.	1.12 Calculate kinetic energy of a moving object. 1.13 Convert between common energy units.	Worked Example 1.4; Problem 1.60 Problems 1.94 and 1.95
1.9 • Accuracy	If measurements are accurate, they are close to the	1.14 Specify the number of significant	Worked Example

Helping students relate chemical reasoning to mathematical operations

WORKED EXAMPLE 19.3

Using Half-Life to Calculate an Amount Remaining

Phosphorus-32, a radioisotope used in leukemia therapy, has a half-life of 14.26 days. What percent of a sample remains after 35.0 days?

IDENTIFY

Known	Unknown
$t_{1/2} = 14.26$ days	Percent of sample remaining (N_t/N_0) $\times 100$
$t = 35.0$ days	

STRATEGY

The ratio of remaining (N_t) and initial (N_0) amounts of a radioactive sample at time t is given by the equation

$$\ln\left(\frac{N_t}{N_0}\right) = -kt$$

Taking N_0 as 100%, N_t can then be obtained. The value of the rate constant can be found from the equation $k = 0.693/t_{1/2}$.

SOLUTION

The value of the rate constant is calculated using the half-life.

$$k = \frac{0.693}{14.26 \text{ days}} = 4.860 \times 10^{-2} \text{ days}^{-1}$$

Substituting values for t and for k into the equation gives

$$\ln\left(\frac{N_t}{N_0}\right) = (-4.860 \times 10^{-2} \text{ days}^{-1})(35.0 \text{ days}) = -1.70$$

Taking the natural antilogarithm of -1.70 then gives the ratio N_t/N_0 :

$$\frac{N_t}{N_0} = \text{antiln}(-1.70) = e^{-1.70} = 0.183$$

Since the initial amount of ^{32}P was 100%, we can set $N_0 = 100\%$ and solve for N_t :

$$\frac{N_t}{100\%} = 0.183 \quad \text{so} \quad N_t = (0.183)(100\%) = 18.3\%$$

After 35.0 days, 18.3% of a ^{32}P sample remains and $100\% - 18.3\% = 81.7\%$ has decayed.

CHECK

We can estimate the answer by considering half-life. Since phosphorus-32 has a half-life of 14.26 days and the time is 35 days, we know the time of the reaction is more than two half-lives. After two half-lives, 75% has reacted and 25% remains. Since the time is over two half-lives, we would estimate that less than 25% remains, which agrees with the answer of 18.3%.

► **PRACTICE 19.7** What percentage of ^{14}C ($t_{1/2} = 5715$ years) remains in a sample estimated to be 16,230 years old?

► **APPLY 19.8** Cesium-137 is a radioactive isotope released as a result of the Fukushima Daiichi nuclear disaster in Japan in 2011. If 89.2% remains after 5.00 years, what is the half-life?

Worked Examples Numerous Worked Examples show the approach for solving different types of problems using a stepwise procedure.

Identify The first step helps students identify key information and classify the known or unknown variables. This step frequently involves translating between words and chemical symbols.

Strategy The strategy describes how to solve the problem without actually solving it. Failing to articulate the needed strategy is a common pitfall; this step involves outlining a plan for solving the problem.

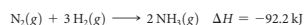
Solution Once the plan is outlined, the key information can be used and the answer obtained.

Check Uses both your practical knowledge of the world and knowledge of chemistry to evaluate your answer.

WORKED EXAMPLE 9.2

Calculating Internal Energy Change (ΔE) for a Reaction

The reaction of nitrogen with hydrogen to make ammonia has $\Delta H = -92.2$ kJ. What is the value of ΔE in kilojoules if the reaction is carried out at a constant pressure of 40.0 atm and the volume change is -1.12 L?



IDENTIFY

Known	Unknown
Change in enthalpy ($\Delta H = -92.2$ kJ)	Change in internal energy (ΔE)
Pressure ($P = 40.0$ atm)	
Volume Change ($\Delta V = -1.12$ L)	

STRATEGY

We are given an enthalpy change ΔH , a volume change ΔV , and a pressure P and asked to find an energy change ΔE . Rearrange the equation $\Delta H = \Delta E + P\Delta V$ to the form $\Delta E = \Delta H - P\Delta V$ and substitute the appropriate values for ΔH , P , and ΔV .

CHECK

The sign of ΔE is similar in size and magnitude ΔH , which is to be expected because energy transfer as work is usually small compared to heat.

► **PRACTICE 9.3** The reaction between hydrogen and oxygen to yield water vapor has $\Delta H = -484$ kJ. How much PV work is done, and what is the value of ΔE in kilojoules for the reaction of 2.00 mol of H_2 with 1.00 mol of O_2 at atmospheric pressure if the volume change is -24.4 L?



SOLUTION

$$\Delta E = \Delta H - P\Delta V$$

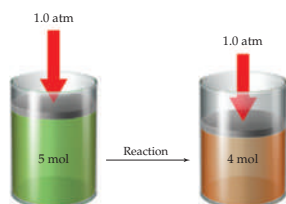
where $\Delta H = -92.2$ kJ

$$P\Delta V = (40.0 \text{ atm})(-1.12 \text{ L}) = -44.8 \text{ L} \cdot \text{atm}$$

$$= (-44.8 \text{ L} \cdot \text{atm}) \left(101 \frac{\text{J}}{\text{L} \cdot \text{atm}} \right) = -4520 \text{ J} = -4.52 \text{ kJ}$$

$$\Delta E = (-92.2 \text{ kJ}) - (-4.52 \text{ kJ}) = -87.7 \text{ kJ}$$

► **Conceptual APPLY 9.4** The following reaction has $\Delta E = -186$ kJ/mol.

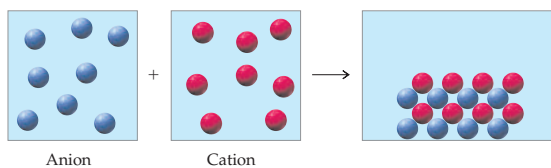


- (a) Is the sign of $P\Delta V$ positive or negative? Explain.
 (b) What is the sign and approximate magnitude of ΔH ? Explain.

Conceptual WORKED EXAMPLE 4.7

Visualizing Stoichiometry in Precipitation Reactions

When aqueous solutions of two ionic compounds are mixed, the following results are obtained:



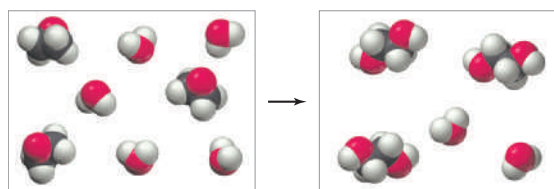
(Only the anion of the first compound, represented by blue spheres, and the cation of the second compound, represented by red spheres, are shown.) Which cation and anion combinations are compatible with the observed results?

Anions: NO_3^- , Cl^- , CO_3^{2-} , PO_4^{3-}

Cations: Ca^{2+} , Ag^+ , K^+ , Cd^{2+}

Conceptual Worked Examples and Conceptual Questions

Worked Conceptual Examples are included throughout each chapter to emphasize the conceptual nature of problem solving, often using molecular illustrations. Conceptual problems are now always preceded by Conceptual Worked Examples.



- Identify the limiting and the excess reactant.
- How many molecules of excess reactant are left over after the reaction occurs?
- How many molecules of product can be made?

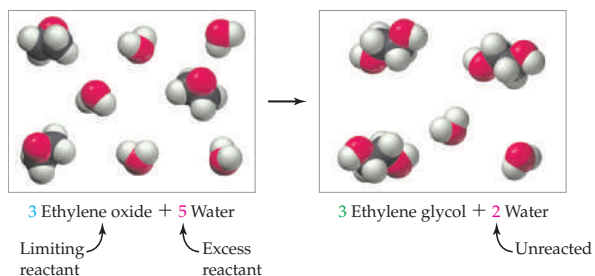
STRATEGY

Count the numbers of reactant and product molecules and use coefficients from the balanced equation to relate them to one another.

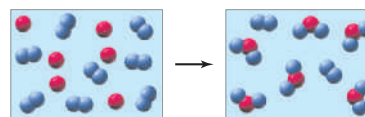
SOLUTION

- Count the number of each type of molecule in the box on the reactant side of the equation. There are 3 ethylene oxide molecules and 5 water molecules. According to the balanced equation the stoichiometry between the reactants is 1:1. Therefore, 5 ethylene oxide molecules would be needed to react with 5 water molecules. Since there are only 3 ethylene oxide molecules, it is the limiting reactant, and water is in excess.
- Count the number of water molecules on the product side of the equation. There are 2 water molecules that have not reacted, and water is called the excess reactant.
- Count the number of ethylene glycol molecules on the product side of the equation. There are 3 ethylene glycol molecules present.

Therefore, the reaction of 3 ethylene oxide molecules with 5 water molecules results in 3 ethylene glycol molecules with 2 water molecules left over.



- ▶ **Conceptual PRACTICE 3.13** The following diagram represents the reaction of A (red spheres) with B_2 (blue spheres):



- Write a balanced equation for the reaction.
- Identify the limiting and excess reactant.
- How many molecules of product are made?

Conceptual Practice and Apply questions located at the end of selected Worked Examples assess understanding of principles rather than the ability to simply plug numbers into a formula.

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Before Class

The screenshot shows a question titled "QUESTION 4" with the prompt "The name of the molecule shown is _____". A chemical structure of cyclopropylmethanol is displayed. The answer options are: cyclopropanol, methylene cyclopropanol, cyclopropylmethanol, hydroxymethylcyclopropane, and I DON'T KNOW YET. The correct answer, "cyclopropylmethanol", is highlighted. A "next question" button is visible at the bottom.

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The screenshot shows a "Chapter 12 Reading Quiz Question 4" with the following text: "Part A For reaction $A + B \rightarrow C + D$, the reaction rate decreases from 1.80 M/s to 0.20 M/s when [A] decreases from 3 M to 1 M, the reaction rate does not change when [B] increases from 1 M to 2 M. Which of the following is the correct rate law for the reaction?" The answer options are: rate = $k[A]^2[B]$, rate = $k[A][B]$, rate = $k[A]^2$, and rate = $k[B]^2$. A "Submit" button and "Hints" link are visible at the bottom.

Reading Quizzes give instructors the opportunity to assign reading and test students on their comprehension of chapter content. Reading Quizzes are often useful to provide a common baseline for students prior to coming to class, thereby saving time on lower level content and allowing instructors to use in-class time on more challenging topic.

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Joseph Topich, *Virginia Commonwealth University*

This manual contains worked out solutions to all in-chapter problems and even-numbered end-of-chapter problems.

Study Guide (ISBN: 0133888819)

James Zubricky, *University of Toledo*

The Study Guide includes learning goals, an overview, progressive review section with worked examples, and self-tests with answers.

Laboratory Manual (ISBN: 013388662X)

Sandra Chimon-Peszek, *Calumet College of St. Joseph*

The Laboratory Manual contains over 20 experiments that focus on real-world applications. Each experiment corresponds with one or more topics covered in each chapter.

For Instructors

Instructor Resource Center (ISBN: 013388659X)

Available for download on the Pearson catalog page at www.pearsonhighered.com

Mark Benvenuto, *University of Detroit Mercy*

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- All illustrations, tables, and photos from the text in JPEG format
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- TestGen computerized software with the TestGen version of the Testbank
- Word files of the Test Item File

Solutions Manual (ISBN: 0133892298)

Joseph Topich, *Virginia Commonwealth University*

The solutions manual provides worked-out solutions to all in-chapter, conceptual, and end-of-chapter questions and problems. With instructor's permission, this manual may be made available to students.

Instructor Resource Manual (ISBN: 0133886603, Download Only)

Charity Lovitt, *University of Washington, Bothell*

The Instructor manual contains teaching tips, common misconceptions, lecture outlines, and suggested chapter learning goals for students, as well as lecture/laboratory demonstrations and literature references. It also describes the various resources, such as printed test bank questions, animations, and movies that are available to instructors.

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Christine Hermann, *Radford University*

The Test Bank contains more than 4,500 multiple choice, true/false, and matching questions.



Chemistry

SEVENTH EDITION

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Instruments for scientific measurements have changed greatly over the centuries. Modern technology has enabled scientists to make images of extremely tiny particles, even individual atoms, using instruments like this atomic force microscope.



What are the unique properties of nanoscale ($1 \text{ nm} = 10^{-9} \text{ m}$) materials?

The answer to this question can be found in the **INQUIRY** ►► on page 23.

Chemical Tools: Experimentation and Measurement

CONTENTS

- 1.1 ► The Scientific Method in a Chemical Context: Improved Pharmaceutical Insulin
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- 1.9 ► Accuracy, Precision, and Significant Figures in Measurement
- 1.10 ► Rounding Numbers
- 1.11 ► Calculations: Converting from One Unit to Another

STUDY GUIDE



▲ The sequence of the approximately 5.8 billion nucleic acid units, or *nucleotides*, present in the human genome has been determined using instruments like this automated DNA sequencer.

Life has changed more in the past two centuries than in all the previously recorded span of human history. The Earth's population has increased sevenfold since 1800, and life expectancy has nearly doubled because of our ability to synthesize medicines, control diseases, and increase crop yields. Methods of transportation have changed from horses and buggies to automobiles and airplanes because of our ability to harness the energy in petroleum. Many goods are now made of polymers and ceramics instead of wood and metal because of our ability to manufacture materials with properties unlike any found in nature.

In one way or another, all these changes involve **chemistry**, the study of the composition, properties, and transformations of matter. Chemistry is deeply involved in both the changes that take place in nature and the profound social changes of the past two centuries. In addition, chemistry is central to the current revolution in molecular biology that is revealing the details of how life is genetically regulated. No educated person today can understand the modern world without a basic knowledge of chemistry.

1.1 ► THE SCIENTIFIC METHOD IN A CHEMICAL CONTEXT: IMPROVED PHARMACEUTICAL INSULIN

By opening this book, you have already decided that you need to know more about chemistry to pursue your future goals. Perhaps you want to learn how living organisms function, how medicines are made, how human activities can change the environment, how alternative fuels produce clean energy, or how to make materials with novel properties. A good place to start is by learning the experimental approach used by scientists to make new discoveries.

Let's examine the development of Humalog[®], a billion-dollar medicine, to illustrate the scientific method and how chemical principles are applied in the pharmaceutical industry. Humalog[®] was commercialized by Eli Lilly and Company in 1996 and is one of several insulin drugs available to people with diabetes. Do not worry if you do not understand all the details of the chemistry yet as our focus is on the process of modern interdisciplinary research.

Diabetes is caused by inadequate production and/or use of insulin, a hormone involved in the body's metabolism of glucose. High blood glucose levels can lead to severe long-term consequences such as cardiovascular disease, kidney failure, and blindness. Insulin was discovered in 1921 by Dr. Frederick Banting and research associate Charles Best, leading soon after to insulin therapy for diabetic patients. Prior to the commercial availability of insulin in 1923, onset of Type I diabetes meant certain death, and insulin's ability to restore health was so dramatic that it was described as "the raising of the dead." Insulin was initially produced by extracting it from the pancreas glands of pigs and cattle, but beginning in the 1980s recombinant DNA technology was used to make enough human insulin to treat a large number of patients worldwide.

While insulin treatment was once considered a miracle therapy, there are several limitations to the use of human insulin as a drug. **FIGURE 1.1** compares the time profile for insulin

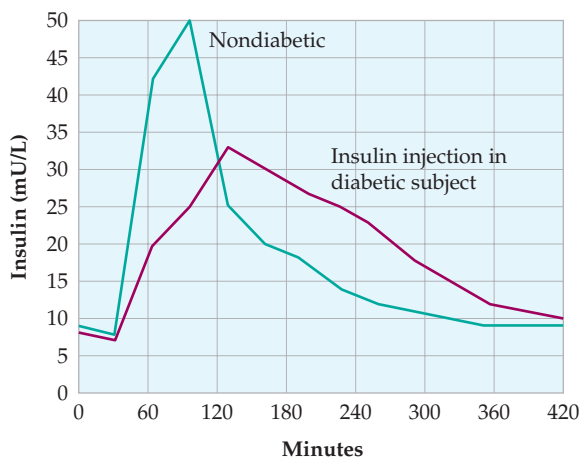
► FIGURE 1.1

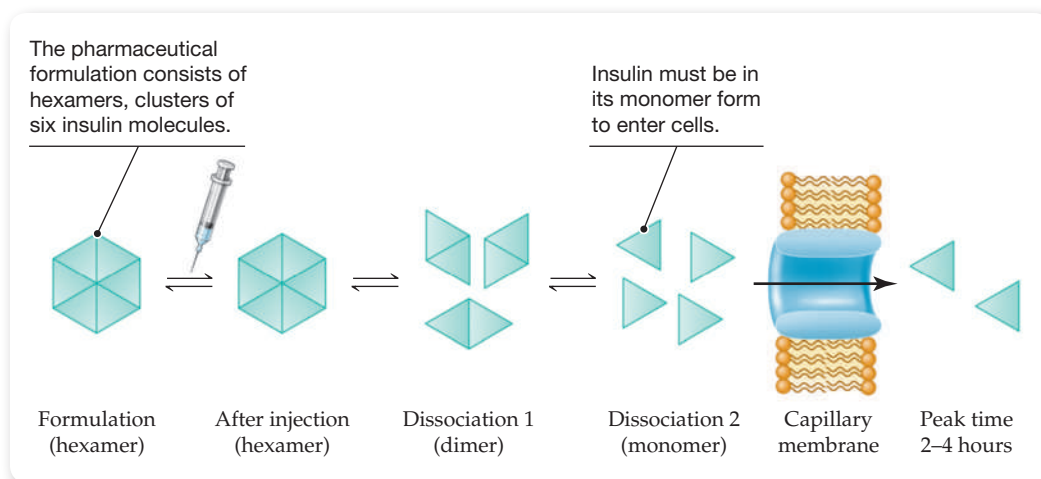
Comparison of insulin profiles. The rise and fall of insulin levels in the blood of a nondiabetic individual and a patient taking an injection of human insulin are shown over time.

Figure It Out

What are the main differences in the time profile for injected insulin when compared to natural insulin release? How do these differences affect treatment of diabetes?

Answer: For injected insulin, the peak concentration is later and the peak shape is more broad than naturally released insulin. These differences lead to high blood sugars initially, but a potential for severe low blood sugar several hours later.





◀ **FIGURE 1.2**
Hexamer dissociation after insulin injection. As concentration decreases, insulin hexamers break apart into dimers and then monomers which enter cells through the capillary membrane.

concentration in the blood of a diabetic patient to that of a nondiabetic individual. After a person eats, the peak in insulin concentration in the natural physiological process is sharper and faster than the peak after injection of insulin. This leads to two major problems involving the use of insulin as a drug. Insulin doses depend on the quantity and type of food eaten, but the slow time profile means injections must be given 30 minutes *before* a meal. Failure to adhere to recommended timing can result in large increases in blood glucose (hyperglycemia). Also, because injected insulin will act to lower blood glucose long after food is digested, diabetics must take care to avoid dangerous low blood sugar events (hypoglycemia), which can cause confusion, unconsciousness, and seizures.

Why does the exact same molecule, human insulin, behave differently when produced naturally in the body than when taken in drug form? Differences in the insulin profiles seen in Figure 1.1 are explained by the relatively high concentration of insulin in the pharmaceutical formulation. The drug's shelf life (that is, its stability) is extended when prepared in higher concentrations. Increased stability results from aggregation of insulin *monomers*, single molecules, into *hexamers*, clusters of six insulin molecules. As shown in **FIGURE 1.2**, the hexamers *dissociate*, or break apart, into monomers as insulin becomes diluted in the body. Only the monomeric form can enter the cell by crossing the capillary membrane, causing a time lag in bioavailability. The peak concentration occurs 2 to 4 hours after injection.

Many different principles from chemistry that you will learn about in this book are central to the pharmacological properties of insulin. What, for example, would cause molecules to attract one another and form clusters like the insulin hexamer? In Chapter 8, Bonding Theories and Molecular Structure, you will learn about forces that give molecules like insulin their specific shapes and functions, and cause them to attract one another. Chapter 4, Reactions in Aqueous Solutions, describes how to calculate solution concentrations important in both drug formulations and in the human body. Rates of reactions—such as the time required for hexamer dissociation—and important factors that influence them are explored in Chapter 13, Kinetics. In Chapter 14, on equilibrium, we discuss the control of reversible processes like hexamer formation and the extent to which molecules reside in one state (hexamer) or the other (monomer). We turn now to how knowledge of these and many other scientific concepts was acquired: the scientific method.

The Scientific Method

Dr. Richard DiMarchi, at Eli Lilly and Company, led a team of scientists in the discovery of an improved or “fast acting” insulin, Humalog®. Scientific research begins with a driving question that is frequently based on experimental observations or the desire to learn about the unknown. In this case, measurements of the time profile of injected insulin led to the question, “How can we make a pharmaceutical formulation of human insulin that mimics the body’s natural release profile?” A general approach to research is called the **scientific method**. The scientific method is an iterative process involving the formulation of questions and conjectures arising from observations, careful design of experiments, and thoughtful analysis of results. The scientific method involves identifying ways to test the validity of new ideas and



▲ Dr. Richard DiMarchi led a team of scientists in the discovery of the “fast acting” insulin, Humalog®.

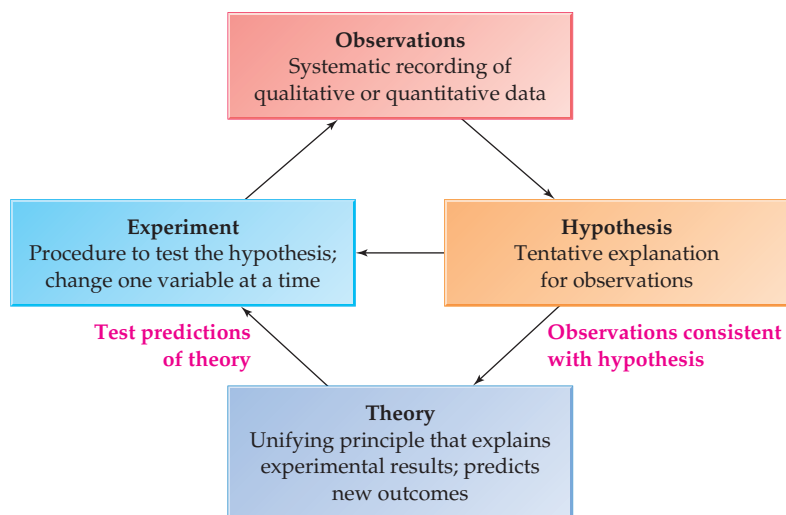
► FIGURE 1.3

The scientific method. An iterative experimental approach is used in scientific research. Hypotheses and theories are refined based on new experiments and observations.

Figure It Out

What is developed when numerous experimental observations support a hypothesis?

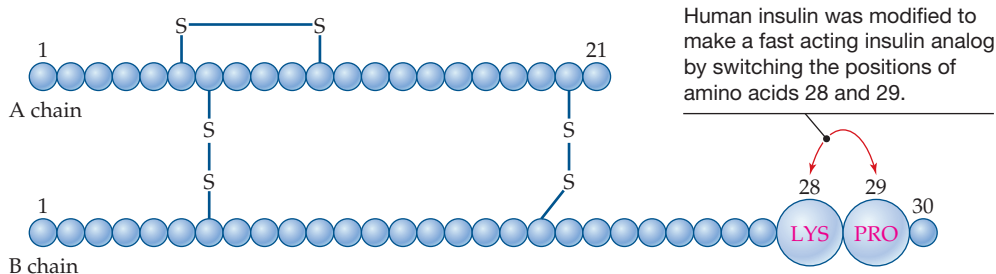
Answer: Theory.



seldom is there only one way to go about it. The main elements of the scientific method, outlined in **FIGURE 1.3**, are the following:

- **Observations** are a systematic recording of natural phenomena and may be **qualitative**, descriptive in nature, or **quantitative**, involving measurements.
- A **hypothesis** is a possible explanation for the observation developed based upon facts collected from previous experiments as well as scientific knowledge and intuition. The hypothesis may not be correct, but it must be testable with an experiment.
- An **experiment** is a procedure for testing the hypothesis. Experiments are most useful when they are performed in a *controlled* manner, meaning that only one variable is changed at a time while all others remain constant.
- A **theory** is developed from a hypothesis consistent with experimental data and is a unifying principle that explains experimental results. It also makes predictions about related systems and new experiments are carried out to verify the theory.

Keep in mind as you study chemistry or any other science that theories can never be absolutely proven. There's always the chance that a new experiment might give results that can't be explained by present theory. All a theory can do is provide the best explanation that we can come up with at the present time. Science is an ever-changing field where new observations are made with increasingly sophisticated equipment; it is always possible that existing theories may be modified in the future. Many iterations of the scientific method were required in creating a new analog of insulin that would have a time profile similar to natural insulin. The general hypothesis was that the chemical structure of insulin was responsible for aggregation and modifying it could change properties. In the case of Humalog[®], Dr. DiMarchi devised a hypothesis based on observations of the chemical similarity between human insulin and another human hormone called insulin-like growth factor 1 (IGF-1). Both of these hormones are **peptides**, molecules that consist of molecules called **amino acids** linked together in a chain. The structure of IGF-1 was of interest because it exists in solution only in the form of monomers, which results in rapid uptake by cells. A simplified structure of Humalog[®], a "fast acting" analog of human insulin is:



LOOKING AHEAD...

The chemical structure of **amino acids** and **peptides** is described in Chapter 23.

Each amino acid is represented by a single circle, and the overall molecule consists of 51 total amino acids. Both the human insulin and Humalog[®] molecule consist of two chains, A and B. It was known that in IGF-1, the B chain contained lysine at position 28 and proline at position 29, and that these two amino acids are found in natural human insulin in exactly the reverse order. The hypothesis was that *switching the order of amino acids at positions 28 and 29 on the B chain* would minimize hexamer formation while retaining the biological activity of insulin. Known chemistry was used to synthesize a new analog of insulin, called *Lispro*, in which the two amino acid positions are reversed. Insulin Lispro, marketed as Humalog[®], was indeed more “fast acting” than injected human insulin. It aggregated to a lesser extent, resulting in a time profile more closely matching physiological insulin release. Upon successfully concluding clinical trials, including studies for safety and toxicity, doctors worldwide began prescribing Humalog[®] for treatment of diabetes. Millions of patients in more than 100 countries have benefited from the science that went into its discovery.

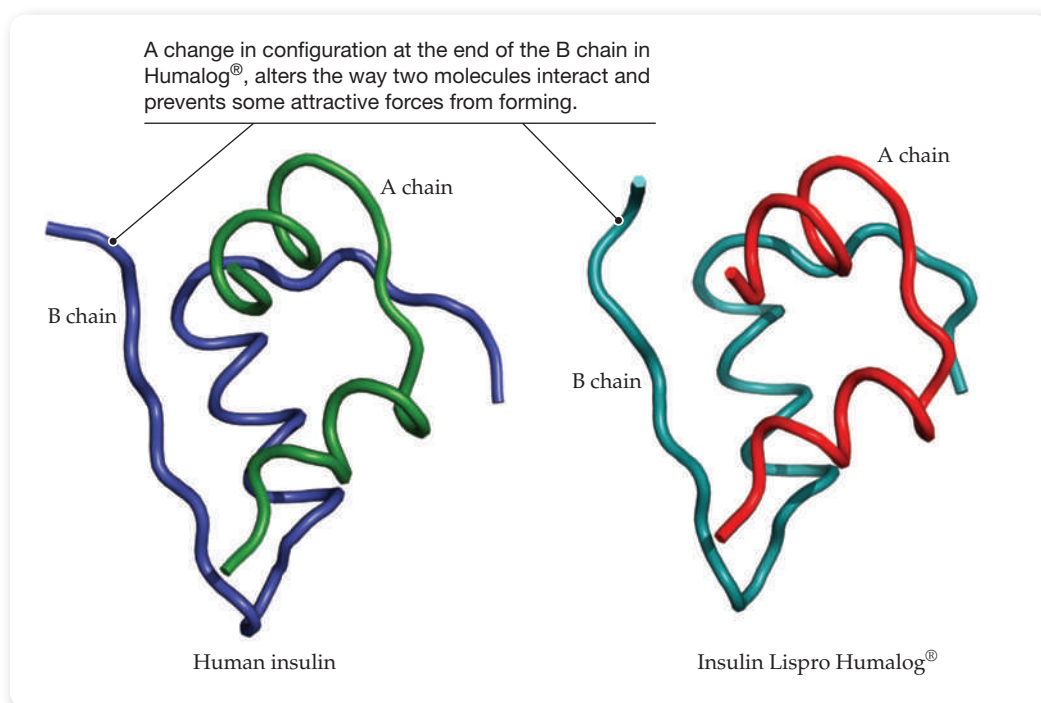
Visualizing Chemical Behavior with Molecular Models

How can simply switching the position of two amino acids in an insulin analog result in such drastically different pharmacological properties? A theory to explain this remarkable result was needed. Chemists often make use of molecular models to help develop a theory and to visualize structure–function relationships. **Molecular models** are simplified versions of the way atoms are connected and reveal their three-dimensional arrangement. **FIGURE 1.4** is a ribbon model of Humalog[®] and human insulin, showing only the position of atoms in the “backbone” of the molecule. A comparison of the structure of these two forms of insulin can help explain the minimized aggregation of the analog. Notice that the configuration at the end of the B chain is significantly different in the two forms of insulin. A bend occurs at the end of the human insulin chain, but not in Humalog[®]. When the amino acids are switched as in Humalog[®], the B chains on adjacent molecules cannot approach closely, preventing some attractive forces from forming. This leads to less self-association and faster dissociation once the insulin analog has been injected. Other than the end of the B chain, the structure of the two molecules is nearly identical, giving Humalog[®] essentially the same biological activity as human insulin.

In summary, the hypothesis that switching the amino acids at positions 28 and 29 in the B chain of human insulin to create fast-acting insulin was upheld with experimental observations. A theory to explain these observations was developed by experimentally determining

LOOKING AHEAD...

Common types of **molecular models** used to depict molecules will be described in Section 2.10.



◀ **FIGURE 1.4**

Ribbon model for human insulin and insulin Lispro. A ribbon model is a useful simplification for depicting how the change in position of lysine and proline alters the backbone configuration at the end of the B chain in Humalog[®].

chemical structures and examining molecular models to interpret their meaning. Models showed that the last five amino acids in the B chain were important in aggregation but not biological activity. A prediction could then be made that an insulin analog missing these five amino acids would have a rapid time profile and excellent biological activity. When the analog was prepared, observations supported the prediction, but this analog lacked the stability needed for a drug formulation. Other analogs were prepared, but in the end Humalog® was found to have the most desirable properties. Research laboratories all over the world use the scientific method to discover new phenomena and develop new products.

1.2 ► EXPERIMENTATION AND MEASUREMENT

Chemistry is an experimental science. But if our experiments are to be reproducible, we must be able to fully describe the substances we're working with—their amounts, volumes, temperatures, and so forth. Thus, one of the most important requirements in chemistry is that we have a way to measure things.

Under an international agreement concluded in 1960, scientists throughout the world now use the International System of Units for measurement, abbreviated **SI** for the French *Système Internationale d'Unités*. Based on the metric system, which is used in all industrialized countries of the world except the United States, the SI system has seven fundamental units (**TABLE 1.1**). These seven fundamental units, along with others derived from them, suffice for all scientific measurements. We'll look at three of the most common units in this chapter—those for mass, length, and temperature—and will discuss others as the need arises in later chapters.

One problem with any system of measurement is that the sizes of the units often turn out to be inconveniently large or small. For example, a chemist describing the diameter of a sodium atom (0.000 000 000 372 m) would find the meter (m) to be inconveniently large, but an astronomer describing the average distance from the Earth to the Sun (150,000,000,000 m) would find the meter to be inconveniently small. For this reason, SI units are modified through the use of prefixes when they refer to either smaller or larger quantities. Thus, the prefix *milli-* means one-thousandth, and a *millimeter* (mm) is 1/1000 of 1 meter. Similarly, the prefix *kilo-* means one thousand, and a *kilometer* (km) is 1000 meters. [Note that the SI unit for mass (kilogram) already contains the *kilo-* prefix.] A list of prefixes is shown in **TABLE 1.2**, with the most commonly used ones in red.

Notice how numbers that are either very large or very small are indicated in Table 1.2 using an exponential format called **scientific notation**. For example, the number 55,000 is written in scientific notation as 5.5×10^4 , and the number 0.003 20 as 3.20×10^{-3} . Review Appendix A if you are uncomfortable with scientific notation or if you need to brush up on how to do mathematical manipulations on numbers with exponents.

Notice also that all measurements contain both a number and a unit label. A number alone is not much good without a unit to define it. If you asked a friend how far it was to the nearest tennis court, the answer “3” alone wouldn't tell you much, 3 blocks? 3 kilometers? 3 miles? Worked Example 1.1 explains how to write a number in scientific notation and represent the unit in prefix notation.

TABLE 1.1 The Seven Fundamental SI Units of Measure

Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Temperature	kelvin	K
Amount of substance	mole	mol
Time	second	s
Electric current	ampere	A
Luminous intensity	candela	cd

TABLE 1.2 Some Prefixes for Multiples of SI Units. The most commonly used prefixes are shown in red.

Factor	Prefix	Symbol	Example
$1,000,000,000,000 = 10^{12}$	tera	T	1 teragram (Tg) = 10^{12} g
$1,000,000,000 = 10^9$	giga	G	1 gigameter (Gm) = 10^9 m
$1,000,000 = 10^6$	mega	M	1 megameter (Mm) = 10^6 m
$1000 = 10^3$	kilo	k	1 kilogram (kg) = 10^3 g
$100 = 10^2$	hecto	h	1 hectogram (hg) = 100 g
$10 = 10^1$	deka	da	1 dekagram (dag) = 10 g
$0.1 = 10^{-1}$	deci	d	1 decimeter (dm) = 0.1 m
$0.01 = 10^{-2}$	centi	c	1 centimeter (cm) = 0.01 m
$0.001 = 10^{-3}$	milli	m	1 milligram (mg) = 0.001 g
*0.000 001 = 10^{-6}	micro	μ	1 micrometer (μm) = 10^{-6} m
*0.000 000 001 = 10^{-9}	nano	n	1 nanosecond (ns) = 10^{-9} s
*0.000 000 000 001 = 10^{-12}	pico	p	1 picosecond (ps) = 10^{-12} s
*0.000 000 000 000 001 = 10^{-15}	femto	f	1 femtomole (fmol) = 10^{-15} mol

*For very small numbers, it is becoming common in scientific work to leave a thin space every three digits to the right of the decimal point, analogous to the comma placed every three digits to the left of the decimal point in large numbers.

WORKED EXAMPLE 1.1

Expressing Measurements Using Scientific Notation and SI Units

Express the following quantities in scientific notation and then express the number and unit with the most appropriate prefix.

- (a) The diameter of a sodium atom, 0.000 000 000 372 m
 (b) The distance from the Earth to the Sun, 150,000,000,000 m

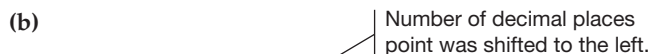
STRATEGY

To write a number in scientific notation, shift the decimal point to the right or left by n places until you obtain a number between 1 and 10. If the decimal is shifted to the right, n is negative and if the decimal is shifted to the left, n is positive. Then multiply the result by 10^n . Choose a prefix for the unit that is close to the exponent of the number written in scientific notation.

SOLUTION

- (a)  Number of decimal places point was shifted to the right.

$$0.000\ 000\ 000\ 372\text{m} = 3.72 \times 10^{-10}\text{ m} = 372\text{ pm}$$

- (b)  Number of decimal places point was shifted to the left.

$$150,000,000,000.\text{ m} = 1.5 \times 10^{11}\text{ m} = 150\text{ Gm}$$

► **PRACTICE 1.1** Express the following quantities in scientific notation and then express the number and unit with the most appropriate prefix.

- (a) The diameter of an insulin molecule, 0.000 000 005 m
 (b) The circumference of the Earth at the Equator, 40,075,017 m

► **APPLY 1.2** Express the following quantities in scientific notation using fundamental SI units of mass and length given in Table 1.1.

- (a) The diameter of a human hair, 70 μm .
 (b) The mass of carbon dioxide emitted from a large power plant each year, 20 Tg.

1.3 ► MASS AND ITS MEASUREMENT

Mass is defined as the amount of *matter* in an object. **Matter**, in turn, is a catchall term used to describe anything with a physical presence—anything you can touch, taste, or smell. (Stated more scientifically, matter is anything that has mass.) Mass is measured in SI units by the **kilogram** (**kg**; $1 \text{ kg} = 2.205 \text{ U.S. lb}$). Because the kilogram is too large for many purposes in chemistry, the metric **gram** (**g**; $1 \text{ g} = 0.001 \text{ kg}$), the **milligram** (**mg**; $1 \text{ mg} = 0.001 \text{ g} = 10^{-6} \text{ kg}$), and the **microgram** (**μg**; $1 \text{ μg} = 0.001 \text{ mg} = 10^{-6} \text{ g} = 10^{-9} \text{ kg}$) are more commonly used. (The symbol μ is the lowercase Greek letter mu.) One gram is a bit less than half the mass of a new U.S. dime.

$$\begin{aligned} 1 \text{ kg} &= 1000 \text{ g} = 1,000,000 \text{ mg} = 1,000,000,000 \text{ μg} && (2.205 \text{ lb}) \\ 1 \text{ g} &= 1000 \text{ mg} = 1,000,000 \text{ μg} && (0.035 27 \text{ oz}) \\ 1 \text{ mg} &= 1000 \text{ μg} \end{aligned}$$

The standard kilogram is set as the mass of a cylindrical bar of platinum–iridium alloy stored in a vault in a suburb of Paris, France. There are 40 copies of this bar distributed throughout the world, with two (Numbers 4 and 20) stored at the U.S. National Institute of Standards and Technology near Washington, D.C.

The terms *mass* and *weight*, although often used interchangeably, have quite different meanings. *Mass* is a physical property that measures the amount of matter in an object, whereas *weight* measures the force with which gravity pulls on an object. Mass is independent of an object's location: your body has the same amount of matter whether you're on Earth or on the moon. Weight, however, *does* depend on an object's location. If you weigh 140 lb on Earth, you would weigh only about 23 lb on the moon, which has a lower gravity than the Earth.

At the same location on Earth, two objects with identical masses experience an identical pull of the Earth's gravity and have identical weights. Thus, the mass of an object can be measured by comparing its weight to the weight of a reference standard of known mass. Much of the confusion between mass and weight is simply due to a language problem. We speak of “weighing” when we really mean that we are measuring mass by comparing two weights. **FIGURE 1.5** shows balances typically used for measuring mass in the laboratory.

1.4 ► LENGTH AND ITS MEASUREMENT

The **meter (m)** is the standard unit of length in the SI system. Although originally defined in 1790 as being 1 ten-millionth of the distance from the equator to the North Pole, the meter was redefined in 1889 as the distance between two thin lines on a bar of platinum–iridium alloy stored near Paris, France. To accommodate an increasing need for precision, the meter was redefined again in 1983 as equal to the distance traveled by light through a vacuum in $1/299,792,458$ second. Although this new definition isn't as easy to grasp as the distance between two scratches on a bar, it has the great advantage that it can't be lost or damaged.



▲ The mass of a U.S. dime is approximately 2.27 g.

► **FIGURE 1.5**

Some balances used for measuring mass in the laboratory.



One meter is 39.37 inches, about 10% longer than an English yard and much too large for most measurements in chemistry. Other more commonly used measures of length are the **centimeter (cm)**; $1 \text{ cm} = 0.01 \text{ m}$, a bit less than half an inch), the **millimeter (mm)**; $1 \text{ mm} = 0.001 \text{ m}$, about the thickness of a U.S. dime), the **micrometer (μm)**; $1 \mu\text{m} = 10^{-6} \text{ m}$, the **nanometer (nm)**; $1 \text{ nm} = 10^{-9} \text{ m}$, and the **picometer (pm)**; $1 \text{ pm} = 10^{-12} \text{ m}$. Thus, a chemist might refer to the diameter of a sodium atom as 372 pm ($3.72 \times 10^{-10} \text{ m}$).

$$1 \text{ m} = 100 \text{ cm} = 1000 \text{ mm} = 1,000,000 \mu\text{m} = 1,000,000,000 \text{ nm} \quad (1.0936 \text{ yd})$$

$$1 \text{ cm} = 10 \text{ mm} = 10,000 \mu\text{m} = 10,000,000 \text{ nm} \quad (0.3937 \text{ in.})$$

$$1 \text{ mm} = 1000 \mu\text{m} = 1,000,000 \text{ nm}$$

1.5 ► TEMPERATURE AND ITS MEASUREMENT

Just as the kilogram and the meter are slowly replacing the pound and the yard as common units for mass and length measurement in the United States, the **Celsius degree ($^{\circ}\text{C}$)** is slowly replacing the degree **Fahrenheit ($^{\circ}\text{F}$)** as the common unit for temperature measurement. In scientific work, however, the **kelvin (K)** has replaced both. (Note that we say only “kelvin,” not “kelvin degree.”)

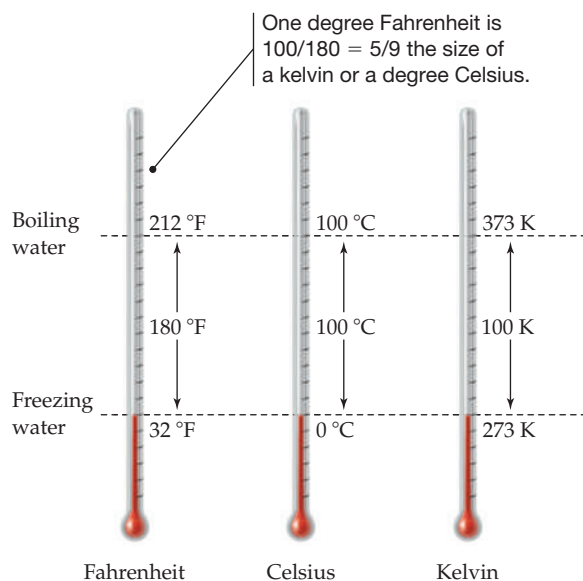
For all practical purposes, the kelvin and the degree Celsius are the same—both are one-hundredth of the interval between the freezing point of water and the boiling point of water at standard atmospheric pressure. The only real difference between the two units is that the numbers assigned to various points on the scales differ. Whereas the Celsius scale assigns a value of 0°C to the freezing point of water and 100°C to the boiling point of water, the Kelvin scale assigns a value of 0 K to the coldest possible temperature, -273.15°C , sometimes called *absolute zero*. Thus, $0 \text{ K} = -273.15^{\circ}\text{C}$ and $273.15 \text{ K} = 0^{\circ}\text{C}$. For example, a warm spring day with a Celsius temperature of 25°C has a Kelvin temperature of $25 + 273.15 = 298 \text{ K}$.

Relationship between the Kelvin and Celsius scales

$$\text{Temperature in K} = \text{Temperature in } ^{\circ}\text{C} + 273.15$$

$$\text{Temperature in } ^{\circ}\text{C} = \text{Temperature in K} - 273.15$$

In contrast to the Kelvin and Celsius scales, the common Fahrenheit scale specifies an interval of 180° between the freezing point (32°F) and the boiling point (212°F) of water. Thus, it takes 180 degrees Fahrenheit to cover the same range as 100 degrees Celsius (or kelvins), and a degree Fahrenheit is therefore only $100/180 = 5/9$ as large as a degree Celsius. **FIGURE 1.6** compares the Fahrenheit, Celsius, and Kelvin scales.



◀ **FIGURE 1.6**

A comparison of the Fahrenheit, Celsius, and Kelvin temperature scales.

Figure It Out

Which represents the largest increase in temperature: $+10^{\circ}\text{F}$, $+10^{\circ}\text{C}$, or $+10 \text{ K}$?

Answer: Temperature changes of $+10^{\circ}\text{C}$ or $+10 \text{ K}$ are equal and larger than $+10^{\circ}\text{F}$.



▲ The length of the bacteria on the tip of this pin is about $5 \times 10^{-7} \text{ m}$ or 500 nm.